TOPICAL REVIEW

Probing multiband superconductivity by point-contact spectroscopy

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Abstract

Point-contact spectroscopy was originally developed for the determination of the electron–phonon spectral function in normal metals. However, in the past 20 years it has become an important tool in the investigation of superconductors. As a matter of fact, point contacts between a normal metal and a superconductor can provide information on the amplitude and symmetry of the energy gap that, in the superconducting state, opens up at the Fermi level. In this paper we review the experimental and theoretical aspects of point-contact spectroscopy in superconductors, and we give an experimental survey of the most recent applications of this technique to anisotropic and multiband superconductors.

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

1. Introduction

Point-contact spectroscopy (PCS) was developed more than 35 years ago as an experimental tool to investigate the interaction mechanisms between electrons and phonons in metals. Yanson [1] was the first to observe that small microconstrictions between two metals show nonlinearities in the $I–V$ characteristic (and in the second derivative $d^2V/dI^2$) that are the hallmark of inelastic scattering of electrons by phonons. The point-contact technique was later used to study all kinds of scattering of electrons by elementary excitation in metals, like magnons and so on [2, 3]. When one of the sides of a point contact is a superconductor, quantum phenomena such as quasiparticle tunneling or Andreev reflection (see section 4.1) occur at the interface, depending on the height of the potential barrier between the two electrodes. As a result, the $I–V$ shows—in addition to the features related to inelastic electron scattering—much stronger nonlinearities that give rise to particular structures in the first derivative $dI/dV$ (that is, in the differential conductance) which contain fundamental information on the excitation spectrum of the quasiparticles, i.e. on the superconducting energy gap and its properties in the direct and reciprocal space. For this reason, and apparently in spite of its simplicity, point-contact spectroscopy has become an important, sometimes unique, tool for the investigation of superconducting materials. In some recent cases, PCS has provided precious spectroscopic information on newly discovered superconductors when more complex, technologically demanding techniques such as scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) were still hindered by the absence of single-crystal samples of sufficient size. There are a number of excellent reviews that deal with the theoretical and experimental aspects of point-contact spectroscopy in normal metals and superconductors [2–4]. An extensive and comprehensive review was dedicated especially to point-contact results in cuprates [5]. The present review is therefore focused on the most recent applications of point-contact spectroscopy to the study of multiband superconductors. A general theoretical introduction is provided, whose aim is to explain in a simple, experimentally oriented way, and with a consistent notation, theoretical models of increasing complexity for the interpretation of point-contact data in superconductors.

2. Fabrication of point contacts

A point contact is simply a contact between two metals, or a metal and a superconductor, whose radius is smaller than
the electron mean free path, and this in most cases means that the contact is nanometric. Historically, point contacts were fabricated in a number of ways [3]. The pioneering technique exploited by Yanson [1] for PCS was based on the realization of microshorts in the dielectric layer of a tunnel junction between two metals. Another technique widely used, especially in superconductors (but that allows only the creation of homocontacts between two electrodes of the same material), is the break-junction technique in which a single sample is broken at low temperature into two pieces that are then brought back into contact. More recently, point contacts have been made by lithographical creation of a small hole in a thin membrane on both sides of which a metal film is then deposited. But the most often used technique simply consists in bringing the two electrodes in contact by using a micromechanical apparatus. In the most common configuration, often called ‘needle–anvil’, the sample to be studied is one of the electrodes and the other is a metallic tip, electrochemically or mechanically sharpened, which is gently pressed against the sample surface (figure 1(a)). Typically, the tip has an ending diameter of some tens of micrometers and it is easily deformed during the contact [6]. This means that, except in very special cases [7], parallel contacts are very likely to form between the sample and the tip [8]. In general, this is not detrimental to spectroscopy, unless the sample is highly inhomogeneous on a length scale comparable with the tip end [8]. The needle–anvil technique has several advantages: (i) it is non-destructive and several measurements can be carried out on the same sample and (ii) the resistance of the contact can be controlled to some extent by fine tuning of the pressure applied by the tip. Its main drawbacks are the poor thermal and mechanical stability of the junction and the fact that, if the sample is very small (tens of micrometers, as can happen with single crystals), the whole procedure becomes extremely difficult. For these reasons, since 2001 we adopted the so-called ‘soft’ point-contact technique, in which the contact is made between the clean sample surface and a small drop (about 50 μm in diameter) of Ag paste or a small In flake. The Ag or In counter electrode is connected to current and voltage leads through a thin Au wire (10–25 μm in diameter) stretched over the sample, as depicted in figure 1(b). Despite the large ‘footprint’ of the counter electrode (in particular in the case of Ag paste) if compared to the electronic mean free path, these contacts very often provide spectroscopic information. This clearly means that, on a microscopic scale, the real electrical contact occurs only here and there through parallel nanometric channels connecting the sample surface with the In flake or with individual grains in the Ag paste, whose size is 2–10 μm. With respect to the needle–anvil technique, the ‘soft’ one does not involve any pressure applied to the sample and this can sometimes be very useful, as we will show in section 5.3. The resistance of the as-made contacts is usually already in the suitable range for Andreev reflection to occur. If needed, it can be tuned by applying voltages (≈50 ms) or current pulses until a spectroscopic contact is achieved. This effect (sometimes called ‘fritting’ [9]) is well known in standard electrotechnics. The pulses have the effect of destroying some of the existing microjuncions and/or creating new ones by piercing a small oxide layer on the surface of either electrode. The contacts are mechanically and thermally very stable so that, for example, PCS measurements can be performed even in a cryocooler. Moreover, they can also be made on the thin side of small single crystals, allowing directional point-contact spectroscopy even in samples too small or brittle for the needle–anvil technique. Often (but not always) the conductance curves of ‘soft’ point contacts are more broadened than those obtained by the needle–anvil technique. As we will show, this is probably related to inelastic scattering near the interface, possibly by an oxide layer on the surface of Ag grains or of the sample. As a matter of fact, the same holds for contacts made with the Au wire alone, or even with a tip, whenever the pressure applied by the tip on the sample is small.

3. Point-contact spectroscopy in the normal state

The uniqueness of point-contact spectroscopy in the normal state is due to its ability to provide spectroscopic, energy-resolved information on the inelastic scattering of quasiparticles with elementary excitations like phonons, magnons and so on by using a very simple and cheap experimental set-up. To do so, however, some important experimental requirements must be fulfilled. The relevant quantity is the Knudsen ratio \( K = \ell / a \), where \( \ell \) is the electron mean free path \( (1/\ell = 1/\ell_e + 1/\ell_i \) where \( \ell_e,i \) are the elastic and inelastic mean free paths) and \( a \) is the contact radius. From now on it will be assumed that the shape of the contact is a circular orifice with radius \( a \) in an otherwise completely reflecting barrier. Unless otherwise specified, we will especially refer to homocontacts (i.e. contacts between two electrodes made of the same metal). Depending on the value of the Knudsen ratio, different regimes of conduction are possible, as described in the following.

3.1. Regimes of conduction in a point contact

3.1.1. Ballistic regime. In the ballistic regime the electron mean free path \( \ell \) is much larger than the contact radius \( a \) or \( K \gg 1 \). The applied voltage \( V \) accelerates electrons within the distance of a mean free path. The electrons will then flow through the contact ballistically (with no scattering) gaining kinetic energy equal to \( eV \) (see figure 2(a)). In this way, the energy of the injected electrons is perfectly known.
and corresponds to the voltage applied to the junction. The resistance of the contact in such a situation was calculated by Sharvin [10] and is equal to

$$R_S = \frac{4\rho\ell}{3\pi a^2}$$  (1)

where \(\rho\) is the resistivity of the material under study. Since in metals \(\rho \propto \ell^{-1}\), \(R_S\) is independent of the electron mean free path and depends only on the contact geometry. As a matter of fact, in the free-electron approximation it can also be written as

$$R_S = \frac{2\hbar}{e^2k_F^2a^2}$$  (2)

with \(k_F\) being the Fermi momentum [11]. In the \(k\) space, the (supposed spherical) Fermi surface (FS) expands for forward electrons by a quantity \(eV\) (see figure 2(a)). Inelastic scattering events taking place in the bottom electrode give rise to a measurable (negative) correction to the current only if they cause the backflow of carriers through the orifice. The backscattered electron must jump back onto the shrunken FS and this is possible only if it can lose an energy \(eV\) in the scattering process. This explains why in the ballistic regime the applied voltage sets the energy scale of the spectroscopic investigation.

The first-order correction to the current due to the backscattered electrons is [2, 3]

$$\delta I = -\frac{2\pi e}{h}\Omega_{\text{eff}}N(0) \int_0^{eV} dE \int_0^{E} dE' S(E - E')$$  (3)

where \(\Omega_{\text{eff}} = 8a^3/3\) is the effective volume in which the inelastic scattering of electrons contributing to \(\delta I\) occurs, \(N(0)\) is the density of states at the Fermi level and

$$S(E) = \frac{N(0)}{32\pi^2} \int \frac{d^2k}{k^2} \int \frac{d^2k'}{k'^2} |g_{kk'}|^2 K(k, k') \delta(E - E_k + E_{k'})$$  (4)

is the spectral function for the relevant interaction, which results from an integration over all the initial and final electron states of the scattering matrix elements \(|g_{kk'}|\) weighted by an efficiency function \(K(k, k')\) which accounts for the direction of the incoming and the inelastically scattered electron. It can be shown [2, 3] that

$$\frac{d^2I}{dV^2} = -\frac{2\pi e^3}{h}\Omega_{\text{eff}}N(0)S(eV).$$  (5)

A direct determination of the spectral function by means of PCS \(I-V\) measurements is thus possible. If the elementary excitations are phonons, \(S(eV)\) is the so-called ‘point-contact electron–phonon spectral function’ \(\alpha_{pc}^2 F(eV)\) which differs only slightly (due to the efficiency function \(K(k, k')\)) from the thermodynamic Eliashberg function \(\alpha^2F(eV)\). In this case, using the formulæ of the free-electron model, one obtains

$$\frac{d^2I}{dV^2} = -\frac{16ae}{3hv}\alpha_{pc}^2 F(eV).$$  (6)

It is worth mentioning that, according to equation (6), one expects the experimental \(-d^2I/dV^2\) to rapidly fall to zero above the Debye energy. Very often this is not the case [2–4] and a considerable background is found, which has been attributed to the presence of non-equilibrium phonons. It is, however, possible to correct for the background and to determine the \(\alpha_{pc}^2 F(eV)\) function [2]. This method has allowed extracting the electron–phonon spectral function in many normal metals [3], but can be applied also to superconductors above the critical temperature or driven normal by means of a magnetic field. Some examples will be discussed in section 5.2.3 for the case of MgB\(_2\) and in section 5.4 for the case of borocarbides.

3.1.2. Thermal regime. Opposed to the ballistic regime is the thermal (or Maxwellian) one in which \(\ell \ll a\) (see figure 2(c)).

Some authors [3] prefer to identify this regime by the condition

![Figure 2. Schematic diagram of the contributions to the current in a point contact obtained by solving the Boltzmann equation. (a) Zeroth-order Sharvin current (no scattering). (b) Diffusive regime (only elastic scattering in the contact area). (c) Thermal regime with inelastic scattering in the contact region. The right sides of the figures show electron distribution functions at the center of the contact for the three main regimes: (a) ballistic regime. The FS is formed by two half-spheres with different radii, i.e. defined by the surfaces at energy \(E\) and \(E + eV\). (b) Diffusive regime. The elastic scattering redistributes the electrons over the sphere but only in an energy shell with a width given by \(eV\). (c) Thermal regime. The inelastic scattering reduces the shift in energy space as is usual for normal transport in a conductor.](image-url)
In this case, the resistance of the junction (already calculated by Maxwell) depends on the resistivity of the metal [2]:

$$\rho_{\text{M}} = \frac{\rho}{2a}$$  \hspace{1cm} (7)

Joule heating occurs in the contact region and causes a local increase in temperature. The maximum temperature $T_{\text{max}}$ at the center of the contact can be estimated by using the following expression [2]:

$$T_{\text{max}}^2 = T_{\text{bath}}^2 + V^2/4L$$ \hspace{1cm} (8)

where $T_{\text{bath}}$ is the bath temperature and $L$ is the Lorenz number. In this case, at any finite bias the contact resistance is related to the resistivity of the material at $T_{\text{max}} > T_{\text{bath}}$. Since in metals $\rho$ increases with temperature, the $I$–$V$ curves become S-shaped and the conductance decreases with bias [8]. Any spectroscopic information on the electron inelastic scattering is lost. Since the standard transport theory for bulk materials applies also to the contact, the FS is only slightly shifted in the direction of the electric field, as in figure 2(c).

3.1.3. Intermediate regime. Between the two aforementioned extreme regimes, the resistance of the contact can be expressed by a simple interpolation formula derived by Wexler [12]:

$$R = \frac{4\rho\ell}{3\pi a^2} + \frac{\Gamma(K)}{K} \frac{\rho}{2a} = \frac{2\hbar}{\pi^2 k_F^2 a^2} + \frac{\Gamma(K)}{K} \frac{\rho}{2a}$$ \hspace{1cm} (9)

Here the first term is the Sharvin resistance and the second is the Maxwell resistance, multiplied by a function of the Knudsen ratio $K$. $\Gamma$ is always of the order of unity. If the two metals are different (i.e., for a heterocontact), the resistance of the contact can be written as [13, 14]

$$R = \frac{2\hbar}{\pi^2 a^2 k_{F,\text{min}}^2} + \Gamma(K) \frac{\rho_{1} + \rho_{2}}{4a}$$ \hspace{1cm} (10)

assuming a spherical Fermi surface for both metals 1 and 2. Here $k_{F,\text{min}} = \min[k_{F,1}, k_{F,2}]$ and

$$\tau = \frac{4\hbar v_{F,1} v_{F,2}}{(v_{F,1} + v_{F,2})^2}.$$ \hspace{1cm} (11)

In both equations (9) and (10) the prevalence of the Sharvin or Maxwell term depends only on the size of the contact. For a junction between given materials, the Maxwell contribution dominates in large contacts, while the Sharvin one becomes more and more important on decreasing $a$.

Between the thermal and ballistic regime one can also define the so-called diffusive regime in which the elastic mean free path $\ell_{e}$ of the electrons is small compared with the contact radius $a$ but the diffusion length $\Lambda = \sqrt{\ell_{e} a}$ for inelastic scattering is still bigger than $a (a \ll \Lambda)$. The quasiparticles can now experience elastic scattering processes inside the contact region but not inelastic ones, as shown in the left panel of figure 2(b). The scattered electrons redistribute the quasiparticles isotropically over the FS, in an energy shell of width $eV$ (right panel of figure 2(b)). Though energy-resolved information is still available, the effective volume $\Theta_{\text{eff}}$ (see equation (3)) in which the inelastic scattering of electrons gives rise to the backflow current is now reduced by a factor of the order of $a/\ell$ with respect to the ballistic regime. This is due to the fact that the probability for an electron to cross the contact, undergo an inelastic scattering event and then flow back through the orifice is reduced by elastic scattering in the contact region. The intensity of the spectroscopic signal (proportional to $-d^2I/dV^2$) is thus strongly reduced. Moreover, a different efficiency function must be used in the spectral function $S(E)$ (see equation (4)), since the elastic scattering relaxes the requirement of momentum conservation.

3.2. Determination of the conduction regime of a real point contact

The radius of a real point contact (for example, made by pressing a metallic tip against the sample surface) is unknown and, in general, experimentally inaccessible. As a matter of fact, the size of the actual contact is not related to the apparent contact area or to the footprint of the tip [8]. The problem arises of how to check whether the contact is ballistic or not. One possibility is to admit that the resistance of the contact $R_N$ can be written as in the Sharvin formula, i.e., $R_N = (4\rho\ell)/(3\pi a^2)$, where the product $\rho\ell$ refers to the bank with the smaller Fermi energy (see equation (10)) and that, in a NS junction, is generally the superconducting one. The condition $a \ll \ell$ can then be turned into a condition on the contact resistance:

$$R_N \gg \frac{4\rho}{3\pi \ell}.$$ \hspace{1cm} (12)

Alternatively, one can (very crudely) evaluate the contact radius $a$ by means of

$$a = \sqrt[3]{\frac{4\rho_0 \ell}{3\pi R_N}}$$ \hspace{1cm} (13)

and then compare it to $\ell$. This estimation is based on the assumption that only one contact is present. In almost all real cases, because of the rather likely formation of parallel contacts, the value of $a$ obtained in this way is nothing other than an upper limit to the size of the contacts (whose number is unknown). As a matter of fact, in this case $R_N$ is the resistance of the parallel as a whole and the resistance of individual contacts is necessarily larger than that. This means that, if $a$ estimated from equation (13) is smaller than $\ell$, the contact (either single or multiple) is necessarily ballistic. If instead $a \gg \ell$, this does not necessarily mean that the contact is not ballistic. In these cases, the conductance curves ($dI/dV$ versus $V$) can help in understanding what is the regime of conduction. If the conductance shows a downward curvature, for example, heating may occur in the contact. If the conductance shifts on heating may occur in the contact. If the conductance shows a downward curvature, for example, heating may occur in the contact. If the conductance shows a downward curvature, for example, heating may occur in the contact. If the conductance shows a downward curvature, for example, heating may occur in the contact..
increasing temperature, this may mean that a Maxwell term (proportional to the resistivity) is playing a role.

In the case of point contacts on superconductors, as we will see later on, some specific features show up in the conductance curves when the contact is not ballistic (see section 4.4.1). Moreover, a critical temperature of the junction smaller than the bulk $T_c$ can be due to a surface-degraded layer but also, more banally, to Joule heating in the contact (so that the actual temperature of the contact $T_{\text{max}}$ is higher than that of the bath).

4. Point-contact Andreev-reflection spectroscopy (PCAR) in the superconducting state

4.1. Andreev reflection

Let us consider a normal metal (N) brought in direct contact with a superconductor (S), with no potential barrier between them. Let us apply to this junction a voltage $V < \Delta/e$. $\Delta$ being the energy gap in the S side. If the contact is ballistic, the whole voltage drop occurs at the interface. An electron coming from the N side will not be able to propagate through the interface because only Cooper pairs exist in this energy range in S. But if a hole is reflected and two electrons are transmitted in S as a Cooper pair (figure 3) the total charge and current is constant and does no longer depend on the applied voltage. Instead, the electrons with energy higher than the gap are transmitted through the interface (see figure 3) giving a voltage-dependent current. The total current for $eV \gg \Delta$ is thus [6]

$$I \propto e\nu_F(eV - \Delta) + 2e\nu_F\Delta \approx \frac{V}{R_S} + \frac{\Delta}{eR_S}$$  \hspace{1cm} (14)

The second term on the right-hand side of equation (14) is called 'excess current' and is the hallmark of the superconducting state even at energies much higher than the gap. This result is exact only if the gap rises from zero up to the bulk value over a distance larger than the superconducting coherence length $\xi$. If the gap is instead modeled as a sharp barrier at the interface an additional term equal to $\Delta/3eR_S$ must be included.

Because of Andreev reflection, the conductance of the junction turns out to be doubled for $V < \Delta/e$. This clearly suggests a simple way to determine the energy gap in the S side by point-contact spectroscopy. This technique is often referred to as point-contact Andreev-reflection spectroscopy (PCAR). From the solution of the Bogoliubov–de Gennes equations near an N/S interface [17] it is possible to note that Andreev reflection does not occur abruptly at the interface but over a length scale of the order of $\xi$. In general $\xi$ is also the length over which $\Delta$ is depressed due to the proximity effect generated by N on S. However, if the contact size is smaller than $\xi$ this effect can be neglected.

