Point-Contact Andreev-Reflection Spectroscopy in the Fe-based Superconductor LaFeAsO$_{1-x}$F$_x$

**M. Tortello · D. Daghero · G.A. Ummarino ·
R.S. Gonnelli