As already mentioned, PCAR requires that the gain in energy of the electrons crossing the junction is well defined. This is true in the ballistic regime but, also, in the diffusive one. If one wants to measure the gap by PCAR, it is clear that the voltage across the junction will reach values of the order of, and even greater than, the gap $\Delta$. If the contact is ballistic, using the value for the carrier density in the free-electron model, it is possible to show [5] that the velocity of electrons across the contact, at $V \simeq \Delta/e$, is of the order of the depairing velocity in the superconductor. In other words, the current density becomes overcritical in the contact. Just outside the contact the current spreads out, its density decreases and will reach the critical value a short distance away from the actual junction [18, 19], as shown in figure 4(a). If the size of the overcritical region is smaller than the coherence length $\xi$ the spectroscopy is still possible [5], because superconductivity cannot be quenched over distances smaller than $\xi$. Therefore it is necessary to adopt contacts (see figure 4(a)) which are smaller than the electron mean free path (to avoid heating effects) and smaller than the coherence length (to avoid the proximity effect and destruction of superconductivity in the contact region) [5].

4.2. The Blonder, Tinkham and Klapwijk (BTK) model

Even if Andreev reflection was discovered in the early 1960s, it was only in 1982 that Blonder, Tinkham and Klapwijk [20] (from now on referred to as BTK) gave a complete, even though simplified, theoretical discussion of the phenomenon, including the effect of a finite transparency of the interface.
The most noticeable simplification is that the model is 1D, i.e. all the involved momenta are normal to the interface (here supposed to lie in the yz plane) and thus parallel to the x axis. The barrier is represented by a repulsive potential \( U_0 \delta(x) \) located at the interface, which enters in the calculations through the dimensionless parameter

\[
Z = \frac{U_0}{\hbar v_F}, \quad (15)
\]

Of course, the smaller Z is, the more transparent is the barrier. The parameter Z was originally meant to represent the effect of a typical oxide layer in a point contact, the localized disorder in the neck of a short microbridge or the intentional oxide barrier in a tunnel junction. According to the BTK model, calculated at \( T = 0 \), the electron coming from the N side can undergo four processes whose probabilities are:

- **A** \( \Rightarrow \) probability of Andreev reflection. The probability decreases with increasing \( Z \) for \( eV < \Delta \) and is always small for \( eV > \Delta \);
- **B** \( \Rightarrow \) probability of normal specular reflection. This probability increases with \( Z \), i.e. on decreasing the barrier transparency;
- **C** \( \Rightarrow \) probability of transmission in S as an electron-like quasiparticle (ELQ). The probability decreases if \( Z \) increases but it is always zero for \( eV < \Delta \);
- **D** \( \Rightarrow \) probability of transmission with FS crossing (i.e. as a hole-like quasiparticle, HLQ). The probability is small for \( eV > \Delta \) and always zero for \( eV < \Delta \).

Of course the sum of the four probabilities must be equal to 1. Figure 3 shows the particular case of a barrierless (\( Z = 0 \)) N/S junction at \( T = 0 \), where only the terms A and C are present.

It can be shown that the expression of the total current across the junction, at \( T = 0 \), is given by [6]

\[
I_{NS} = I_0 \int_{-\infty}^{\infty} [f(E - eV) - f(E)][1 + A(E) - B(E)] dE. \quad (16)
\]

where \( f(E) \) is the Fermi distribution function, \( A(E) \) and \( B(E) \) are the coefficients giving the probability of Andreev and ordinary reflection, and the quantity \( [1 + A(E) - B(E)] \) (which is the transmission probability) is often indicated by \( \sigma(E) \). Note that, although \( \sigma(E) \) is formally written only as a function of A and B, the contribution of C and D has been taken into account in the calculations. \( I_0 \) is a constant which depends on the area of the junction, on the density of states and on the Fermi velocity. The derivative of the current with respect to the bias, \( dI_{NS}/dV \), provides the conductance of the junction. When divided by the conductance of the same junction **when the superconductor is in the normal state**, \( dI_{NN}/dV \), this gives the normalized conductance of the junction, \( G \) (which is the outcome of PCAR experiments).

Here, instead of giving the explicit expressions for the probabilities \( A, B, C \) and \( D \) that can be found easily in the literature [3, 5, 20], we prefer to show in detail the results of a different approach [21] that allows writing the AR normalized conductance at \( T = 0 \),

\[
G = \langle dI/dV \rangle_{N/S} / \langle dI/dV \rangle_{NN}
\]

as a function of the quantities \( N_0(E) = E / \sqrt{E^2 - \Delta^2} \) and \( N_\delta(E) = \Delta / \sqrt{\Delta^2 - E^2} \), whose real parts are the BCS quasiparticle and pair density of states, respectively.

We can start from the definition of the transparency \( \tau_N \) of the barrier in the BTK approximation of current injection totally perpendicular to the N/S interface:

\[
\tau_N = \frac{1}{1 + Z^2} \quad (17)
\]

and then we introduce the function

\[
\gamma(E) = \sqrt{\frac{E - \sqrt{E^2 - \Delta^2}}{E + \sqrt{E^2 - \Delta^2}}} = \frac{E - \sqrt{E^2 - \Delta^2}}{\Delta} \quad (18)
\]

It is trivial to show that

\[
\gamma(E) = \frac{N_\delta(E) - 1}{N_0(E)} \quad (19)
\]

Note that \( \gamma(E) \) is a complex function even if the gap \( \Delta \) is real, as in the BCS case, since \( N_\delta(E) \) and \( N_0(E) \) become imaginary for \( E < \Delta \). By using these definitions it is possible to demonstrate that the BTK conductance at \( T = 0 \) is given by

\[
\sigma(E) = \tau_N \frac{1 + \tau_N |\gamma(E)|^2 + (\tau_N - 1)|\gamma(E)|^2}{1 + (\tau_N - 1)|\gamma(E)|^2} \quad (20)
\]

The calculated normalized conductance \( G(E) = \sigma(E)/\tau_N \) is shown in figure 5(a) for various values of \( Z \). In a perfectly transparent junction (\( Z = 0 \), pure Andreev regime) the conductance within the gap (\( |eV| \leq \Delta \)) is doubled with respect to the normal-state one. When \( Z > 0 \), two peaks appear at \( |eV| \leq \Delta \) and their amplitude increases on increasing \( Z \) while the zero-bias conductance (ZBC) is depressed. Finally, at \( Z \gtrsim 10 \), the normalized conductance at \( T = 0 \) practically coincides with the BCS quasiparticle density of states, i.e. the real part of \( N_\delta(E) \). Indeed, it can be demonstrated that the results of the BTK model for \( Z \to \infty \) coincide with the standard results of the theory for NIS (I = insulator) tunnel junctions. Hence, the BTK
model can reproduce, by simply changing a parameter, all the different experimental situations corresponding to different transparencies at the N/S interface, from zero to infinity.

Equation (20) is particularly useful to discuss the extensions of the simple BTK formalism we will present in the following sections. As a matter of fact, it should be borne in mind that, even if widely used as a simple tool for fitting the experimental PCAR spectra, the original BTK model is based on a large number of approximations and simplifications, i.e.

1. All the calculations are made at $T = 0$.
2. The problem is 1D, i.e. the current injection is only perpendicular to the plane interface.
3. The barrier is ideal and presents a null thickness.
4. The Fermi surfaces of both materials in N and S sides are spherical.
5. The Fermi velocities are the same on both sides.
6. The superconductor is supposed homogeneous and isotropic. Because of the mono-dimensionality, the gap $\Delta$ entering the equations is actually the gap in one single direction and represents ‘the’ gap only if the order parameter is isotropic (i.e. it has an s-wave symmetry).
7. The N/S interface is atomically flat (somewhat implicit in the 1D current injection).

In the following we will show that most of these restrictions can be easily relaxed, giving a more realistic tool for the analysis of PCAR experiments in a variety of unconventional superconductors.

4.3. Beyond the BTK model

4.3.1. Finite temperature. The calculation of the differential conductance of an N/S junction at finite temperature is quite an easy task. It can be simply accomplished by introducing in the equation for the current the standard convolution with the Fermi function at finite $T$, $f(E, T)$, and then taking the derivative of the current with respect to the bias voltage, i.e.

$$\frac{dI_{NS}}{dV}(V) = I_0 \frac{d}{dV} \int_{-\infty}^{+\infty} \left[ f(E - eV, T) - f(E, T) \right] \sigma(E) dE$$

where $\sigma(E)$ is given by equation (20). In figure 5(b) the effect of the thermal broadening on the normalized conductance is calculated by using a temperature-independent gap $\Delta = 3 \text{ meV}$ and $Z = 0.2$. On the increase of $T$ the two peaks typical of the AR at $Z \neq 0$ are smeared out, finally leaving a single zero-bias maximum. If the (supposed BCS) temperature dependence of the gap $\Delta(T)$ is taken into account in the expressions of $N_q(E)$ and $N_c(E)$, i.e. in the $\sigma(E)$, the curves become as shown in figure 6(b). The AR features now correctly disappear at the critical temperature of the contact (usually equal or very close to the $T_c$ of the superconductor).

The prefactor $I_0$ of equation (21) is expressed in terms of the normal density of states of the two materials and thus could, at least in principle, depend on temperature and on energy: in this case it should be brought inside the integral and would no longer simplify when normalizing. This could be the case when the normal-state conductance is found experimentally to change with temperature or to be voltage-dependent, as it is in high-$T_c$ cuprates [5] and in the recently discovered Fe-based superconductors (see section 5.3). However, one usually assumes for simplicity that $I_0$ is constant and uses the expression for the normalized conductance to fit the experimental PCAR spectra. From the experimental point of view, however, these cases present the extra problem of defining what is the normal-state conductance to be used for the normalization, as we will show in section 5.3.

4.3.2. 2D or 3D BTK model. If the current injection was really only perpendicular to the interface as the BTK model...
assumes, one could in principle probe the $k$ dependence of the gap by making directional PCAR (DPCAR) measurements on the different crystallographic planes of high-quality superconducting single crystals. Actually, charge carriers can approach the interface from any direction and the only condition set by the AR theory is that the component of the $k$ vector parallel to the interface is conserved in all processes. This implies, for example, that the reflected hole comes back in N with $k$ opposite to that of the incident electron and traces back its trajectory until the first scattering event in N occurs (see figure 4(a)). In the S side a Cooper pair propagates essentially in the same direction as the incident electron (neglecting the small refraction due to the expansion of the FS). Calling $\theta_N$ the angle between the direction of the incident electron and the normal to the interface, the conservation of transverse momenta leads to the following dependence of the transparency $T_N$ on $\theta_N$:

$$t_N(\theta_N) = \frac{\cos(\theta_N)^2}{\cos(\theta_N)^2 + Z^2}. \quad (22)$$

Of course equation (22) coincides with equation (17) for $\theta_N = 0$. In figure 4(b) the angular dependence of the normalized transparency (i.e. $t_N(\theta_N)/t_N(0)$) is shown for different values of $Z$. When $Z = 0$ all the quasiparticles are transmitted with the same unitary probability in the whole half-space $-\pi/2 \leq \theta_N \leq \pi/2$, but on the increase of $Z$ the transmission becomes progressively weaker and more directional around the perpendicular to the interface. Strictly speaking, the injection is always in the whole half-space but one can decide to conventionally fix a threshold (e.g. 75% of the maximum transparency) to determine an equivalent injection angle $\theta^*$. In the limit $Z \gg 10$ (tunnel regime) one gets $\theta^* \approx \pm 30^\circ$, i.e. the tunneling process is certainly highly directional. For the typical $Z$ values observed in real PCAR experiments ($\sim 0.2-0.5$), $\theta^*$ ranges between $\pm 70^\circ$ and $\pm 52^\circ$, thus showing the reduced directionality of the PCAR technique. In addition to these ‘theoretical’ limitations, some practical problems have to be taken into account. Irrespective of the way the PC are realized (needle–anvil or ‘soft’ technique) the contact footprint has a relatively large area (some hundreds of square microns). If this area contains crystal-growth terraces, defects, pits or cracks the probability to have some contacts along a different crystallographic direction becomes high. Directional PCAR spectroscopy can give reliable results only if very high-quality single crystals with highly regular (and large) surfaces parallel to the crystallographic planes are used. Despite these limitations, we will show in the experimental survey (section 5) that recent DPCAR experiments were able to precisely determine the anisotropic properties of the gap in several unconventional superconductors.

As shown in equation (22) the barrier transparency depends on the direction of the incoming electron in the N side. By introducing this expression in equation (20), integrating over the whole half-plane and properly normalizing, we get the normalized conductance at $T = 0$ [21]:

$$G_{2D}(E) = \frac{\int_{-\pi/2}^{\pi/2} \sigma(E, \theta_N) \cos \theta_N d\theta_N}{\int_{-\pi/2}^{\pi/2} t_N(\theta_N) \cos \theta_N d\theta_N}. \quad (23)$$

The calculation of $G_{2D}$ at any temperature can be done as in equation (21) by a convolution with the Fermi function.

When the system has rotational symmetry around the axis normal to the interface (i.e. the gap is isotropic and the FS is spherical) this approach can be considered as the 3D extension of the BTK model. Figure 6(a) shows the comparison of two normalized conductances at $T = 0$ and 4 K calculated with the standard 1D BTK model and with its 3D version. The angular integration leads to a remarkable depression of the AR signal when $0 < Z < 10$. Obviously, when $Z = 0$ (completely transparent junction) or $Z > 10$ (tunneling regime) the two approaches yield the same results. In figure 6(b) a complete temperature dependence of the normalized conductance calculated by using the 3D model

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**Figure 6.** (a) Normalized conductance curves calculated at $T = 0$ and 4 within the 1D BTK model [20] (dashed lines) and within its 3D generalization [21] (solid lines) using $\Delta = 3$ meV and $Z = 0.2$. (b) Temperature dependence of the conductance curves calculated within the 3D BTK model with $Z = 0.2$ and assuming for the gap a BCS temperature dependence with $\Delta(T = 0) = 3$ meV and $T_c = 19.73$ K.
and assuming a BCS $\Delta(T)$ dependence is reported. It is trivial to show that the 3D normalized conductance practically coincides with the 1D one calculated for a properly enhanced $Z$ value. Probably this fact explain why the standard 1D model is still largely used in fitting the experimental data. Nevertheless, problems can arise when comparing the $Z$ values obtained by the two different approaches, particularly in the cases where the value of $Z$ has remarkable consequences on the interpretation of the physical process occurring at the interface, as, for example, in the study of ferromagnet–superconductor PCAR junctions.

4.3.3. Fermi velocity mismatch at the interface. In a realistic system the Fermi velocities will be different on the two sides of the contact. The mismatch of the Fermi velocities gives rise to carrier reflections at the interface even when no barrier is present. This effect was initially introduced in the original BTK theory [6] by adopting an effective barrier parameter:

$$Z_{\text{eff}} = \sqrt{Z^2 + \frac{(1 - r)^2}{4r}}$$

where $r = v_F1/v_F2$ is the ratio of the Fermi velocities in the superconducting and in the normal side. The normal-state resistance at high voltage is given by $R_N = R_S(1 + Z_{\text{eff}}^2)$, where $R_S$ is the Sharvin resistance [6].

In the 3D version of the model [21] the situation is more complex. To account for the possibility of different effective masses in N and S, the parameter $r$ of equation (24) is replaced by $\lambda_0 = k_S/k_N$. The ‘refraction’ of quasiparticles at the interface is due to the conservation of transverse momentum, i.e., $\sin(\theta_N) = \lambda_0 \sin(\theta_S)$, where $\theta_N$ and $\theta_S$ are the incidence and transmission angles, respectively. Under these conditions it is possible to show [21] that the normal transmission probability (equation (22)) becomes

$$\tau_N(\theta_N, \theta_S) = \frac{4\lambda_0 \cos \theta_N \cos \theta_S}{\cos \theta_N + \lambda_0 \cos \theta_S} \cos \theta_N \cos \theta_S + 4Z^2.$$ (25)

By introducing this expression in the formula for the superconducting transmission probability (equation (20)) and expressing $\theta_S$ as a function of $\theta_N$ by using the ‘refraction’ relation $\sin(\theta_N) = \lambda_0 \sin(\theta_S)$, one formally obtains the same expression for the normalized conductance $G_{23}(E)$ as in equation (23) that now, however, accounts for the mismatch in the Fermi velocities. Incidentally, when $\lambda_0 < 1$, i.e., $k_N > k_S$, a ‘reflection’ of electrons occurs at the interface for injection angles $|\theta_N| > \sin^{-1} \lambda_0$. In this case the integral in $\theta_N$ has to be restricted to this limit angle [21]. It seems that the condition $\lambda_0 < 1$ could easily apply in the case of a superconductor with a small or very small FS and, thus, this problem could be important in new unconventional superconductors. In the opposite case, $\lambda_0 < 1$, $\theta_N$ can vary in the whole half-plane while the range of $\theta_S$ is restricted. Anyway, whatever the approach to the problem is, it turns out that the global effect of a mismatch of Fermi velocities at the interface is simply described by a sort of ‘renormalization’ of the $Z$ values of the kind described in equation (24). As a consequence, apart from extreme and hypothetical cases showing very large (or very small) $\lambda_0$ values, the effect of the mismatch cannot be separated from the standard experimental variability of $Z$ values, unless one is able to determine the true $Z$ value at the interface.

4.3.4. The broadening parameter. Even if the BTK model allows a correct interpretation of some experiments in low-temperature superconductors [6], in most cases it predicts much sharper gap features than those actually observed in the low-temperature conductance curves. This means that the AR structures in the experimental spectra are not only depressed in amplitude but also spread in energy. This effect can be attributed to the reduction of the quasiparticle lifetime, resulting from: (i) the imaginary part of the quasiparticle self-energy: this term is ‘intrinsic’ but very small, as discussed in the tunnel regime by Dynes et al [22], and (ii) inelastic quasiparticle scattering processes occurring near the N/S interface (surface degradation, contamination, etc, either at the N or the S side) [23]. This term is ‘extrinsic’ and much larger than the previous one. By properly solving the Bogoliubov–de Gennes equations in the presence of an inelastic scattering term, it has been shown [7, 23] that it is possible to globally take these effects into account by including in the BTK model a single broadening parameter $\Gamma$ in the form of an imaginary part of the energy, i.e., $E \rightarrow E + i\Gamma$. $\Gamma$ can thus be considered as the sum of the ‘intrinsic’ lifetime parameter $\Gamma_i = h/\tau_i$ and the ‘extrinsic’ one $\Gamma_x = h/\tau_x$, $\tau_i, \tau_x$ being the corresponding intrinsic and extrinsic lifetimes. There is actually a third possible origin of broadening of the conductance curves that can be accounted for by using $\Gamma$, i.e. a distribution of gap values (in anisotropic superconductors). In this case, $\Gamma$ simulates the effect of a convolution of the theoretical conductance with the gap distribution (an example is presented in section 5.4). Finally, as discussed in section 5.2.2, $\Gamma$ can also be used, as a first approximation, to simulate the pair-breaking effect of a magnetic field.

Introducing $\Gamma$ in the BCS quasiparticle density of states leads to the modified expression [22, 23]:

$$N(E, \Gamma) = \text{Re} \left[ \frac{E + i\Gamma}{\sqrt{(E + i\Gamma)^2 - \Delta^2}} \right].$$ (26)

$\Gamma$ enters the BTK model or its generalizations through $N_0(E)$ and $N_0(E)$ in equation (19), thus modifying $\sigma(E, \theta_N)$ and the conductance $G_{23}(E)$ (equation (23)). Figure 7(a) depicts the normalized conductance $G_{23}(E)$ calculated using $Z = 0.25$ and different values of the ratio $\Gamma/\Delta$. The broadening effect of $\Gamma$ cannot be reproduced by any combination of parameters of the standard BTK theory unless one convolutes the zero-temperature conductance with the Fermi function at a fictitious temperature higher than the actual one. This approach is sometimes implicitly used indeed when the experimental smearing of the curves is treated in terms of a Gaussian broadening. Such a procedure is not theoretically founded and mixes the actual thermal smearing with the other broadening effects, which are instead well distinct. Finally, even if it is a common (and reasonable) opinion that the best conductance curves should allow a fit with $\Gamma/\Delta \lesssim 0.5$, large
4.3.5. Energy dependence of the order parameter. It is well known that the mean-field BCS definition of a constant superconducting order parameter $\Delta$ is only a crude approximation of the physical reality. In the Eliashberg approach, even in the weak-coupling regime $\Delta$ is a function of the energy and shows a small energy-dependent imaginary part. The signatures of this energy dependence on the normalized tunneling (or AR) conductance curves are visible. By solving the Eliashberg equations for the strong-coupling regime starting from the electron–phonon spectral function $\alpha^2 F(E)$ and the Coulomb pseudopotential $\mu^*$ (direct solution) it is possible to obtain the full energy dependence of the order parameter $\Delta(E) = \text{Re} \Delta(E) + i \text{Im} \Delta(E)$.

The imaginary part of $\Delta(E)$ increases at the increase of the coupling and accounts for the finite lifetime of Cooper pairs. By introducing the function $\Delta(E)$ into the expression for the quasiparticle density of states (equation (26) with $\Gamma = 0$), small deviations from the BCS DOS at the typical phonon energies are observed, due to the electron–phonon interaction (EPI). It is well known that the inverse procedure also works (but only approximately in multiband superconductors! [24]), i.e. starting from the EPI structures in the experimental tunneling conductance it is possible to obtain $\alpha^2 F(E)$ and $\mu^*$ by the inverse solution of the Eliashberg equations.

Since the results of the BTK theory (and its modifications discussed so far) coincides with the ones of BCS theory for superconducting tunneling in the limit of large $Z$, it is easy to predict that the introduction of $\Delta(E)$ into the BTK expressions will lead to EPI structures in the normalized conductance for any $Z$ value in the ballistic regime. This is indeed the case, as can be explicitly demonstrated [25]. A simplified approach to the problem was presented in [26], where simple asymptotic expressions for the normalized conductance at $eV \gg \Delta$ in the tunnel ($Z \to \infty$), ballistic and diffusive regimes were obtained by taking into account phonon self-energy effects on the order parameter. Let us instead show here an example of the complete procedure applied to a ‘classic’ strong-coupling superconductor. First, we calculated the $\Delta(E)$ function of lead starting from its EPI spectral function (top curve in figure 7(c)) and assuming $\mu^* = 0.11$. $\Delta(E)$ was thus introduced in the expressions of $N_g(E)$ and $N_p(E)$, finally leading to the point-contact normalized conductance shown in figure 7(b) for different $Z$ values. As expected, the normalized conductance at $eV \lesssim \Delta_{Pb}$ coincides with the standard BTK one [26]. At $eV \approx \Delta_{Pb} + E_{ph}$ (where $E_{ph}$ represents the range of energies where $\alpha^2 F(E)_{Pb} \neq 0$) the EPI structures appear for any $Z$ value but their amplitude increases with $Z$. Figure 7(c) shows the sign-changed first derivative of the normalized conductance $-dG/dV = -d^2J_{NS}/dV^2$ versus $V$ compared to the $\alpha^2 F(E)_{Pb}$ (top curve). Even if the EPI structures shift to higher energies and their amplitude is depressed on the decrease of $Z$, the use of DPCAR spectroscopy in very high-quality single crystals to access quantitative information on the $\alpha^2 F(E)$ and its dependence on direction, temperature and applied magnetic fields proved to be a feasible task [26].

$$\Gamma \text{ values might sometimes be necessary (for example, in the presence of a wide gap distribution). This does not necessarily prevent the determination of the gap by means of a fitting procedure, which is indeed possible even when } \Gamma/\Delta > 1 \text{ (especially if } Z \text{ is sufficiently large).}$$

4.3.6. Anisotropic order parameter. The assumption of an isotropic (s-wave) order parameter (OP) makes the BTK model particularly simple, but this constraint must be relaxed if one wants to describe systems in which the OP is instead anisotropic, i.e. it depends on the wavevector $k$ in the reciprocal space. This happens, for example, in high-$T_c$ cuprates, where at least one component of the OP has a d-wave symmetry [5]. Generally speaking, the anisotropy of the OP can have two different origins: (i) the OP has a true $k$ dependence (at least along some planes of high symmetry) on the single FS sheet where it opens and (ii) different isotropic OPs open on different sheets of the FS of a multiband system. Strictly speaking, in the latter case the OP is not anisotropic but appears so when
Figure 8. (a), (b) Polar plot of the magnitude of the OP in the case of anisotropic s-wave symmetry (a) and \( d_{xy} \) symmetry (b). The sign of the OP is indicated by + and −. The angle \( \alpha \) (here equal to \( \pi/4 \)) between the crystallographic \( a \) axis and the \( x \) axis (normal to the interface) is also shown. (c), (d) Normalized conductance curves at \( T = 1 \) K calculated within the generalized 2D BTK model [21] with \( \alpha = 0 \) for different values of \( Z \) and in the same OP symmetries as in (a) and (b).

it is measured by techniques with null or poor resolution in the \( k \) space. Of course, more complex cases with multiple anisotropic gaps can, in principle, occur, which could probably be elucidated only by experimental techniques with full \( k \)-space resolution (e.g. high-resolution ARPES). In this section, we will show how to account for a single anisotropic OP within the 2D BTK model. The more complex effect of multiple OPs on different FS sheets and the influence of the shape of the FS itself will be addressed in section 4.3.7.

The problem of introducing the OP anisotropy into the expression of the superconducting transmission probability \( \sigma(E, \theta_N) \) was solved in [21] in the most general case. Here we will give a simplified ‘operative’ description of the general results. Let us suppose for simplicity that the OP has a \( k \) dependence only in the \( k_x k_y \) plane and that \( x \) is the direction normal to the flat junction interface. Let the system have a translational invariance along the \( k_z \) axis so that the problem reduces to a two-dimensional one, i.e. the FS is a cylinder. We also suppose that the current injection occurs in the plane \( xy \) (\( ab \)-plane contact) and that \( \lambda_0 = 1 \), i.e. there is no refraction of quasiparticles at the interface and both the integration angles \( \theta_N \) and \( \theta_S \) span in the range \([-\pi/2, \pi/2]\). Let the OP \( \Delta \) be a function of the angle \( \theta_S \) with which electron-like quasiparticles (ELQ) are injected in \( S \). The specific expression of \( \Delta(\theta_S) \) depends on the kind of symmetry the OP shows in the \( k \) space. To take into account the possible rotation of the crystallographic \( a \) axis with respect to the normal to the interface (\( x \) axis) we also introduce the angle \( \alpha \) (see figures 8(a) and (b)). Since ELQ and HLQ are injected in \( S \) with angles \( \theta_S \) and \( -\theta_S \), respectively, they feel different OPs, namely \( \Delta_+ = \Delta(\theta_S - \alpha) \) (for ELQ) and \( \Delta_- = \Delta(-\theta_S - \alpha) \) (for HLQ). Under these conditions, the superconducting transmission probability becomes [21]

\[
\sigma(E, \theta_S) = \frac{\tau_N}{1 + \tau_N |\gamma_+(E)c^\dagger_+(E)c^\dagger_-(E)\gamma_-(E)|^2} \text{exp}(i\phi_0) \tag{27}
\]
where
\[ γ_±(E) = \frac{E - \sqrt{E^2 - |\Delta_±|^2}}{|\Delta_±|} \]
and \( \varphi_± = (\varphi_− - \varphi_+) \), \( \varphi_± \) being the phases of \( \Delta_± \). When \( \Delta_± \) are real quantities, then their phase can be either 0 or \( \pi \) (depending on the sign) and the same holds for \( \varphi_± \). The choice of \( \alpha \) determines the \( \theta_3 \) intervals in which the phase difference \( \varphi_± \) is 0 or \( \pi \). If \( \Delta_± \) do not show sign changes as a function of \( \theta_3 \), then \( \varphi_± = 0 \) independently of \( \alpha \). \( \tau_N \) appearing in equation (27) has the same expression shown in equation (25). Putting \( \sigma(E, \theta_3) \) in equation (23) one finally obtains the total (integrated) normalized conductance at \( T = 0 \). The convolution with the Fermi function as in equation (21) will finally give the theoretical curves to be compared with the experimental results at any \( T \).

The experimental results at any \( T \) will finally give the theoretical curves to be compared with the experimental results at any \( T \). The convolution with the Fermi function as in equation (21) will finally give the theoretical curves to be compared with the experimental results at any \( T \).

4.3.7. True shape of the Fermi surfaces and momentum dependence of the pair potential. Taking into account in the calculations for the PCAR conductance the true shape of the Fermi surfaces in N and in S, the possible k dependence of the pair potential and the possible existence of multiple sheets of the FS—where the OP can assume different values—is a rather complicated task, from both the conceptual and the numerical point of view. Let us proceed step by step following the approach reported in [27, 28]. We will neglect possible interference effects between bands that can lead to the formation of bound states at the surface as discussed in [29].

First of all, the materials used in the N side are usually good conductors (Au, Ag, Pt, Cu, Al) for which the approximation of a spherical FS is reasonable. So here we restrict the analysis to the shape of the FS in the superconducting material. In the most general case the FS is divided into different sheets. Let us label them with the subscript \( i \) and call \( n \) the unitary vector in the direction of the total injected current, perpendicular to the contact interface. As a consequence the components along the direction \( n \) of the Fermi velocities at wavevector \( \mathbf{k} \) in the \( i \)th FS sheet of the superconductor are \( v_{i \mathbf{k}} \cdot \mathbf{n} = v_{i k, n} \), where \( v_{i \mathbf{k}} = \frac{1}{2}[V_k(E_i(\mathbf{k}))]. \) Of course, due to the previous approximation, the corresponding quantity in the normal metal is \( v_{N k, n} = v_N \cdot \mathbf{n} \), \( v_N \) being the (constant in magnitude) Fermi velocity in the normal material. The \( i \)th component of the total current flowing through a perfectly transparent \((Z = 0)\) interface with no mismatch of the Fermi velocities \((\lambda_0 = 1)\) in a ballistic PCAR experiment on a superconductor with isotropic OP is thus [27]

\[ I_i \propto \langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS} = \int_{FS} D_{i \mathbf{k}} v_{i k, n} \, dS_i = S_i \sigma_i \]

where \( D_{i \mathbf{k}}(E_F) = 1/|4\pi|^3|V_k(E_i(\mathbf{k}))| \) is the density of states of the \( i \)th band at the Fermi energy and wavevector \( \mathbf{k} \) in S, \( dS_i \) is the elementary area on the FS in S and \( \langle \rangle_{FS} \) is the integral over the \( i \)th FS sheet. The integral in equation (28) is limited to values \( v_{i k, n} > 0 \). Obviously \( S_i \sigma_i \) has the meaning of area of the projection of the \( i \)th FS sheet along the \( \mathbf{n} \) direction, i.e., on the interface plane perpendicular to \( \mathbf{n} \). It is the area of the \( i \)th FS sheet of the superconductor ‘seen’ along the direction \( \mathbf{n} \).

Of course, under these restrictive conditions every contribution to the total conductance from the \( i \)th FS sheet can be evaluated by using the same kind of integral, i.e., proportional to the projected area \( S_i \). If the total conductance ‘seen’ along the direction \( \mathbf{n} \) is \( \langle \sigma(E) \rangle_{FS} = \sum \sigma_i(\mathbf{E})/\langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS} = \sum \sigma_i(\mathbf{E}) S_i \sigma_i \) and the total normalized conductance is

\[ \langle G(E) \rangle_{FS} = \sum \sigma_i(\mathbf{E}) \langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS}/\langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS} = \sum \sigma_i(\mathbf{E}) S_i \sigma_i \]

where \( \sigma_i(\mathbf{E}) \) is the BTK superconducting transmission probability (equation (20)) of the \( i \)th FS sheet. In the case of different OPs \( \Delta_i \) on the different sheets of the FS the total normalized conductance will be dominated by the contribution of the \( \sigma_i(\mathbf{E}) \) that corresponds to the largest FS projected area along the \( \mathbf{n} \) direction. As a consequence, directional PCAR experiments at \( Z = 0 \) and \( \lambda_0 = 1 \) can give information on the distribution and values of the isotropic OPs on the different FS sheets in a multiband, multigap superconductor. It is quite obvious to expect similar results also in the more general case of an anisotropic OP and of \( Z \neq 0 \) and \( \lambda_0 \neq 1 \), but the calculation of the normalized conductance is now much more complex.

First of all, if the OPs on the FS sheets are anisotropic, i.e., \( \Delta_i = \Delta_{i \mathbf{k}}(\mathbf{k}) = \Delta_{i \mathbf{k}} \) (but still \( Z = 0 \) and \( \lambda_0 = 1 \)), then the superconducting transmission probability becomes a function of \( \mathbf{k} \) and cannot be anymore extracted from the integral over the FS. The total normalized conductance thus becomes

\[ \langle G(E) \rangle_{FS} = \sum \sigma_i(\mathbf{E}) \langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS}/\langle D_{i \mathbf{k}} v_{i k, n} \rangle_{FS} \]

where \( \sigma_i(\mathbf{E}) \) is always expressed by equation (20) but using functions \( N_{ik}^n(E) = E/\sqrt{E^2 - \Delta_{ik}^2} \) and \( N_{ik}^n(E) = \Delta_{ik}/\sqrt{E^2 - \Delta_{ik}^2} \) which substitute for the standard ones in the definition of \( \gamma(E) \) in equation (19). If the barrier has a finite transparency and there is an N/S Fermi velocity mismatch, the normal transmission probability of the barrier \( \tau_N \) is no longer identically 1. According to the standard 2D extension
of the BTK model shown before, \( \tau_N \) (which we here call \( \tau \) for simplicity of notation) is given by equation (25) which can be conveniently rewritten as a function of the projections of the Fermi velocities along the \( n \) direction [27]:

\[
\tau_{ik,n} = \frac{4v_{ik,n}v_{N,n}}{(v_{ik,n} + v_{N,n})^2 + 4\lambda_0^2v_N^2}.
\]

By introducing this transmission probability inside the integrals over the FS both at the numerator and denominator of equation (29) and taking into account that \( D_{ik}v_{ik,n}/v_k \) we finally obtain the total normalized conductance at \( T = 0 \) in the most general case:

\[
\langle G(E) \rangle_{\eta|n} = \frac{\sum_i \sigma_{ik,n}(E)\sum_{n=1}^{4\lambda_0^2v_{N,n}}v_{N,n}/v_{ik,n} + v_{N,n})^2 + 4\lambda_0^2v_N^2}{\sum_i \sum_{n=1}^{4\lambda_0^2v_{N,n}}v_{N,n}/v_{ik,n} + v_{N,n})^2 + 4\lambda_0^2v_N^2}.
\]

where a subscript \( n \) has been added to the expressions of \( \sigma_{ik}(E) \) and \( Z \) just to include the possibility of having different \( Z \) values along the different crystallographic directions, a thing that is often observed in DPCAR experiments. In the case of large \( Z \) (tunneling regime) the weighting factor inside both the FS integrals of equation (31) reduces to \( D_{ik}v_{ik,n}^2 \) and the calculations are simplified. As previously, the presence of isotropic OPs on every FS sheet allows extracting \( \sigma_i(E) \) from the integrals. This is the approach recently followed by Brinkman et al in [28], where the total normalized conductance of MgB\(_2\) has been written as a weighted sum of the partial conductances of the \( \sigma \) and \( \pi \) bands using the squares of the plasma frequencies along the different crystallographic directions as weighting factors. Of course, independently of the isotropic or anisotropic properties of the OPs, if the current injection in a point-contact (or tunneling) experiment was a fully directional process the gap should not be seen along that direction where the FS has a null projected area.

Actually, as we have seen in the previous sections, this is not the case, i.e. only a partial directionality is always present, which depends on the \( Z \) and \( \lambda_0 \) values. This explains why \( c \)-axis tunneling experiments on superconductors with a quasi-2D FS (cylinder parallel to \( k_z \)) actually are able to measure the gap averaged over the \( ab \) plane. If the gap value \( \Delta_{ik} \) and the Fermi velocity \( v_k \) are known at any \( k \) point of the \( i \)th FS sheet by first-principles calculations or by high-resolution ARPES experiments, then equation (31) allows the calculation of the PCAR normalized conductance at \( T = 0 \) for a current injection along any crystallographic direction. An example of the results of this procedure [30] is shown in figure 9, which shows the distribution of the pair potential values over the three different sheets of the FS of CaC\(_6\) obtained by first-principles calculations [31] (left panel) and the theoretical AR normalized conductance at \( T = 0 \) for current injection along the \( a \) axis (\( Z_a = 0.75 \)) and along the \( c \) one (\( Z_c = 1 \)) (right panel). The theoretical curves of figure 9, where properly broadened by \( \Gamma \) values close to the experimental ones, turned out to reproduce very well the experimental DPCAR results in CaC\(_6\) [30], as will be shown in section 5.5.

4.4. Non-ideal effects in the contact

4.4.1. Dips. The PCAR differential conductance often shows unexpected sharp dips at voltage values larger than the superconducting gap, but sometimes very close to it, as shown in figure 10(a). These dips are related to the superconducting properties of the S electrode since they never show up in NN junctions, but the BTK theory is unable to reproduce them. On increasing temperature, they generally shift to lower energies and generally affect the shape of the gap structures, as shown in figure 10(a). For example, they can make a broad maximum centered at zero bias look like a sharp zero-bias conductance peak.
whose relative weight depends on generally the sum of a Sharvin and a Maxwell contribution, according to Wexler’s formula, the point-contact resistance is the dips are related to the regime of conduction through the withdrawing the tip in small steps, and found indeed that progressively reducing the diameter of the point contact by N/S contacts (made with the needle–anvil technique) on who measured the evolution of the PCAR spectra of various Z

\[ Z \text{= } \frac{Z_0}{\Gamma_1} \text{ featuring clear dips. All the curves but the } \]

Figure 10. (a) Temperature evolution of the conductance curve of an Ag-paste contact on an Mg$_{2}$Ge$_{3}$Al$_{11}$B$_{3}$ single crystal (normal-state resistance $R_N = 13 \Omega$) featuring clear dips. All the curves but the bottom ones are vertically offset for clarity. (b) Upper curves (shifted for clarity): the theoretical conductance curve obtained within the diffusive model with $Z = 0$ (solid line) is well reproduced by that obtained within the BTK model with the same parameters but with $Z = 0.59$ (dashed line). Lower curves: conductance curve calculated in the diffusive model with $Z = 0.5$ (solid line) and its BTK fit (dashed line) that requires $Z = 1$. In all cases, the other parameters of the models are always the same: $T = 0.4 \text{ K}$, $\Delta = 1 \text{ meV}$ and $\Gamma = 0.2 \text{ meV}$.

It is commonly accepted that these dips indicate a non-ideal conduction through the contact. The detailed mechanism leading to their emergence was studied by Sheet et al. [32] who measured the evolution of the PCAR spectra of various N/S contacts (made with the needle–anvil technique) on progressively reducing the diameter of the point contact by withdrawing the tip in small steps, and found indeed that the dips are related to the regime of conduction through the junction, but also to the bias current. As a matter of fact, according to Wexler’s formula, the point-contact resistance is generally the sum of a Sharvin and a Maxwell contribution, whose relative weight depends on $a$. If $a$ is large, the dominant term is the Maxwell one, which contains the bulk resistivity of the two electrodes (equation (10)). As long as the current flowing through the contact is small, the resistivity of the superconductor is zero; however, when the current reaches the critical value ($I_c$) in the S side, a normal-state region can be created in S close to the junction, as discussed in section 4.1. If this happens, the resistivity of the superconductor starts playing a role and enters equation (10), giving a sharp increase in the voltage across the junction and a dip in the differential conductance. The same mechanism can be described as being due to the sudden disappearance of the excess current. Numerical simulations of the conductance, obtained by summing the $I$–$V$ curves of a ballistic contact (given by BTK) to those of a typical bulk superconductor, indeed give results in good agreement with observations [32].

An alternative explanation of the dips as being due to a proximity effect was given in [33]. The idea is that, if a proximity layer with depressed order parameter $\Delta_{\text{prox}}$ is present at the interface, Andreev reflection is limited to energies $eV < \Delta_{\text{prox}}$, while quasiparticles can enter the S side only when $eV > \Delta_{\text{bulk}}$. This gives rise to dips in the conductance curves at energies between $\Delta_{\text{prox}}$ and $\Delta_{\text{bulk}}$, which also necessarily shift to lower energies on increasing temperature because of the temperature dependence of the gaps. Reference [33] also provides a model for the fit of the conductance curves that requires $\Delta_{\text{bulk}}$, $\Delta_{\text{prox}}$ and $Z$ as adjustable parameters and can be generalized to include a broadening term $\Gamma$.

Very often, when analyzing conductance spectra with dips, a BTK fit is done ignoring the dips. However, even if this procedure introduces only a small error in the determination of the gap when the dips are small, it has been shown [32] that a considerable overestimation of the gap can occur when they become large.

4.4.2. Diffusivity in the contact. In section 3.1.3 we mainly discussed the effects of a diffusive contact in the case of an N/N junction. In N/S junctions, the diffusivity in the contact has been theoretically addressed by Mazin et al [34, 35] and turns out to affect only the Z parameter. For instance, the conductance of a diffusive junction with a given barrier parameter $Z$ can be fitted with a ballistic (BTK) model with an effective $Z^* > Z$. This is shown in figure 10(b) where the conductance curves obtained within the diffusive model (solid lines) are compared with those calculated with the standard BTK model (dashed lines). All the curves are calculated for $\Gamma = 0.2 \text{ meV}$, $\Delta = 1 \text{ meV}$ and $T = 0.4 \text{ K}$. The upper curves show that the conductance in the diffusive model with $Z = 0$ is well reproduced by the BTK model with $Z = 0.59$. Analogously, the lower curves indicate that, when $Z = 0.5$ is introduced in the diffusive model, the obtained conductance corresponds reasonably to that obtained within the BTK model, but with $Z = 1$. This conclusion is also, and even more, true at higher temperatures and for higher values of the lifetime broadening, i.e. when the curves are more smeared out.

4.4.3. Inelastic scattering in the vicinity of the contact. The inelastic scattering due to some layer with different composition at the N/S interface has been clearly singled out experimentally in [36] where ballistic Andreev-reflection measurements were performed in Cu–Pb junctions with and without a very thin (≈2 nm) Pt layer in between. The PCAR curves of the Cu/Pt/Pb junctions were shown to be more broadened than those of the Cu–Pb contacts, and were well fitted by the BTK model by systematically using larger $\Gamma$ values—though giving a good determination of the gap
amplitude (note that, already in the original paper by Plecenik et al [23], $\Gamma$ was introduced in the BTK model to take into account exactly these effects).

Something similar is likely to happen in the ‘soft’ point contacts, whose normalized conductance curves show a reduced amplitude and a larger broadening than those obtained with the conventional needle–anvil technique. To identify the scattering layer in this case, we carefully measured the temperature dependence of the resistivity of the particular Ag paint used for the contacts. We found a residual resistivity at low temperature of 0.34 m$\Omega$ cm (about $10^5$ times higher than that of pure Ag) and an enormously increased slope of $\rho(T)$ at higher temperature. The former indicates a huge contribution of intergrain connectivity to the resistivity and the latter a drastic reduction of the inelastic mean free path on the grain surface, which could well give rise to the observed broadening of the conductance curves. It must be said, however, that a contribution from a layer at the surface of the sample cannot be completely ruled out, and is instead proved by the fact that a similar broadening has been observed also in some PCAR spectra taken with the needle–anvil technique. This will be further discussed in the experimental survey (see sections 5.2.1 and 5.3).

4.4.4. Spreading resistance. For spectroscopic measurements to be reliable, electrons must not lose a significant energy while traveling through the electrodes. If at least one of the electrodes is highly resistive, a so-called spreading resistance $R_{sp}$ must be considered in series with the contact resistance, and this results in a shift of the conductance peaks to higher energies, leading to an overestimation of the gap [8, 37]. Actually, a spreading resistance $R_{sp}$ is always present but usually plays a role only in measurements performed in thin films, while in bulk or highly conductive samples it is much smaller than the contact (junction) resistance and can thus be neglected. In the case of ‘soft’ point contacts, one can wonder whether the Ag paste between the Au wire and the sample surface can give a significant contribution to $R_{sp}$. Actually, the resistance of the Ag-paste spot (approximately modeled as a cylinder with a diameter of 50 $\mu$m) is as small as 0.086 $\Omega$ even if a (largely overestimated) thickness of 50 $\mu$m is assumed. This value is clearly negligible when compared to the contact resistance that is usually in the range 5–100 $\Omega$ (depending on the material under study).

5. Point-contact spectroscopy in multiband superconductors

5.1. Two-band model for superconductivity

The first theoretical study of multiband superconductivity dates back to the late 1950s when Suhl et al [38] generalized the BCS theory to the simple case of a superconductor with two overlapping bands. The corresponding BCS Hamiltonian contains two intraband terms of the kind $\sum_{kk'} V_{ij} c_{ij}^\dagger c_{i-k-k'} c_{j-k-k'}$ and two interband terms of the kind $\sum_{kk'} V_{ij} c_{ij}^\dagger c_{i-k-k'} c_{j-k-k'}$ (where $ij = 1, 2$ is the band index). $V_{ij}$ is the (constant in the BCS approach) averaged pairing potential which results from boson emission and absorption by an $i-j$ process, minus the corresponding shielded Coulomb interaction. In the absence of interband coupling ($V_{ij} = 0$), the two bands would be completely independent, each featuring its own BCS gap and critical temperature. In the opposite case (only interband coupling, $V_{ii} = 0$) the critical temperature is the same, but there are still two gaps unless the partial density of states is the same in the two bands ($N_1 = N_2$). In general, through interband coupling the band with the higher superconducting temperature raises the critical temperature of the weaker, or even induces superconductivity in a nonsuperconducting band. The critical temperature is defined as $k_BT_c = 1.14k_B\rho \lambda^{-1/\omega}$, where $\lambda_{eff}$ is the effective coupling constant and is simply the maximum eigenvalue of the matrix $\Delta_{ij} = V_{ij}/\lambda_{eff}$, where $\lambda$ is the density of states at the Fermi energy (per spin) in the $j$th band.

![Figure 11: Temperature dependence of the gaps $\Delta_1$ and $\Delta_2$ in a two-band BCS model, calculated in the cases of: no interband coupling (solid lines); weak interband coupling (dotted lines) and strong interband coupling (dashed–dotted lines). The intraband coupling constants are arbitrary; here we used those for MgB$_2$.](image)

Figure 11 shows the temperature dependence of the (normalized) gaps as a function of the normalized temperature in the BCS two-band model in different cases: (i) bands completely decoupled ($V_{ij} = 0$, solid lines). The $T_c$s of the bands depend on the relevant intraband coupling; (ii) weakly coupled bands (dashed lines). While $\Delta_1$ follows the same standard BCS temperature dependence (but with $2\Delta_1/k_BT_c > 3.53$), $\Delta_2$ features a high-temperature tail and closes at the same $T_c$ as $\Delta_1$, and (iii) strongly coupled bands (dashed–dotted lines). The small gap still deviates from a BCS-like behavior but smoothly decreases on heating, to finally close rather quickly at $T_c$. The gap ratios $2\Delta_1/k_BT_c$ for the two gaps are greater and smaller than the single-band BCS value of 3.53, respectively. As we will show in the following experimental survey, PCAR measurements in multiband superconductors have provided examples of all these three cases.

5.2. Magnesium diboride

After the publication of the theory for two-band superconductivity, some of its consequences on various measurable quanti-
ties were calculated and possible marks of multiband superconductivity were found in conventional materials like Nb [39, 40]. In 1980 clearer experimental evidence of multiband superconductivity was found in Nb-doped SrTiO$_3$ [41] by means of tunnel spectroscopy. Despite the fundamental importance of the result, the very low transition temperature of this compound (a few hundred mK) made its experimental investigation rather demanding and prevented its study from becoming very popular. The situation changed completely in 2001 when superconductivity below 39 K was discovered in MgB$_2$, which remains up to now the most known and the most studied example of multiband superconductor. MgB$_2$ has a layered structure with graphite-like, honeycomb B layers intercalated by Mg planes with hexagonal close-packed structure [42]. Its electronic structure includes four $\sigma$ bands originating from $sp^2$-hybrid B orbitals and two $\pi$ bands due to the overlapping of the residual $p_z$ orbitals. The Fermi surface is made up of nearly-2D cylinders around the $\Gamma-A$ line (due to the $\sigma$ bands) and a 3D tubular network related to the $\pi$ bands [43].

Superconductivity develops in the $\sigma$ bands below $T_c = 39$ K mainly because of their coupling to the $E_{\text{2g}}$ phonon modes [44], and is induced in the $\pi$ bands through interband coupling.

The key role of this two-band-system structure was soon witnessed by the failure of all the conventional single-band theories in describing the phenomenology of MgB$_2$ [42, 45]. An effective two-band model was then proposed, in which the four bands were grouped into two band systems ($\sigma$ and $\pi$). The anisotropic effective coupling constant for superconductivity $\lambda_{\text{eff}} = 1.01$ actually indicates an intermediate coupling regime which is best described by the Eliashberg theory [46–48].

The calculation of the gaps within a two-band Eliashberg model [28] gave $\Delta_{\sigma} = 7.1$ meV and $\Delta_{\pi} = 2.7$ meV (see figure 12). Similar values can be obtained within a BCS approach [45].

An interesting feature of multiband superconductivity in MgB$_2$ is the role played by impurity scattering in the intraband and interband channels. According to Anderson’s theorem [49], it can be shown [50] that, at least for small impurity concentrations, the intraband non-magnetic scattering has no effect on $T_c$ and the gaps. The interband scattering, on the other side, has a pair-breaking effect and thus decreases the critical temperature $T_c$. According to the two-band model, in the limit of very strong interband scattering (dirty limit) a complete isotropization is asymptotically achieved, and the two gaps assume the same value so that one single gap is actually observed (dotted line in figure 12(a)).

This is often referred to as ‘gap merging’. According to Eliashberg calculations in [28], at low temperature $\Delta_{\text{dirty}} = 4.1$ meV with a corresponding reduced $T_c = 25$ K. For the sake of completeness, figure 12(a) also shows the results of a fully anisotropic Eliashberg calculation, based on the actual momentum dependence of the electron–phonon coupling calculated ab initio [51].

This approach gives two distinct and non-overlapping distributions of gap values with averages 6.8 and 1.8 meV. The differences from the two-band model arise from details in the calculations that are not worth discussing here. In any case, all calculations show that the gap values on the two band systems are sufficiently different to be also distinguishable experimentally.

According to the discussion of section 4.3.7, the shape of the FS (and in particular of the quasi-2D $\sigma$-band sheets) suggests a dependence of the PCAR or tunneling spectra on the direction of (main) current injection. Brinkman et al. [28] calculated the conductance curves of an ideal MgB$_2$–I–N junction with various barrier transparencies within the Eliashberg theory. They expressed the normalized conductance $G$ of the junction as the (weighted) sum of the BTK contributions of the two band systems: $G = w_{\sigma}G_{\sigma} + (1 - w_{\sigma})G_{\pi}$ [28]. As expected, the weight $w_{\sigma} = 1 - w_{\pi}$ depends on the direction of current injection. For $I \parallel c$ (and parallel to the axis of the nearly cylindrical $\sigma$-band sheets) $w_{\pi}$ is no more than 1% so that only the small gap $\Delta_{\pi}$ should give detectable structures in the conductance curve. For $I \parallel ab$, $w_{\pi}$ is maximum and equal to 33%, so that four peaks corresponding to the small and large gaps $\Delta_{\pi}$ and $\Delta_{\sigma}$ are found in the conductance curves [28]. Note that the theoretical values of the conductance curve.

In this calculation, interference effects between bands were not taken into account. In a recent paper [29], it has instead been shown that such effects can, in principle, give rise to observable features in the Andreev conductance spectra not only in iron pnictides, where the order parameter changes sign on different bands, but also in MgB$_2$, where the order parameter has the same sign on both $\sigma$ and $\pi$ bands.
$w_\sigma$ are referred to ideal tunneling current injection; slight differences are expected in PCAR experiments where the angle of effective current injection as defined in section 4.3.2 can be considerably larger.

5.2.1. Determination of the gaps in MgB$_2$. The earliest PCAR investigations carried out in MgB$_2$ polycrystals gave evidence of a single isotropic (s-wave) gap. Schmidt et al. [58] obtained $\Delta = 4.3$–4.6 meV, while Kohen et al. [56] measured a gap $\Delta = 3.8$–4.0 meV in higher-resistance contacts, while in a lower-resistance junction a smaller gap ($\Delta = 3$ meV) was found, with reduced $T_c = 29$ K. Laube et al. [59] obtained an accumulation of gap values around 1.7 and 7 meV but never observed both of them in the same spectrum. Plecenik et al. [60] studied the Andreev-reflection curves of MgB$_2$/N junctions obtained in different ways, whose fit with the modified BTK model (with $\Gamma = 0.8$ meV) gave a gap $\Delta = 4.2$ meV. A discontinuity in the temperature evolution of the gap suggested the existence of parallel contacts in clean and dirty regions of the sample, with a gap $\Delta_S = \Delta_\pi = 2.6$ meV closing at $T_c \approx 38$ K and a gap $\Delta_\text{dirty} = 4.0$ meV closing at $T_c = 22$ K, respectively. The absence of $\Delta_\pi$ was probably due to a preferred $c$-axis current injection. The presence of a degraded layer on the sample surface suggested in [56] and [60] was confirmed by PCAR measurements performed with electrochemically sharpened tips of different hardness [61], which showed indeed a decrease in the height of the conductance peaks (from 1.8 down to 1.25) and an increase in $\Gamma$ from zero up to 1.2 meV on decreasing the pressure in the contact region from about 0.6 down to 0.1 GPa. Spectra taken with the ‘soft’ pressureless technique had a height of only 1.15, and their fit with a single-gap BTK model gave $\Gamma \approx 3$ and $\Delta_\text{dirty} = 4$–5 meV with a reduced $T_c$. A reduced $T_c$ was found also in [52], together with an increase in $\Gamma$ and $Z$ on decreasing the barrier transparency. All these results indicate an extrinsic contribution to $\Gamma$ from inelastic carrier scattering in the barrier, not easily accountable for in the theoretical model, and possibly due to a degraded or reconstructed layer covering the sample which can be broken by a tip but remains intact when the pressure is small or absent [61]. Indeed, it was shown experimentally [36] that this effect can be simply accounted for by increasing the broadening parameter(s) in the modified BTK model.

With the improvements in the sample quality, spectra with multiple-gap features were readily obtained in films and polycrystals [52, 53], which allowed a fit by the two-band BTK model. In principle, the fitting function contains seven parameters: the two gap amplitudes $\Delta_\sigma$ and $\Delta_\pi$, the broadening parameters $\Gamma_\sigma$ and $\Gamma_\pi$, two barrier parameters $Z_\sigma$ and $Z_\pi$, plus the weight $w_\sigma$ (so that $w_\sigma = 1 - w_\pi$) for a total of seven parameters. Some authors decided to use only one $Z$ for both bands [52, 53] but, owing to the different Fermi velocities in the two bands, keeping $Z_\sigma$ and $Z_\pi$ as independent parameters is more general. Some authors also take $\Gamma_\sigma = \Gamma_\pi$ or even replace them with a convolution of the $T = 0$ conductance with a Gaussian of width $\omega$ [52]. Others (including us) prefer instead to calculate the conductance at the correct temperature and add $\Gamma_\sigma$ and $\Gamma_\pi$ as imaginary parts of the energy in the BTK equation [23] to account for all the sources of broadening discussed in section 4.3.4. Despite the number of free parameters, reliable values of the gaps can be obtained. This is certainly true for $\Delta_\pi$ which is quite strictly determined by the energy position of the relevant conductance peaks. The same holds for $\Delta_\sigma$ when the relevant peaks are observable—that means, for $I \parallel ab$ [28]. When the structures related to the large gap are only smooth shoulders (as in $c$-axis contacts or in $ab$-plane contacts at higher temperature), the uncertainty on $\Delta_\sigma$ increases. The evaluation of this uncertainty is not straightforward, because of the complex expression for the conductance in the two-band BTK model and the number of parameters. Indeed, an automated fitting procedure is destined to fail and one has to manually search for the parameters that allow minimizing the chi-squared or the sum of squared residuals (SSR). Once the ‘best’ fit is found, a range of parameters that give ‘acceptable’ fits must be determined. This can be done by fixing a level of confidence for the chi-squared or allowing a per cent increase in the SSR. Then, the fit has to be repeated many times by changing all the free parameters so as to find the maximum variation of the gaps compatible with the fixed limits. Several fits made independently by different people normally ensure a good estimate of this range. Fortunately, some physical constraints limit the range of variability of some parameters. For example, $w_\sigma$, $Z_\sigma$, and $Z_\pi$ should not depend on either the temperature and the magnetic field; the intrinsic (lifetime) part of $\Gamma_\sigma$ and $\Gamma_\pi$ can increase with temperature, but their usually much larger extrinsic part, related to the interface properties, should probably not.

Figure 12(b) reports the experimental results of various PCAR experiments in MgB$_2$. In all cases apart from [57] a two-band fit was used. All the datasets approximately agree with each other, apart from the early data by Bugoslavsky in thin films which show a reduced $T_c$. The error bars are indicated only for some datasets and clearly increase on approaching $T_c$ because of the thermal smearing of the gap features. Because of the same effect, one may wonder whether the two gaps really close at the same temperature, since at high temperature the spectra show only a broad maximum and the two-band fit could be questioned. A conclusive answer to this issue and in favor of the two-gap model in MgB$_2$ was found already in 2001 by Szabó et al [53], who performed PCAR measurements in polycrystalline samples (squares in figure 12(b)), obtaining gap values in very good agreement with theoretical predictions. They found that the application of magnetic fields to the junctions resulted in a much faster suppression of the $\pi$-band features with respect to the $\sigma$-band ones. At high temperature or in $c$-axis contacts where no $\sigma$-band features are apparent, the disappearance of the dominant $\pi$-band structures allows unveiling the underlying $\sigma$-band contribution, with the emergence of two more well-resolved maxima related to $\Delta_\pi$ even at $T = 30$ K.

The synthesis of single crystals large enough to be used for PCAR allowed a step forward in the experimental investigation of multiband superconductivity in MgB$_2$, and in particular a study of the anisotropy of the spectra [28] by controlling the direction of (main) current injection. The soft-PCAR technique
allowed us to make the contacts either on the flat surface of the crystals (c-axis contacts in the following, according to the nominal direction of current injection) or on their thin (50–100 μm) side (ab-plane contacts), which is very difficult by using a tip.

Figure 13 shows two examples of conductance spectra measured in the ab-plane and c-axis contacts whose normal-state resistance is indicated in the labels. Note that for all contacts with $R_N > 10$ Ω the rather large mean free path of these samples ($\ell = 80$ nm) ensures the fulfillment of the conditions for ballistic conduction (see section 3.1.1) even if a single contact is hypothesized. Clearly, if several parallel contacts are present, they must be necessarily ballistic [55]. The spectra are normalized, i.e. divided by the differential conductance at $T_A$ ($T_A$ being the critical temperature of the junction). The experimental curves in figure 13 clearly show the predicted anisotropy [28], but the non-perfect directionality of PCAR prevents the weight of the $\pi$-band conductance from assuming the theoretical extremal values ($w_\pi = 0.66$ for ab-plane tunneling and $w_\pi = 0.99$ for c-axis tunneling). This is particularly clear in c-axis contacts, where the single-gap BTK fit (dashed line) does not work well and a two-band fit (solid line) is instead necessary (with $w_\pi < 0.99$). The values of the fitting parameters are indicated in the labels. The temperature dependence of the gaps obtained in different contacts on single crystals [55] is shown in figure 12(b) (left triangles).

5.2.2. PCAR in magnetic field. As mentioned above, the first PCAR measurements in MgB$_2$ in the presence of a magnetic field were carried out by Szabó et al [53] in polycrystals. Figure 14 shows the magnetic field dependence of the low-temperature PCAR spectra for contacts with a large ab-plane contribution (a) and a dominant c-axis contribution (b). In the first case, the peaks related to $\Delta_\pi$ are fast depressed by weak fields and become barely detectable at $B = 1$ T, at which the large-gap maxima are still clearly visible. In the second case, where no clear peaks related to $\Delta_\pi$ are observed in zero field [62], the suppression of the $\pi$ gap at 1–1.5 T causes an apparent outward shift of the conductance peaks (from about 3 to 5 meV in figure 14) that then starts to shrink, because of the suppression of the $\pi$ bandgap. Actually, the use of polycrystals made it impossible to control the direction of both the probe current and the magnetic field. This is not irrelevant because of the anisotropy of the critical fields in MgB$_2$ [63–65]. Indeed, PCAR measurements in single crystals [55, 66, 67] showed that: (i) a field of about 1 T ‘completely’ suppresses the small gap irrespective of the field direction. This does not mean that the $\pi$ band becomes nonsuperconducting, but simply that the $\pi$-band contribution to the conductance at about 1 T is very little affected by a field of 1 T, either parallel or perpendicular to the ab plane [55]; (iv) in c-axis contacts, the suppression of the $\pi$-band contribution to the conductance at about 1 T is accompanied by an outward shift of the conductance peaks and by an abrupt decrease in the amplitude of the spectrum.

A quantitative study of the effect of the field on the gaps requires a fit of the experimental curves. Here the main problem is: can the BTK model or its generalized version be used to fit the conductance curves when a magnetic field is present? In conventional superconductors, Naidyuk et al [68] showed that the pair-breaking effect of the field can be mimicked, within a generalized BTK model, by the broadening parameter $\Gamma$. In other words, the total broadening parameter $\Gamma$ can be considered as the sum of an intrinsic (field-independent) $\Gamma_i$ (due to self-energy and inelastic scattering effects, see section 4.3.4) and an extrinsic $\Gamma_f(B)$ due to the magnetic field. This approach assumes that the pair-breaking effect of the field can be completely represented by the broadening $\Gamma_f(B)$ while its effect on the DOS is negligible in a first-order approximation.
Incidentally, the possibility to obtain information also on the change the resulting macroscopic superconducting properties. 

\[ \text{gaps from the conductance curves not only have given good agreement with theory. As a matter of fact, the attempts to use the BTK model to obtain the field dependence of the theoretical DOS curves become much more similar to those given by the standard BTK-lifetime model; (ii) as we will show in the following, the model seems to fit much better the experimental curves than the calculated ones, giving results in good agreement with theory. A matter of fact, the attempts to use the BTK model to obtain the field dependence of the gaps from the conductance curves not only have given good results, but have been able to extract quantitative information about the diffusivities in the two bands} \]

\[ \text{This information is crucial since, as shown in [69–71], varying the ratio of electron diffusivities in the two bands will change the resulting macroscopic superconducting properties. Incidentally, the possibility to obtain information also on the interband coupling by means of PCAR measurements in the presence of a supercurrent parallel to the interface has been recently proposed [76].} \]

\[ \text{Figure 15 shows the PCAR spectra of ab-plane contacts on MgB}_2\text{ single crystals, in magnetic fields parallel to the c axis. The curves of panel (a) were obtained in a 'soft' point contact [77], while the curves of panel (b) were measured by Naidyuk et al with a Cu tip [73]. In panel (a), the experimental curves (thick lines) are compared to the two-band generalized BTK fit (thin lines). The fit was carried out with the two-band BTK model up to about 1 T, while above this field the \( \pi \)-band features became undetectable so that we took \( \sigma_\pi \equiv 1 \), in agreement with our previous findings in single crystals [66, 67] and with those by Szabó et al. The curves in panel (b), instead, were fitted with both the \( \sigma \) and the \( \pi \) contributions up to the highest field. A similar result was also obtained by Bugoslavsky et al in epitaxial thin films of MgB}_2, where the \( \pi \) bandgap was found to survive up to 5 T [72].} \]

\[ \text{The values of the gaps extracted from the fit are shown in figure 15(c) as solid and open symbols. The data are compared to the predictions by Dahm et al [70] in the clean limit (solid lines) as well as to those by Koshelev and Golubov [71] in the dirty limit (dashed lines) in the particular case where the diffusivities in the two bands are \( D_\sigma = 0.2 D_\pi \), which is the case that allows best fitting the data in panel (a). The fit of the experimental PCAR curves seems to work very well and the resulting values of \( \Delta_\sigma \) are perfectly compatible with the expected field dependence. In all cases [72, 77] the broadening parameters of the BTK model, \( \Gamma_\sigma \) and \( \Gamma_\pi \), increase linearly with field, giving further support to the distinction between intrinsic lifetime broadening and field-induced broadening (proportional to \( B \)).} \]

\[ \text{According to figure 15(c), a fast suppression of the \( \pi \) bandgap features in weak fields [53, 55, 62, 66, 78] indicates that the \( \pi \)-band diffusivity of the samples under study is a few times greater than the \( \sigma \)-band one. Since the theoretical field dependence of the gaps in the clean limit [70] is identical to that predicted by the dirty-limit model in the case \( D_\sigma = D_\pi \) (equal diffusivities) [71], the difference between our results (a) and those by Naidyuk (b) or Bugoslavsky [72] are simply due to sample-dependent variations in the diffusivity ratio \( D_\sigma / D_\pi \), which occurs also in different crystals from the same batch [77].} \]

\[ \text{A check of internal consistency of the results described above was achieved by studying the partial averaged zero-bias density of states (ZBD) in the two bands, \( N_\sigma (0) \) and \( N_\pi (0) \), whose magnetic field dependence is predicted to depend on the diffusivity ratio [71]. In [77] we used the gaps \( \Delta_\sigma \) and \( \Delta_\pi \), the weight \( w_\pi \) and the field-induced broadening} \]
regions of the sample (vortex cores) [79]. Hence, what PCAR measures is an effective average over the vortex lattice and the conductance of the point contact should be considered as being the sum of a ‘normal channel’ and of a ‘superconducting channel’ contributions. In MgB$_2$, the normalized conductance in magnetic field thus becomes

$$G(V) = w_\pi \{ [n_\pi + (1 - n_\pi)G_\pi]$$

$$+ (1 - w_\pi)\{ [n_\sigma + (1 - n_\sigma)G_\sigma]\} \right) \right) \right)$$

(32)

where $n_\pi$ and $n_\sigma$ represent the fraction of normal-state core excitation and were thus identified [79] with the partial ZBD $N_\pi$ and $N_\sigma$. To reduce the number of free fitting parameters, the authors assumed $Z_\pi = Z_\sigma$ and used the convolution with a Gaussian of width $\omega$ to account for both the thermal smearing and inelastic interface scattering. $Z$ and $w_\pi$ were fixed to their zero-field values. The values of $n_\sigma$ and $n_\pi$ obtained from the fit of different series of conductance curves, in magnetic fields either parallel or perpendicular to the $c$ axis, are reported in figure 19(b). The data in $B \parallel c$ approximately agree with the theoretical curves (solid lines) for $D_\sigma = 0.5D_\pi$. This is consistent with the field dependence of the gaps shown in (c), which shows the persistence of the small gap up to 5 T [72]. Note that the field dependence of $\Delta_\pi$ and $\Delta_\sigma$ does not depend on the field direction (indicating that the $\pi$ band diffusivity is isotropic) while the $\alpha$-band quantities show a marked anisotropy.

Another interesting way to determine the diffusivity ratio $D_\sigma/D_\pi$ from a PCAR experiment is described in [73], where the excess current $I_{exc}$—obtained by integration of the reduced $dI/dV$ after subtraction of the background—is directly plotted as a function of the magnetic field. The result is reported in figure 19(d) for the curves in figure 19(b). Let us just recall here for convenience that the excess current is approximately $I_{exc} \cong \Delta/eR_N$; when a magnetic field is applied, a fraction $N(0, B)$ of the contact becomes nonsuperconducting (vortex cores) and does not contribute any longer to $I_{exc}$. Taking into account the presence of two bands (whose partial ZBD behave differently in the field) Naidyuk et al arrived at the expression

$$I_{exc}(B) \propto w_\pi \Delta_\pi(B) \{ 1 - N_\pi(0, B) \}$$

$$+ (1 - w_\pi)\{ \Delta_\sigma(B) \{ 1 - N_\sigma(0, B) \} \} \right) \right)$$

(33)

that was used to fit the experimental data. In this function, the gap values $\Delta_\pi(B)$ and $\Delta_\sigma(B)$ as well as the ZBD $N_\pi(0, B)$ and $N_\sigma(0, B)$ are taken from the theoretical curves of [71] suitably scaled to the actual critical field. The zero-field values of the gaps and the weight were obtained from the fit of the zero-field Andreev spectra. Figure 19(d) shows that the experimental values of $I_{exc}$ are in good agreement with the theoretical predictions in the case $D_\sigma = D_\pi$, which further confirms the conclusion drawn from the magnetic field dependence of the gaps in figure 19(c). It is worth mentioning that, both in [77] and [73], different contacts resulted in different values of the diffusivity ratio and the curves shown here are just an example.

The low-temperature magnetic field dependence of the gaps in single crystals shown in figure 19(c) indicates that, in these samples, a field of 1 T makes the PCAR spectra look as if the small gap was completely suppressed, but does not
Figure 16. (a), (b) Magnetic field dependence of the zero-bias density of states evaluated from PCAR. (a) The total ZBD obtained by simulating the zero-temperature tunneling conductance curves (from [77]) (symbols) compared to the theoretical prediction in the dirty limit for $D_\sigma = 0.2 D_\pi$. The perfect agreement confirms the result given by the field dependence of the gaps in figure 15(c). (b) The partial ZBD $n_\pi$ and $n_\sigma$ obtained from the fit of the conductance curves with the model by Bugoslavsky et al. [79], compared to the theoretical predictions in the case $D_\sigma = 0.5 D_\pi$ (solid lines). The dashed line is an estimate of the expected behavior of $N_\sigma$ for the case $H \parallel ab$. The results agree with the gap measurements in the same samples (shown in (c)) with the persistence of the small gap up to 5 T. (d) Magnetic field dependence of the excess current $I_{exc}$ (from [73]). Symbols: experimental values of $I_{exc}$ from integration of the conductance curves in figure 15(b). Lines: $I_{exc}(B)$ calculated from equation (33) based on the theoretical predictions of [71].

The process works well at 4.2 K and can be extended to higher temperatures with some caution, because of temperature-dependent anisotropy of the critical fields in MgB$_2$ [63–65]. In particular, the field must be parallel to the $ab$ plane [66, 67]; in this case the single-band BTK fit of the PCAR spectra in a field of 1 T (see figure 17(b)) gives values of $\Delta_\pi$ that agree very well with those determined by the two-band fit of the zero-field curves (figure 17(a)), apart from a much smaller uncertainty. The fit of the difference $G_{exp}(B = 0) - G_{exp}(B = 1 T)$ (figure 17(c)) gives very good results for the small gap $\Delta_\pi$ as well. The resulting temperature dependence of the gaps [55] is shown in figure 17(d).

In [67] we also determined by means of PCAR the temperature dependence of the critical field $B_{c2 || c}$ and $B_{c2 || ab}$, identified with the field that suppresses superconductivity and restores the normal-state conductance. For $T > 0.8 T_c$, a fit of the spectra with a function like $G(B = 1 T) = w_\pi 1 + (1 - w_\pi) G_\sigma (B = 1 T)$ is thus possible and gives a gap $\Delta_\pi$ which coincides with the zero-field one—but has a smaller uncertainty because of the reduced number of fitting parameters. If now one subtracts the experimental normalized spectrum $G_{exp}(B = 1 T)$ from the zero-field one, $G_{exp}(B = 0)$, one obtains a curve that only contains the zero-field $\pi$-band contribution and can thus be fitted by a three-parameter function like $G(B = 0) - G(B = 1 T) = w_\pi [G_\pi (B = 0) - 1]$ from which the small gap $\Delta_\pi$ can be obtained with a small uncertainty. In this fitting process, all the parameters must be adjusted to ensure a consistency between the different fits. The final result, as shown in [55], is a rather strict determination of the gaps, that turn out to be $\Delta_\pi = 2.80 \pm 0.05$ meV and $\Delta_\sigma = 7.1 \pm 0.1$ meV, in excellent agreement with theoretical predictions of [28].

seriously affect the $\sigma$ bandgap. A fit of the spectra with a function like $G_\sigma (B = 1 T) = \frac{1}{2} [G_\sigma (B = 0) + G_\sigma (B = 1 T)]$ is thus possible and gives a gap $\Delta_\sigma$ which coincides with the zero-field one—but has a smaller uncertainty because of the reduced number of fitting parameters. If now one subtracts the experimental normalized spectrum $G_{exp}(B = 1 T)$ from the zero-field one, $G_{exp}(B = 0)$, one obtains a curve that only contains the zero-field $\pi$-band contribution and can thus be fitted by a three-parameter function like $G_\pi (B = 0) = \frac{1}{2} [G_\pi (B = 0) + G_\pi (B = 1 T)]$ from which the small gap $\Delta_\pi$ can be obtained with a small uncertainty. In this fitting process, all the parameters must be adjusted to ensure a consistency between the different fits. The final result, as shown in [55], is a rather strict determination of the gaps, that turn out to be $\Delta_\pi = 2.80 \pm 0.05$ meV and $\Delta_\sigma = 7.1 \pm 0.1$ meV, in excellent agreement with theoretical predictions of [28].
Figure 17. (a) Temperature dependence of the zero-field conductance curves $G(B=0)$ of a c-axis contact on an MgB$_2$ single crystal (symbols) and the relevant two-gap BTK fit. (b) Same as in (a), but in a field of 1 T applied parallel to the ab plane. The $G(B=1\,\text{T})$ curves are compared to the relevant fit with a single-gap BTK model containing only the $\sigma$-band contribution to the Andreev conductance. (c) Temperature dependence of the difference $G(B=0) - G(B=1\,\text{T})$, compared to the relevant single-gap BTK fit that contains only the $\pi$-band Andreev-reflection conductance. (d) Temperature dependence of the gaps $\Delta_\sigma$ and $\Delta_\pi$ extracted from the single-gap BTK fits of the partial $\sigma$ and $\pi$-band conductances (panels (b) and (c), respectively). Data taken from [66] and [81].

5.2.3. Determination of the electron–phonon spectral function by PCS. Point-contact spectroscopy in the normal and superconducting state of MgB$_2$ was also used to obtain the electron–phonon spectral function and elucidate the role of the in-plane B stretching mode E$_{2g}$ in determining the superconducting properties of this compound. In [82], Yanson et al investigated the point-contact spectra in c-axis-oriented films, in the superconducting ($T < T_c$) and in the normal ($T > T_c$) state. They directly measured the differential resistance ($dV/dI$) as well as the second derivative of the $I–V$ curves, i.e. $d^2V/dI^2$, which is proportional to the electron–phonon spectral function $\alpha^2 F_\omega(\omega)$ (see section 3.1.1). The authors observed clear structures in the superconducting state, with a signature of the E$_{2g}$ mode of the same amplitude as other phonon peaks. Owing to the preferential current injection along the c axis, this is in agreement with the calculated $\alpha^2 F_\omega(\omega)$ [83]. However, these structures were found to disappear at $T > T_c$ where only much smaller nonlinearities persisted. This indicates a superconducting origin of the structures, i.e. due to the energy dependence of the order parameter (‘elastic’ or self-energy term) rather than to the actual inelastic e–ph scattering. This point was also addressed theoretically in [26] where a simple asymptotic formula for the order parameter self-energy effects in the superconducting point contact was derived. Later, the same authors performed
by means of fields as high as 9 T. In low-temperature, zero-
least a partial suppression of superconductivity at 4.2 K
smaller critical field of crystals with respect to films allowed
\[
\frac{\partial^2 V}{\partial t^2}
\]
and
2
5.2.4. Effect of chemical doping on the gaps of MgB
Eliashberg functions
\[\alpha\]
the quantities needed to describe MgB$_2$ are manifold:
doping in MgB$_2$ always gives a decrease in
experimentally. As we will see in the following, chemical
can be either calculated from first principles or determined
and some of them (like the DOS, the phonon spectrum)
those of other sources of
T
role) or to an increase in interband scattering. Fortunately,
Gammas 20 mV that were claimed to reflect bulk (isotropic)
phonons, and were put in connection with the first two maxima
in the phonon density of states or
phonons, which, however, play a minor
30 and 50 mV that were claimed to reflect bulk (isotropic)
mode, largely smeared by the e–ph coupling, as observed by x-
ray inelastic scattering [85]. The \[\partial^2 V/\partial t^2\] spectra of contacts
with a predominant e-axis tunneling contribution showed
instead much weaker structures such as shallow maxima at
30 and 50 mV that were claimed to reflect bulk (isotropic)
phonons, and were put in connection with the first two maxima
in the phonon density of states or
T
structures related to the large gap
become less and less
dependence of the conductance curves can be more conclusive
in this sense: an outward shift of the conductance peaks is a
strong indication in favor of two gaps. Another problem
is the determination of the actual doping content, especially
in the case of light atomic species (Li, C), which makes the
trend of the gaps versus the doping content rather uncertain.
Moreover, the doping content is intrinsically inhomogeneous
on the scale probed by PCAR so that different contacts on the
same sample can even show different gaps and different $T_c^A$.
For these reasons, we always prefer to report the values of the
gaps as a function of the local critical temperature $T_c^A$.
This representation is also the most suited to compare the results for
different substitutions. For example, one can learn that there is
an interesting universal scaling law of $\Delta_c$ with $T_c^A$, at least
for $T_c^A > 20$ K, independent of the main mechanism of $T_c$
reduction.

Carbon is the only chemical substitution in the site of
boron that the structure of MgB$_2$ accepts. PCAR experiments
in Mg(B$_{1-x}$C$_x$)$_2$ were carried out in nearly single-phase
polycrystals with 0.09 $\leq x \leq$ 0.13 [90, 95] and in single
-crystals grown at high pressure and high temperature [96]
with 0.047 $\leq x \leq$ 0.132. The critical temperature
decreases on C doping, as shown in figure 18, although the
difficulty in determining the actual C content gives rise to some
minor differences in the actual $T_c$ versus $x$ curve for crystals
(Karpinski) and polycrystals (Ribeiro).

Figure 19 shows some examples of normalized PCAR
curves and the relevant fit at different C contents, in
polycrystals and wires [97] and in single crystals [98]. Already
at $x = 0.1$, the experimental curves seem to be fittable by a
single-band BTK model with lifetime broadening. Actually, at
this C content the second gap is still retained [99], as can be
easily shown by applying a magnetic field (see figure 19(b)): as
in pure MgB$_2$, the small gap is rapidly suppressed and

5.2.4. Effect of chemical doping on the gaps of MgB$_2$. Chemical substitutions in MgB$_2$ were tried very soon after the
discovery of superconductivity in this compound [88]. The
huge experimental work carried out in substituted MgB$_2$ has
allowed a deeper understanding of the pure compound, but
has also unveiled a surprisingly rich and complex physics.
Even in the simplest effective two-band model [28, 45]
the quantities needed to describe MgB$_2$ are manifold: four
Eliashberg functions $a^2F_{\alpha \beta} (\omega)$ (where $i, j = \sigma, \pi$) [24], four
quasiparticle scattering rates (intra-band, $\Gamma_{ii}$, and inter-band, $\Gamma_{ij}$), two
densities of states (DOSs) and a prefactor $\mu_0$ to the
Coulomb pseudopotential (which is a $2 \times 2$ matrix whose
elements only contain the densities of states $N_{\sigma}$ and $N_{\pi}$). Not
all these parameters are independent (for example, $\Gamma_{\sigma \sigma} = (N_{\sigma}/N_{\pi}) \Gamma_{\sigma \pi}$, $N_{\sigma, \pi}$ being the zero-bias DOS in the two bands)
and some of them (like the DOS, the phonon spectrum)
can be either calculated from first principles or determined
experimentally. As we will see in the following, chemical
doping in MgB$_2$ always gives a decrease in $T_c$ (see figure 18)
and $\Delta_c$, which can be due either to a variation in the DOS
(in the phonon frequencies, which, however, play a minor
role) or to an increase in interband scattering. Fortunately,
the effects of the latter are rather easily distinguishable from
those of other sources of $T_c$ reduction, since an increase in $\Gamma_{\sigma \pi}$
suppresses $T_c$ and $\Delta_c$ but increases $\Delta_\sigma$. As a consequence,
some indications about the effects of doping on the DOS and on
the interband scattering can be extracted from the analysis of the
doping dependence of the gaps, measured by PCAR, within
the two-band Eliashberg theory. Indications about the relative
role of intraband scattering rates in the two bands can instead
be obtained from the magnetic field dependence of the ZBD
or the excess current, as shown in section 5.2.2. A detailed review
on PCAR measurements in doped MgB$_2$ is reported in [89]; in
the following we will thus give only a general discussion of the
main findings.

In general, a problem with PCAR in doped MgB$_2$ is that
the structures related to the large gap $\Delta_c$ become less and less
clear on increasing the dopant content. The comparison of the
two-band fit to the single-band one can clarify whether two
gaps are still present or not, but sometimes the magnetic field
dependence of the conductance curves can be more conclusive
in this sense: an outward shift of the conductance peaks is a
strong indication in favor of two gaps. Another problem
is the determination of the actual doping content, especially
in the case of light atomic species (Li, C), which makes the
trend of the gaps versus the doping content rather uncertain.
Moreover, the doping content is intrinsically inhomogeneous
on the scale probed by PCAR so that different contacts on the
same sample can even show different gaps and different $T_c^A$.
For these reasons, we always prefer to report the values of the
gaps as a function of the local critical temperature $T_c^A$.
This representation is also the most suited to compare the results for
different substitutions. For example, one can learn that there is
an interesting universal scaling law of $\Delta_c$ with $T_c^A$, at least
for $T_c^A > 20$ K, independent of the main mechanism of $T_c$
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Carbon is the only chemical substitution in the site of
boron that the structure of MgB$_2$ accepts. PCAR experiments
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at $x = 0.1$, the experimental curves seem to be fittable by a
single-band BTK model with lifetime broadening. Actually, at
this C content the second gap is still retained [99], as can be
easily shown by applying a magnetic field (see figure 19(b)): as
in pure MgB$_2$, the small gap is rapidly suppressed and
the large-gap features emerge clearly [97, 98]. As shown in figure 19(b), in single crystals with the highest doping content ($x = 0.132$) the application of the magnetic field makes the conductance peaks decrease in amplitude but no shift in energy is observed as long as the applied field is much smaller than the critical field (this is certainly true for $H \parallel ab$ [98] because C doping increases the critical field). The absence of a shift indicates that, if two gaps are present, they have very similar amplitude—indeed, the two-band BTK fit of all the conductance curves at $x = 0.132$ requires two gap values that are experimentally indistinguishable. The single-band BTK fit shown in figure 19(b) gives a gap $\Delta = 2.8 \pm 0.2$ meV. One could thus conclude that the ‘gap merging’ is obtained in heavily C-doped MgB$_2$, also relying on the fact that: (i) the ratio $2\Delta/k_BT_c = 3.8$ is close to the BCS value; (ii) the conductance curves recorded in this sample at different temperatures all admit a very good single-band BTK fit and (iii) the temperature dependence of the gap $\Delta$ extracted from the fit is perfectly BCS (within the experimental uncertainty) and the critical temperature of the junction, $T_c^A = 19$ K, is in perfect agreement with the bulk $T_c$ measured by DC zero-field-cooling magnetization.

However, the situation is not so simple. Figure 20(a) reports the values of the gaps obtained in C-doped crystals [98] and polycrystals [97, 100, 101] as a function of the critical temperature. It is clear that the two datasets agree rather well as far as $\Delta_\sigma$ is concerned, but disagree on the values and trend of $\Delta_\pi$. In particular, in wires and bulk polycrystalline samples there is no tendency to the gap merging observed instead in single crystals. To analyze the data within the two-band Eliashberg model one can use the $\sigma$- and $\pi$-band DOS and the phonon frequencies calculated for C-doped MgB$_2$ [103], thus leaving $\mu_0$ and $\Gamma_{\sigma\pi}$ as the only adjustable parameters. The overall trend of the gaps in C-doped polycrystals is reproduced by keeping $\Gamma_{\sigma\pi} = 0$ as in pure MgB$_2$, adjusting $\mu_0$ to reproduce the experimental $T_c$ and calculating the corresponding gaps (dashed lines in figure 20(a)). This means that the decrease in $T_c$, $\Delta_\sigma$ and $\Delta_\pi$ in these samples can be completely explained by band filling [104]. In single crystals, instead, the trend of $\Delta_\pi$ can only be reproduced by increasing the interband scattering rate (solid lines in figure 20(a)). This contrasts with the theoretical prediction [105] that substitutions in the $B$ plane (for example, by carbon) preserving the different parity of $\sigma$ and $\pi$ bands have little or no effect on $\Gamma_{\sigma\pi}$. The key to this puzzle could be the presence of microscopic defects in C-doped single crystals, acting as scattering centers, suggested by the doping-induced increase in flux pinning and in the normalized resistance [96]. The nature of these defects and the reason why they should be able to create interband scattering is, however, not completely clear [98]. It is worth mentioning that the analysis of the zero-bias DOS as a function of the magnetic field in C-doped polycrystals, carried out in [101] by using the fitting model developed by Bugoslavsky [79], clearly proves that the ratio $D_\pi/D_\sigma$ increases from 0.2 (pure MgB$_2$) towards 1 on increasing the doping content, indicating that C doping (surprisingly) increases the intraband $\pi$ scattering more than the $\sigma$-band one.

Doping in the Mg site has been obtained with different chemical species: Al, Li, Mn or Fe. The first two are heterovalent and result in electron and hole doping, respectively. According to theoretical predictions, Al should give the maximum increase in interband scattering (for 2% of Al a value of $\Gamma_{\sigma\pi} = 1.1$ meV is predicted, which already has measurable effects on the critical temperature and on the gaps [105]). In contrast, Li should have little or no effect on $\Gamma_{\sigma\pi}$ [105]. PCAR measurements in Mg$_{1-x}$Al$_x$B$_2$ polycrystals [93, 101] and crystals [91] up to $x = 0.2$, carried out with either the conventional or the ‘soft’ technique, showed almost linear decrease of $\Delta_\sigma$ and $\Delta_\pi$ as a function of the Al content, in agreement with the findings of specific-heat
Figure 20. (a) Energy gaps in MgB$_2$ as a function of the critical temperature, measured in single crystals [98] (circles) and polycrystals and wires [97, 100, 101] (triangles). Each point of the single-crystal series is actually the average of different gap values measured in different contacts, whose spread is indicated by the error bar. (b) Energy gaps measured by PCAR in Mg$_{1-x}$Al$_x$B$_2$ as a function of the critical temperature. Circles are taken from [102], squares from [93], down triangles from [101] and up triangles from [91]. In both (a) and (b), dashed–dotted lines represent the gap values calculated within the two-band Eliashberg theory by using the DOS and the phonon frequencies from ab initio calculations. Solid lines indicate the fit of the gaps versus $T_c$ obtained by adding to the model an adjustable interband scattering rate $\Gamma_{\sigma\sigma'}$.

measurements [93]. No clear tendency of the gaps to merge was observed; an extension to higher doping ($x = 0.32$) was later obtained by us in single crystals [102]. All these results are reported, as a function of the critical temperature, in figure 20(b). As in the case of carbon doping, all the datasets agree on the behavior of $\Delta_x$, which is also directly related to the suppression of the critical field by Al doping [93]. Interestingly, this relationship implies the validity of a clean-limit description of the system, as follows from the analysis of the critical field [93, 101] but also from the analysis of the zero-bias DOS as a function of the magnetic field (carried out in [101] by using Bugoslavsky’s fitting model [79]) which shows that the diffusivity ratio of pure MgB$_2$ is preserved on Al doping at least up to $x = 0.20$. The persistence of two gaps even at the highest doping content is not clear in the spectra; the single-band and two-band BTK fits are also very similar to each other although a statistical test (the Fisher F test) clearly indicates that the latter is preferable for any level of confidence. In any case, the magnetic field dependence of the conductance curves shows the outward shift of the conductance maxima on increasing the field [101, 102], which always indicates the presence of two gaps of different amplitude—even though, as explained in [102], the suppression of $H_c2$ by Al doping prevents the separation of the partial $\sigma$ and $\pi$ band contributions to the conductance, as we instead did in pure MgB$_2$.

The dependence of $\Delta_x$ on the critical temperature shown in figure 20(b) can be superimposed to that observed in C-doped MgB$_2$ [101, 102] shown in figure 20(a). The trend of the small gap $\Delta_\pi$ is similar, but not identical, to that observed in C-doped MgB$_2$ polycrystals (see figure 20(a)). Actually, a small tendency to an increase in $\Delta_x$ at low doping content (with a maximum around $T_c^A = 30$ K) is very clear, outside the experimental uncertainty, in our data on single crystals (solid circles). Cooley et al [106] noticed the same trend only in samples produced via a long reaction at high temperature so as to reduce the strain and the inhomogeneity in the Al content. This would indicate that the enhancement in $\Delta_x$ is intrinsic to Al doping but is often masked by other effects, and could explain why it is barely detectable in PCAR results by the Slovak group [91, 101] (triangles) as well as in the results of specific-heat measurements in some polycrystal samples [93, 107]. In any case, this trend cannot be reproduced within the two-band Eliashberg model if only the proper variation in the DOS [108] and in the phonon frequencies due to Al doping [109] are taken into account (dashed lines in figure 20(b)). Although the effect on the DOS is certainly dominant [104], an increase in interband scattering at low Al content in quantitative agreement with expectations [105] is also necessary to catch the experimental trend of $\Delta_x$ in our single crystals. However, in order to fit the data, $\Gamma_{\sigma\pi}$ must again decrease for $x > 0.1$. The reason for this is not completely clear but might be related to extrinsic effects like inhomogeneity and lattice stress (not taken into account in the Eliashberg model) that start playing a role for $x > 0.1$, as suggested in [92, 106] and by the increase in the width of the superconducting transition for $x > 0.1$ [102].

Mn doping is peculiar for two reasons: (i) Mn is homovalent with Mg and (ii) its magnetic moment gives rise to spin-flip, pair-breaking scattering that is considerably larger than the non-magnetic one: indeed, $T_c$ is very rapidly suppressed by small Mn contents (see figure 18). One can thus expect the DOS to be unaffected and the interband non-magnetic scattering to play little role in this compound. PCAR measurements with the soft technique were carried out in single crystals [110] of Mg$_{1-x}$Mn$_x$B$_2$ with $x$ up to 0.015 [112]. The trend of the gaps as a function of $T_c^A$ is shown in figure 21(a). For $x > 0.004$ (i.e. for $T_c^A < 33$ K) the persistence of two gaps was not evident in the conductance curves and had to be proved by using a magnetic field. Unfortunately, Mn doping also suppresses $H_c2$ so that, when $T_c < 17$ K, this procedure becomes unreliable and the conclusion that two gaps persist down to the lowest $T_c^A$ can be based on: (i) the better quality of the two-band fit [110] and (ii) the fact that the presence of a single gap in the low-$T_c^A$ region would imply a sudden change in the slope of the $\Delta_\sigma$ and $\Delta_\pi$ versus $T_c^A$ curves [110] that is not justified by any observed discontinuity in the physical properties of the
compound [112]. The trend of $\Delta_{c}$ and $\Delta_{\sigma}$ versus $T_{c}$ in Mn-doped MgB$_{2}$ is surprisingly similar to that observed in Al-doped samples, apart from the low doping enhancement of $\Delta_{c}$. By the way, $\Delta_{c}$ follows the universal scaling law with $T_{c}$. Unlike in previous cases, the analysis of the data within the two-band Eliashberg model can here give precise information on the magnetic scattering rates, either interband ($\Gamma^{M}_{ij}$) or intraband ($\Gamma^{M}_{\sigma\pi}$). The gap trend can indeed be reproduced very well by using the same phonon spectra, DOS values and Coulomb pseudopotential as in pure MgB$_{2}$, neglecting all non-magnetic scattering rates, and taking $\Gamma^{M}_{\sigma\sigma}$, $\Gamma^{M}_{\pi\pi}$ and $\Gamma^{M}_{\sigma\pi}$ as the only adjustable parameters [110]. The fit of the gaps versus $T_{c}$ indicates a dominant intraband spin-flip scattering in the $\sigma$ band, $\Gamma^{M}_{\sigma\pi}$, with possible smaller contributions from either the $\pi$-intraband $\Gamma^{M}_{\pi\pi}$ or the interband $\Gamma^{M}_{\sigma\pi}$ channels. A large $\sigma-\sigma$ scattering was predicted theoretically as being due to the hybridization of the $\sigma$ bands of MgB$_{2}$ with the d orbitals of Mn [113]. The dominance of this term on the $\pi-\pi$ or $\sigma-\pi$ channels was instead demonstrated by first-principles calculations of the electronic structure of MgB$_{2}$ near an Mn impurity [110].

5.2.5. Effects of irradiation on the gaps of MgB$_{2}$. The effects of the intentional introduction of disorder in MgB$_{2}$ by means of neutron irradiation have been recently discussed in a review [114]. Here we will just quickly mention the results of PCAR measurements in neutron-irradiated Mg$_{11}$B$_{2}$ polycrystals [19]. As explained in [115], the use of isotopically enriched $^{11}$B was necessary to ensure a homogeneous distribution of defects in the bulk and avoid self-shielding effects. Neutron flux densities up to $1.6 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ were used, which suppressed the bulk $T_{c}$ down to 8.7 K. The defect distribution is very homogeneous, as shown by x-ray diffraction and by the small width (0.9 K at most) of the superconducting transition [115]. The PCAR measurements were performed with the ‘soft’ technique [19]. The severe shortening of the electronic mean free path [115] made fulfilling the conditions for ballistic conduction to be more and more difficult. In the most irradiated sample, even the contact with the highest normal-state resistance (40 $\Omega$) turned out to be in the intermediate regime and showed the typical dips at $V > V_{\text{peak}}$ [32], as well as a moderate heating, which was shown to be negligible as long as the voltage drop at the junction was of the order of $V_{\text{peak}}$ [19]. The trend of the gaps as a function of $T_{c}$ is shown in figure 21(b) (circles). In the region of $T_{c}$ around 18–19 K, the results of the two-band BTK fit are shown even though a single-band fit (with $\Delta \approx \Delta_{\sigma}$) is possible as well. The $\Delta_{\sigma}(T_{c})$ and $\Delta_{\pi}(T_{c})$ curves clearly indicate a transition from two-band to single-band superconductivity below 20 K, in excellent agreement with the findings of specific-heat measurements [111] in the same samples (squares). The initial small increase in $\Delta_{c}$ suggests that neutron irradiation increases interband scattering. However, this is not the only effect since a decrease in the $\sigma$-band DOS (indeed observed experimentally [116]) is necessary as well to approximately reproduce the overall trend of the gaps within the two-band Eliashberg model (solid line in figure 21(b)). Actually, the DOS decrease is dominant and can, alone, qualitatively explain the experimental data (dashed lines) and the inclusion of interband scattering only improves the agreement in the high-$T_{c}$ region. The fit in the low-$T_{c}$ region (below 20 K) is poor but cannot be improved since here both gaps are smaller than the BCS value and this is forbidden within the two-band Eliashberg theory (although often observed in disordered superconductors [117]).

5.3. Point-contact spectroscopy in novel Fe-based superconductors

At the beginning of 2008, a new class of Fe-based superconductors with unexpectedly high critical temperatures—with a record $T_{c}$ (up to now) of 57 K—was discovered. These materials are the first real term of comparison for cuprates and thus provide a unique opportunity to test the generality of the theories for high-$T_{c}$ superconductivity and to identify more clearly the conditions for its occurrence. Many compounds of this class have been (and are being) discovered and studied; in the following we will only refer to the most widely studied families of iron–arsenide superconductors. The so-called ‘1111’ family includes the compounds REFeAsO (RE = rare earth) that become superconducting upon doping, with maximum $T_{c} = 55$ K.
as well as the recently discovered oxygen-free $A_{1-x}$RE$_x$FeAsF ($A = \text{Ca, Sr} \ldots$) which shows the record $T_c = 57$ K. The ‘122’ family has the general formula AFe$_2$As$_2$ ($A = \text{Ba, Sr, Ca, Eu}$) and, upon doping, develops $T_c$ up to 38 K. The state of the research on iron pnictides up to May 2009 is (partially) summarized in [118].

Like cuprates, these materials are layered, with alternating RE–O and Fe–As layers, the latter apparently playing the key role for the occurrence of superconductivity. Band structure calculations [119] and ARPES measurements [120] showed that the Fermi surface is quasi-2D, and is generally made up of two or three hole-like sheets around the Γ point of the first Brillouin zone, and two electron-like cylinders at the M point. This immediately suggests, in analogy with MgB$_2$, the possibility of multigap superconductivity and a dependence of the tunneling or PCAR spectra on the direction of current injection. Experimental indications of multigap superconductivity came very soon from measurements of the critical field and NQR in LaFeAsO$_1$–$x$F$_x$ [121–123], from direct ARPES measurements in Ba$_{0.6}$K$_{0.4}$FeAs [120], from NMR in PrFeAsO$_{0.85}$F$_{0.15}$ [124] and so on [118].

The main issue that PCAR spectroscopy has been asked to address is the determination of the number, the amplitude and the symmetry of the order parameter(s). This information is crucial for the development of theoretical models and to test the existing ones.

The first PCAR measurements, carried out with the conventional needle–anvil technique, seemed to support a nodal symmetry of the order parameter, because of the systematic observation of a zero-bias conductance peak (ZBCP). This happened in LaFeAsO$_{0.9}$F$_{0.1}$, where Shan et al. [125] only observed spectra either featureless or with a large ZBCP and much smaller additional features. By fitting the conductance curves with the 2D BTK model [21] (see sections 4.3.2 and 4.3.6), they obtained a d-wave gap $\Delta = 3.9 \pm 0.7$ meV, corresponding to $2\Delta/k_B T_c = 4.11$. Also Wang et al. [126] often observed a ZBCP in polycrystalline SmFeAsO$_{0.9}$F$_{0.1}$ and interpreted it as a signature of nodal gap. All their spectra admitted a fit with the d-wave 2D BTK model, including the few spectra with no ZBCP.

The interpretation of the ZBCP as an indication of nodal symmetry was, however, soon questioned. Yates et al. [127] performed PCAR in oxygen-deficient NdFeAsO$_{0.85}$ with $T_c = 45.5$ K and observed that a ZBCP (always vanishing at $T_c^A$) develops on increasing the pressure applied by the tip (and thus on decreasing $Z$ and $R_0$). This made the authors warn that the ZBCP may be an artifact, not related to the gap symmetry. A temperature dependence of the ZBCP incompatible with a d-wave symmetry was found by the same authors also in TbFeAsO$_{0.9}$F$_{0.1}$ with $T_c = 50$ K, where the presence or absence of the ZBCP was found to even depend on the sample region probed by PCAR [128]. Samuely et al. [129] observed, in NdFeAsO$_{0.85}$F$_{0.15}$, a large predominance of low-temperature spectra without ZBCP. However, the ZBCP was found to emerge at a temperature $T^* \propto 1/Z$, to grow in amplitude until it overwhelms the gap structures (as in [127]), and finally to disappear at $T_c^A$. A ZBCP very robust against the magnetic field was found in low-resistance junctions by Chen et al. [130] who performed PCAR measurements in polycrystalline SmFeAsO$_{0.85}$F$_{0.15}$ with bulk $T_c = 42$ K. In contrast with [125], Chen et al. also found that the ZBCP is very little affected by magnetic fields up to 9 T—which excludes its relationship with a d-wave symmetry of the gap.

The actual nature of this peak is not completely clear. Kondo scattering coming from the magnetic impurities in or near the barrier [125], or to the magnetic moment of Nd or Tb [127, 129], can be excluded. The same holds for intergrain Josephson coupling [131]. Owing to the decrease in $R_N$ that accompanies the increase in tip pressure, one could hypothesize that the ZBCP is due to the contact not being in the ballistic regime so that critical current effects [32] or heating in the contact region occurs. It is true that, as shown in [129], the ZBCP coexists with clear gap features at finite energy [126, 127, 129], but this does not necessarily exclude the possibility of parallel ballistic and thermal contacts. What instead seems to exclude this picture is that soft point-contact measurements carried out in LaFeAsO$_{1-x}$F$_x$ [132, 133] and SmFeAsO$_{0.8}$F$_{0.2}$ [133, 134] never gave evidence of ZBCP, irrespective of the contact resistance, which ranged between a few $\Omega$ and more than 250 $\Omega$ [133]. Therefore the ZBCP is probably related to the pressure rather than to the contact resistance, and this points towards its relationship with local lattice deformations.

Apart from the zero-bias anomaly, the spectra measured by Yates et al. in NdFeAsO$_{0.85}$ show conductance maxima in the low-pressure ZBCP-free spectra (bottom curve in figure 22(a)) which evolve smoothly into shoulders in the high-pressure ones (top curve in figure 22(a)). The position of these features is robust against pressure and, if taken as an indicator of the gap amplitude, it gives $\Delta = 7$ meV corresponding to $2\Delta/k_B T_c = 3.57$. A BTK fit (in s-wave symmetry) of the bottom spectrum in figure 22(a) gives $\Delta \approx 6$ meV. In F-doped Nd-1111 (NdFeAsO$_{0.85}$F$_{0.15}$) [129], the low-temperature spectra are sometimes featureless (bottom curve in figure 22(b)) but more often display conductance peaks at $V = (5-7)$ mV and shoulders at $V = 10$ mV (top curve in figure 22(b)), which makes them strikingly resemble the PCAR spectra in MgB$_2$. Indeed, they were rather well fitted by a two-band BTK model where $G = G_1 + (1 - \alpha)G_2$, $G$ being the normalized junction conductance and $\alpha$ the (unknown) weight of the contribution of band 1. The best-fitting values of the gaps are $\Delta_1 \approx 4-6$ meV and $\Delta_2 \approx 9-13$ meV that, being $T_c = 45$ K, imply gap ratios of 2.6 and 5.7, respectively. Multigap features were clearly observed in Tb-1111 [128], in the form of peaks at about 4.5 and 8 meV (see the top curve in figure 22(c)). The two-band BTK fit of the spectra gave, at low temperature, $\Delta_1 = 5-6$ meV and $\Delta_2 = 8-9$ meV. The PCAR measurements carried out by Wang et al. in polycrystalline SmFeAsO$_{0.85}$F$_{0.15}$ gave two distinct families of spectra, with conductance maxima in different positions. Two of them, with no ZBCP, are shown in figure 22(d). Their fit with a single-band d-wave model gave $\Delta_1 = 10.5 \pm 0.5$ meV and $\Delta_2 = 3.7 \pm 0.4$ meV [126]. Similar gap values were given by the two-band d-wave fit of the only spectrum with clear two-gap structures (and a ZBCP). However, the spectra shown in figure 22(d) also admit a two-band BTK fit in s-wave. Although the very small amplitude of
the signal requires huge values of the broadening parameters, the two s-wave gaps $\Delta_1 \simeq 5 \text{ meV}$ and $\Delta_2 = 14-18 \text{ meV}$ can be obtained, which are much higher than those given by the single-band d-wave fit.

The high-resistance spectra measured by Chen et al in Sm-1111, showing no ZBCP up to $T_A$, can be fitted in the whole temperature range with an s-wave BTK model. The raw conductance curves reported in [130] feature a characteristic left–right asymmetry—also observed in Nd-1111 by Samuely et al [129] and by us in La-1111 [132] and Sm-1111 [134]—probably intrinsic to these materials, as it was in the case of cuprates [5]. The normalized spectra (of which three examples are reported in figure 22(e)) have a very high Andreev signal, always show clear conductance peaks at $V \simeq \pm 7 \text{ meV}$ related to a superconducting gap and often also display additional structures at higher energy that were seen by the authors as extrinsic features and thus disregarded in the fitting procedure. The single-band BTK fit done in [130] clearly reproduces only the two peaks at about 7 meV and, in the best cases, the zero-bias minimum between them. The resulting gap is very robust against the contact resistance and turns out to be almost perfectly BCS, i.e. $\Delta = 6.67 \pm 0.15 \text{ meV}$ at low $T$, corresponding to $2\Delta/k_B T_c = 3.68$.

The existence of a single BCS gap in iron pnictides is actually surprising since, at the present state of knowledge, there seems to be no possible weak-coupling mechanism able to justify the high $T_c$ of these compounds. The electron–phonon coupling is very weak [136] while the coupling mechanisms mediated by spin fluctuations [137] proposed for these materials require a strong interband coupling, and are rather unlikely to give the same BCS gap on all the sheets of the Fermi surface. On the other hand, many results, not only from PCAR, speak in favor of a multiband picture. The same spectra measured by Chen et al may also give indications of multiple gaps, if the additional shoulders at $V > V_{\text{peak}}$ are interpreted as the hallmarks of a larger superconducting gap. This interpretation is questioned by Chen et al because the position and the amplitude of the additional features are contact-dependent [135]. This argument holds in conventional superconductors but, for example, it does not in MgB$_2$ (where the observability of the $\Delta_c$ peaks actually depends on the current direction) or in cuprates (where a large spatial inhomogeneity in the gap values has been observed by STM [138]).

The differential conductance curves measured in ‘soft’ point contacts on SmFeAsO$_{1-x}$F$_x$ polycrystals synthesized at high pressure with $x = 0.20$ ($T_c = 52 \text{ K}$) and $x = 0.09$ ($T_c = 42 \text{ K}$) [134] generally look very similar to those by Chen et al and always present two clear conductance peaks and additional shoulders that we chose not to disregard in the fit. Similar structures, even more marked, were observed by soft PCAR in LaFeAsO$_{1-x}$F$_x$ polycrystals with bulk $T_c = 27 \text{ K}$. The normalization of the spectra prior to fitting is complicated by the fact that: (i) the normal-state spectrum at $T < T^*_c$ is not accessible due to the high $H_T$ [121] and (ii) the normal state at $T_c$ is not flat but shows a zero-bias hump in Sm-1111 and a pseudogap-like feature in La-1111, both progressively washed out on increasing temperature until, around the Néel temperature of the parent compound (about 140–150 K), the conductance becomes flat (but retains its right–left asymmetry). This suggests that the normal-state conductance may change with temperature also below $T_c$.

In the case of Sm-1111, we chose to divide all curves at $T^*_c$ by the authors as extrinsic features and thus disregarded in the fitting procedure. The single-band BTK fit done in [130] clearly reproduces only the two peaks at about 7 meV and, in the best cases, the zero-bias minimum between them. The resulting gap is very robust against the contact resistance and turns out to be almost perfectly BCS, i.e. $\Delta = 6.67 \pm 0.15 \text{ meV}$ at low $T$, corresponding to $2\Delta/k_B T_c = 3.68$.

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curves still feature an asymmetry that might be due to the normalization (i.e. the asymmetry of the normal state might depend on temperature) or might be an intrinsic feature of these compounds, as it was for cuprates. Certainly, it increases the uncertainty in the gaps ($\Delta_2$ in particular) since the model can only fit either side of the experimental spectrum (in this case, the right-hand one).

The temperature dependence of the gaps in La-1111 and Sm-1111 [132–134] is reported in figures 24(a) and (b). In La-1111 (a), three curves are shown, obtained in contacts with different $T_A^c$ and thus possibly made in regions with different local doping. Note that $T_A^c = 31$ K corresponds to the very beginning of the resistive transition. At low temperature, the large gap $\Delta_2$ decreases on increasing $T_A^c$ and apparently disappears at $T_A^c = 31$ K, while the small gap $\Delta_1$ increases. This finding could be compatible with recent predictions of a doping dependence of the gaps [139, 140]; although any conclusion in this sense is definitely premature. The anomalous $T$ dependence of the gaps in La-1111, where $\Delta_2$ seems to close at a $T^* < T_A^c$ above which $\Delta_1$ shows a 'tail', could be due to 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.

This would mean that the superconducting features are progressively weakened starting from the high-bias ones. An indication in this sense is given by the high-temperature curves that are more peaked at zero bias than expected, but if this was the case an apparent decrease in $T_A^c$ with respect to $T_c$ could be expected, which is instead not observed.

Figure 24(b) shows the gap values extracted from the fit of various soft-PCAR curves in Sm-1111 [133, 134]. Here the situation is clearer: $\Delta_1$ almost coincides with that determined by Chen et al [131] (although in our case $T_A^c = 51–53$ K while in [131] $T_c = 42$ K); its values are well reproducible and follow a BCS-like temperature dependence up to $T_A^c$. The trend of $\Delta_2$ versus $T$ in each set of data is compatible with a BCS-like curve, but the absolute values are scattered within a region bounded by two BCS-like curves with $2\Delta_2/k_B T_c = 7–9$. This spread could be both due to the residual asymmetry of the normalized conductance curves and to the uncertainty introduced by the normalization. The possibility has also been explored theoretically that two large gaps exist, of similar amplitude and thus virtually indistinguishable by PCAR [140, 141]. The gaps obtained by fitting Wang’s curves in figure 22(c) (large circles) with a two-band s-wave 2D BTK model turn out to be in agreement with the other results.
In summary, the interpretation of PCAR spectra in 1111 compounds within a multigap picture gives reasonable results, with a certain degree of universality for the different compounds: (i) the low-temperature small gap is a little smaller than BCS in amplitude: $2\Delta_1/k_BT_c$ ranges between 2.23 and 3.44 in La-1111 [132], between 2.54 and 2.95 in Sm-1111 [134] and is around 2.1 in Tb-1111 [128]; (ii) the large gap is larger or much larger than BCS with $2\Delta_2/k_BT_c$ equal to about 4 in Tb-1111, ranging from 6.42 to 8.68 in La-1111 (when $\Delta_2$ is detectable) and from 6.7 to almost 9 in Sm-1111. Such high values are confirmed, among others, by ARPES measurements in Nd-1111 [142] and by infrared ellipsometry in Sm-1111 [143]. They indicate that a non-conventional pairing mechanism is taking place—and indeed they can be obtained within the Eliashberg theory [141] by supposing a spin-fluctuation-mediated pairing mechanism related to the nesting of the Fermi surface [137, 140] and which should give rise to the so-called $\pm$ superconductivity, with nodeless order parameters of opposite sign on the electron-like and hole-like sheets of the Fermi surface. Unfortunately, PCAR in polycrystals cannot give indications about this expected $\pi$-phase change. A definite answer to the single-gap versus multigap debate could come from ARPES, while phase-sensitive techniques are needed to establish whether the symmetry is really $\pm$, but probably these developments will need the growth of large enough single crystals. It must be said that preliminary measurements in $ab$-plane contacts on Sm-1111 single crystals [144] have perfectly confirmed the results mentioned here [134], supporting the existence of two nodeless gaps.

The 122 compounds have been soon grown in the form of large crystals, with markedly layered structure and easily cleavable. ARPES measurements [120] in (Ba, K)Fe$_2$As$_2$ gave unambiguous evidence of multiple nodeless gaps ($\Delta_2 \simeq 12$ meV on the two small hole-like and electron-like FS sheets, and $\Delta_1 \simeq 6$ meV on the large hole-like FS). Directional PCAR measurements with a Pt tip were performed in hole-doped Ba$_{0.55}$K$_{0.45}$Fe$_2$As$_2$ single crystals by the Slovak group [145, 146]. The majority of $ab$-plane point contacts showed a broadened Andreev-reflection feature at zero bias (but no ZBCP) and a pseudogap-like feature in the normal state that persists well above $T_c^d$ and is very similar to that observed in La-1111 [132].

As in La-1111, it is not clear whether the contemporaneous observation of superconducting signatures and a pseudogap-like feature means that they spatially coexist or, instead, they belong to spatially separated superconducting and antiferromagnetic phases [147].

In some contacts, clear double-gap structures were observed, i.e. symmetric peaks at $\pm 2$–$4$ meV and additional shoulders at higher energy (about 10 meV) as in figure 25(a). In these contacts, the normal-state spectrum at $T_c^d$ showed a broad hump at zero bias (bottom curve in figure 25(a)). The conductance curves were then normalized to the normal-state spectrum and fitted with success to a two-band BTK model, as shown in figure 25(b). The low-temperature gaps obtained in several contacts are $\Delta_1 \simeq 2.5$–$4$ meV and $\Delta_2 \simeq 9$–$10$ meV, corresponding to gap ratios $2\Delta_1/k_BT_c = 2.5$–$4$ and $2\Delta_1/k_BT_c = 9$–$10$. Both $\Delta_1$ and $\Delta_2$ were found to follow rather well a BCS-like trend and to close at the same $T_c^d$ (see figure 25(c)). The values of these gaps differ from those observed by ARPES in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [120] $\Delta_1 \simeq 6$ meV and $\Delta_2 \simeq 12$ meV but this difference is partly justified by the different $T_c$ of the samples ($T_c = 37$ K in [120] and $T_c^d = 23$ K in [145]).

The filling effect cannot be simply explained by the thermal broadening of the spectra and continues up to about 70–80 K, the temperature at which the magnetic transition in the system takes place [148].

No trace of gap features were instead observed in $c$-axis contacts (figure 25(d)), but only a V-shaped conductance progressively filled on increasing temperature, with no apparent signature of the $T_c$ crossing. The filling effect cannot be simply explained by the thermal broadening of the spectra and continues up to about 70–80 K, the temperature at which the magnetic transition in the system takes place [148].

This marked anisotropy of the spectra is interesting and it is tempting to associate it with an anisotropy of the FS. However, the 122 compounds seem to have a nearly-3D FS [139, 149] so that the complete absence of gap signature along the $c$ direction is difficult to explain; moreover, as the authors discuss, the inability to observe the gaps in $c$-axis contacts might be as well related to surface contamination or reconstruction.

PCAR measurements were also carried out in the electron-doped system Ba(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$ with bulk $T_c =$ Figure 25. (a) An example of spectra at low temperature (top line) and at $T_c^d$ (bottom line) measured in $ab$-plane contacts in hole-doped Ba-122. (b) The normalized curve (thick line) and the relevant two-gap BTK fit (thin line). (c) Temperature dependence of the gaps. (d) Typical spectra measured in $c$-axis contacts, at low temperature (4.5 K), just above $T_c$ (30 K) and well above $T_c$ (60 K). All the data are adapted from [145] and [146].
23 K [146]. No multigap features were ever observed in this material; the spectra allowed instead a fit to a standard BTK model, although with large broadening, which gave a single isotropic gap of about 5–6 meV. However, ARPES measurements in the same system Ba(Fe12O19)2As2 (\(T_c = 25.5\) K) gave evidence of two nodeless gaps \(\Delta_1 = 4.5\) meV and \(\Delta_2 = 6.7\) meV [150]. Evidence of multiple gaps has also been observed in recent (preliminary) soft-PCAR measurements in the same material.

5.4. PCS and PCAR in borocarbides

Since their discovery in 1994, borocarbides with the formula \(\text{RET}_2\text{B}_2\text{C}_2\) (RE = rare earth, T = transition metal, usually Ni) have been the subject of intensive study. Their crystal structure resembles that of high-\(T_c\) cuprates but their electronic properties are rather those of 3D metals. Point-contact measurements have been performed in these materials both to determine the electron–boson spectral function (which allows clarifying the nature of the superconducting coupling) and to investigate the symmetry of the superconducting state and/or the possibility of multiband superconductivity.

Among the non-magnetic quaternary borocarbides, \(\text{YNi}_2\text{B}_2\text{C}\) is probably the most widely studied. Initially claimed to be an \(s\)-wave superconductor, it has later been found to display a large anisotropy in the superconducting state but basically isotropic normal-state properties, which suggests an anisotropic order parameter. The proposed symmetries were \(s+g\) (or anisotropic \(s\)-wave), with point nodes in the \(ab\) plane (and precisely along the [100] and [010] directions) and the \(d\)-wave symmetry, with nodes both in the \(ab\) plane (in the [100] and [010] direction) and along the \(c\) axis (where instead the \(s+g\) gap has a finite value). However, already in 1998, well before the discovery of MgB2, Shulga et al [151] proposed a two-band model to explain the temperature dependence of the critical fields measured in \(\text{YNi}_2\text{B}_2\text{C}\) and \(\text{LuNi}_2\text{B}_2\text{C}\). As we will see in the following, the debate about the structure and the amplitude of the OP (in these compounds is far from being settled, but the multiband scenario is definitely the most supported by the many experimental results.

Low-\(T\) PCS measurements in the normal state of \(\text{YNi}_2\text{B}_2\text{C}\), obtained by suppressing superconductivity with a magnetic field [152, 156] identified a well-resolved maximum in the second derivative \(d^2V/dI^2\) at 12 meV that corresponds to a soft phonon mode contributing to about 90% of the total electron–phonon coupling. Other phonon peaks at 20, 24 and 32 meV were not observed. This indicates a superconducting coupling mainly mediated by soft phonons, which usually makes an unconventional gap symmetry rather unlikely. Gap measurements in the superconducting state were carried out by PCAR in single crystals [152, 153, 157] and \(c\)-axis-oriented films [158]. In single crystals with \(T_c = 14.6\) K Raychaudhuri et al performed directional PCAR measurements by injecting the current either along the \(a\) or the \(c\) axis. Their conductance curves always admitted a single-band BTK fit that, however, gave clearly different gaps, i.e. a small \(\Delta_{1ab} = 0.37-0.49\) meV and a much larger \(\Delta_{1c} = 1.8-2.2\) meV. The ratio \(\Gamma/\Delta\) was found to be larger for \(I \parallel a\), possibly indicating (see section 4.3.4) a greater angular variation of the gap for \(ab\)-plane contacts, as expected for a \(s+g\) symmetry [153]. The temperature dependence of the large gap, which closes at \(T_c^A = T_c = 14.6\) K, was found to slightly deviate from a BCS-like curve (solid circles in figure 26(a)), which in principle is compatible with a gap with nodes. However, the small gap \(\Delta_{1ab}\) was found to be rapidly suppressed on heating, falling below a BCS-like curve with \(T_c = 14.6\) K (dashed line in figure 26(a)) and to become undetectable above 8 K. The recent measurements of \(\Delta_{1ab}\) down to 300 mK carried out by the same group and shown in figure 26(a) (solid squares) indicate that, for \(T \lesssim 3.5\) K, this gap follows very well a BCS-like curve with \(T_c = 4.75\). As remarked by the authors [153], this temperature dependence is inconsistent with a \(s+g\) symmetry or with any gap function of the form \(\Delta(k) = \Delta_0 f(k)\), and is indeed more compatible with a picture in which the two gaps open on different, weakly coupled bands [38] (see figure 11). The magnetic field dependence gives similar results [157], i.e. the small gap \(\Delta_{1ab}\) is rapidly suppressed by the magnetic field and ‘disappears’ well below \(H_{c2}^{ab}\). This is very similar to
what happens in MgB$_2$ when the diffusivities in the two bands are different [71]. Also the zero-bias DOS, calculated by using $N(E) = \text{Re}[(E + i\Gamma)/\sqrt{(E + i\Gamma)^2 - \Delta^2}]$ and taking $E = 0$, increases with field [157] in a way similar to that predicted by the two-band model for dirty superconductors [71]. If this is the case, the fact that the small gap almost only contributes to the conductance for $I \parallel a$ suggests that it opens on the nearly cylindrical, fast-electron Fermi surface sheets that have the maximum cross section (and dominate the conductance) for $I \parallel a$ but play almost no role for $I \parallel c$ [157]. The multiband picture is also strongly supported by the effect of non-magnetic (Pt) doping on the critical temperature and the upper critical field [159]. The decrease of both $T_c$ and $H_{c2}$ (the latter for either orientations of the field, $H \parallel a$ or $H \parallel c$) and their subsequent saturation on increasing doping was indeed shown to be explainable, within a two-band picture, as being due to an increase in interband scattering as in doped MgB$_2$ [159]. Going back to PCAR measurements, further support to the multiband picture also came from the magnetic field dependence of the excess current $I_{exc}$ obtained by integrating the normalized PCAR spectra in YNi$_2$B$_2$C $c$-oriented films [158] and single crystals [152, 154]. As in MgB$_2$ (see figure 16(d)) $I_{exc}(B)$ shows a positive (although small) curvature. In these measurements, however, the small gap measured by Raychaudhuri et al was never seen. The conductance curves were found to display only one peak (at either positive or negative bias) and were thus fitted to a single-band BTK model giving a distribution of gap values. In single crystals with $T_c = 15.4$ K Naidyuk et al [152] found for the $a$ axis $\Delta_{[100]} = 1.5$–1.7 meV, for the $c$ axis $\Delta_{[001]} = 1.8$–2.5 meV and for the [110] direction $\Delta_{[110]} = 1.0$–2.5 meV. A representative temperature dependence of the gaps for $I \parallel a$ and $I \parallel b$ is shown in figure 26(a) as open symbols.

In LuNi$_2$B$_2$C single crystals, PCAR measurements carried out by Bobrov et al [160] gave spectra with a single conductance peak that was, however, shown to be poorly fitted by a single-band BTK model, and a little better, but still unsatisfactorily, by a two-band one. Two different continuous distributions of gap values were thus used to reproduce the shape of the low-temperature spectra, with $\Delta_{1/2ab}$ ranging between 1 and 3.35 meV (with maxima at 2 and 3.1 meV) and $\Delta_{1/2c}$ ranging from 0.7 to 4 meV (with maxima at 1.8–2 and 2.5 meV). In [154, 161], a more conventional two-gap approach was used to fit the data in either direction, although the spectra always featured a single conductance peak—possibly because the two gaps are too close to each other to be clearly distinguishable. As shown in figure 26(b), a qualitatively similar (but quantitatively different) gap trend as a function of temperature was observed for $I \parallel ab$ (squares) and $I \parallel c$ (circles). The results seem to indicate the existence of two bands with a weak, anisotropic interband coupling [38]. In a more recent PCAR study in LuNi$_2$B$_2$C single crystals [162] the spectra were fitted to a single-band BTK model and gave almost equal gaps in the [001] ($c$ axis, $\Delta_{[001]} \simeq 2.4$ meV) and [110] directions ($\Delta_{[110]} \simeq 2.6$ meV). Both these gaps approximately follow a BCS-like temperature dependence with $2\Delta/k_BT_c$ equal to 3.4 and 3.6, respectively—although an upward deviation of the experimental points was observed at low temperature, as in films [160]. These results may be compatible with those by Naidyuk et al [154] in the ab plane, since the single-band fit can reasonably give an ‘average’ gap with respect to the two-band fit and is probably only weakly sensitive to the faster depression of the small gap. Along the $a$ axis, a rather wide distribution of gap values $\Delta_{[100]} = 1.6–2.5$ meV was observed, all disappearing at the bulk $T_c$—surprisingly similar to the findings by Bashlakov et al [158] in YNi$_2$B$_2$C films.

Various other compounds of the family were studied by PCS in the normal state and PCAR, especially by the Ukrainian group, and it would be impossible to account here for all their results. Let us just briefly mention for its interest the magnetic compound HoNi$_2$B$_2$C with a low-temperature commensurate AFM state whose Néel temperature $T_N = 5.3$ K is smaller than $T_c = 8.5$ K. PCS measurements of $\alpha_{PCS}^2 F(\omega)$ allowed identifying structures at 16, 22, 34 and 50 meV, corresponding to peaks in the photon DOS of isostructural LuNi$_2$B$_2$C, plus a peak at 3 meV related to the magnetic ordered state and indeed disappearing at $T_N$, and a peak at 10 meV possibly due to a coupling of carriers to crystal field excitations [156, 163] (see figure 27). PCAR spectra in the superconducting state first of all showed a negligible dependence on the current direction and admitted a single-band BTK fit; the low-temperature gap is $\Delta_0 = 0.95$ meV, and decreases on increasing temperature following a BCS-like curve but disappears at $T^*_c = 5.6$ K, well below $T_c$. Between $T^*_c$ and $T_c$, an unconventional gapless state was proposed, possibly due to the peculiar spiral magnetic order in this temperature range. Below $T_N$, the superconducting state coexists with an antiferromagnetic order. To explain this phenomenon, a separation of the two phases in the $k$ space has been proposed. In particular, superconductivity below $T_N$ should survive only on a single (isotropic) sheet of the FS with no contributions from the Ho 5d states. This picture has been directly put in connection with the results of critical field and anisotropy measurements as a function of temperature in the same compound [164].
More recently, PCAR measurements have been performed in the ErNi$_2$B$_2$C compound [155], with $T_c = 11$ K and a low-temperature incommensurate antiferromagnetic order with spin density wave between 2 K and $T_N \approx 6$ K. To account for the magnetic pair-breaking effect, a suitable model by Beloborod’ko [165] was used to fit the spectra. The model contains as adjustable parameters $\Delta$ (order parameter, OP), $Z$ (barrier height) and $\gamma$ (magnetic scattering rate). The gap $\Delta_0$ is related to the OP by the formula $\Delta_0 = \Delta(1 - \gamma/2)^{3/2}$ [165].

The single-band fit of the PCAR spectra as a function of temperature gave $\Delta(T = 2$ K) $\approx 1.8$ meV for both $I \parallel ab$ and $I \parallel c$. A two-band fit was also carried out because of the claimed unsatisfactory quality of the single-band one. This fit gives two OPs $\Delta_1 \approx 2$ meV and $\Delta_2 \approx 1.2$ meV whose temperature dependence is shown in figure 26(c). The anisotropy in this case is small, but a very unconventional behavior is observed because of the AFM order below $T_N$. The observation of one or two OPs at low temperature clearly proves the coexistence of superconductivity and AFM order, also observed by laser photoemission. On heating, $\Delta_1$ and $\Delta_2$ first increase (possibly because of the weakening of the AFM order), which is consistent with previous findings by tunnel and laser photoemission spectroscopy as well as with the prediction of some theories of coexistence of superconductivity and antiferromagnetic states [166]. In the paramagnetic state above 6 K, the OPs follow BCS-like curves (whose extrapolation would give $T_{c1} \approx 11.3$ K and $T_{c2} \approx 14.5$ K) and finally abruptly disappear at $T_c = 11$ K. The extrapolated $T_c$ values give for both OPs a ratio $2\Delta/k_BT_c$ in the strong-coupling regime. To fit the curves, the weight of the larger OP $\Delta_2$ also had to be varied in a non-monotonic way, although it generally decreases on heating. The magnetic scattering rates also evolve non-trivially as a function of temperature, and $\gamma_2$ is always greater than $\gamma_1$. These results were interpreted as indicating that: (i) different bands are differently affected by magnetic order; (ii) the part of the FS that develops the larger OP $\Delta_2$ tends to diminish on approaching $T_c$ and (iii) there is an FS separation with distinct superconducting and magnetic bands (or FS sheets); a more detailed analysis of the results in [155] indicates that approximately half of the FS is nonsuperconducting.

It follows from the above that the result of PCAR measurements in borocarbides carried out by different groups are often in disagreement with one another. Moreover, the coexistence of magnetic orders of some kind and superconductivity in some of these compounds prevents any tentative description of this class of compounds as a whole. Nevertheless, various hints strongly suggest multiband superconductivity, with: (i) a conventional phonon-mediated superconducting coupling (at least in non-magnetic ones); (ii) weak interband coupling (in YNi$_2$B$_2$C [153, 157] and in LuNi$_2$B$_2$C [154, 161]) with different gaps and $T_c$; (iii) a generally anisotropic distribution of gap values over the FS, with a larger gap along the $c$ axis and (iv) a separation of superconducting and magnetic order parameters on different sheets of the FS (in HoNi$_2$B$_2$C [163] and ErNi$_2$B$_2$C [155]). The research in this field is still going on and new measurements will certainly help in clarifying this complex situation.

5.5. PCAR in graphite-intercalation compounds

The recent discovery of the new superconducting graphite-intercalation compounds (GICs) CaC$_6$, YbC$_6$ [167] and SrC$_6$ [168] has renewed the interest for this long-known class of compounds. CaC$_6$ shows the highest $T_c = 11.5$ K among them. Its lattice is made up of alternating graphite layers and Ca planes, with a rhombohedral structure [169]. The similarity with MgB$_2$ is striking and indeed the electronic band structure [170] includes the $\sigma$ and $\pi$ bands, though the former are completely filled and play no role in superconductivity. According to first-principles calculations [171, 172] superconductivity arises from the coupling of both Ca and C phonon modes to the carriers of the so-called interlayer band, which is formed by C and Ca orbitals [170]. The Fermi surface [170] consists of $\pi$-band warped cylinders parallel to the $c$ axis, and of interlayer-band FS sheets created by the intersection of some of these cylinders with the nearly spherical Ca orbitals [31]. Unlike in MgB$_2$ (see figure 12(a)) the calculated gap [31] is continuously distributed in energy between 1.1 and 2.3 meV and the mixing of C and Ca states prevents a true multigap superconductivity. However, the gap mapping on the FS shows that it changes from one FS sheet to the other and, is, on average, slightly larger in the 3D interlayer band (actually depending also on the wavevector $\mathbf{k}$ within each sheet). This suggested we use directional soft PCAR in CaC$_6$ single crystals to observe the predicted anisotropy. The extreme sensitivity of CaC$_6$ to air and moisture required us to cleave the sample and make the contact in an inert atmosphere, and to seal the whole sample holder before transferring it to the cryostat. Due to the small $T_c = 11.5$ K and the smallness of the effect to be observed, part of the measurements were carried out at 400 mK [30].

Figure 28(a) shows a $c$-axis and a $ab$-plane PCAR spectrum at $T = 0.4$ K (symbols). The position of the conductance peaks is clearly different and indeed the fit with a single-band 2D BTK model gives $\Delta_{ab} = 1.44$ meV and $\Delta_c = 1.7$ meV. The values of $Z$ are systematically higher in $c$-axis contacts (0.74 $\leq Z \leq 1.01$) than in $ab$-plane ones (0.48 $\leq Z \leq 0.75$), in agreement with the different Fermi velocities in the two directions ($v_{ab} = 0.54 \times 10^6$ m s$^{-1}$, $v_c = 0.29 \times 10^6$ m s$^{-1}$). These spectra are in excellent agreement with $ab$ initio calculations of the Andreev conductance carried out [30] as described in section 4.3.7, equation (31). To allow a comparison with experiment, the theoretical curves with $T = 0$ (shown in figure 9) were smeared with the experimental values of $\Gamma$ (i.e. 0.6 meV for the $ab$-plane contact and 0.8 meV for the $c$-axis one) neglecting the (much smaller) thermal smearing. The results are shown in figure 28 as solid lines. Figure 28(b) shows that the distributions of low-temperature gap values obtained in several $c$-axis and $ab$-plane contacts are approximatively Gaussian and overlap only slightly. The temperature dependence of the gaps is shown, for the spectra in figure 28(a), in panel (c). The gap always follows a BCS-like trend with gap ratio $\Delta_{ab}/k_BT_c = 2.98$ and $\Delta_c/k_BT_c = 3.48$. All these results gave the first direct evidence of gap anisotropy in CaC$_6$ and showed a very nice example of a successful feedback between PCAR experiments and theoretical predictions from $ab$ initio calculations.
the study of cuprates. With the discovery of MgB_2 in 2001, and momentum resolution largely dominated, in the 1990s, other techniques such as STM and ARPES with better spatial spectroscopic tools in the study of superconductors. However, of normal metals, it was soon understood to be a powerful technique, invented in the mid-1970s and, although initially applied to the study of multiband superconductors, starting from MgB_2 (either pure or doped) to continue with borocarbides, graphite-intercalation compounds and the recently discovered Fe-based superconductors. We have shown that PCAR measurements can provide information on the number, the amplitude and the symmetry of the superconducting order parameter(s), but also—when integrated with first-principles calculations and with the Eliashberg theory—on the coupling strengths (both within and between bands), the scattering rates, the densities of states, the k dependence of the gap within the various sheets of the Fermi surface and so on. We have provided the reader with a simple theoretical introduction to PCS and PCAR spectroscopy, showing how the limitations of the original, pioneering Blonder–Tinkham–Klapwijk model (often used even today to fit the point-contact spectra) can be overcome to improve the degree of approximation to the real case and to make PCAR a much sharper tool for the investigation of unconventional superconductors.

6. Conclusions

Multiband superconductivity was theoretically investigated since the 1960s, but it was often considered as an exotic, although interesting, possibility, with little practical relevance because of the feebleness of its effects even in the very few cases when they were detected, or the very small critical temperature of the materials that displayed them [41]. On the other hand, point-contact spectroscopy was invented in the mid-1970s and, although initially applied to the study of normal metals, it was soon understood to be a powerful spectroscopic tool in the study of superconductors. However, other techniques such as STM and ARPES with better spatial and momentum resolution largely dominated, in the 1990s, the study of cuprates. With the discovery of MgB_2 in 2001, multiband superconductivity suddenly became a promising and popular field of research and PCAR spectroscopy rapidly acquired a great relevance thanks to its quick and successful application to this compound. The amount of information this technique has been able to provide, even in samples that were impossible to analyze by STM and ARPES, was probably a surprise for most of the superconducting community. Since then, and thanks to its reliability, simplicity and flexibility, PCAR spectroscopy has played an important role in the investigation of the superconducting properties of many new (and less new) compounds.

In this review we have tried to present the recent applications of PCS and PCAR spectroscopy to the study of multiband superconductors, starting from MgB_2 (either pure or doped) to continue with borocarbides, graphite-intercalation compounds and the recently discovered Fe-based superconductors. We have shown that PCAR measurements can provide information on the number, the amplitude and the symmetry of the superconducting order parameter(s), but also—when integrated with first-principles calculations and with the Eliashberg theory—on the coupling strengths (both within and between bands), the scattering rates, the densities of states, the k dependence of the gap within the various sheets of the Fermi surface and so on. We have provided the reader with a simple theoretical introduction to PCS and PCAR spectroscopy, showing how the limitations of the original, pioneering Blonder–Tinkham–Klapwijk model (often used even today to fit the point-contact spectra) can be overcome to improve the degree of approximation to the real case and to make PCAR a much sharper tool for the investigation of unconventional superconductors.

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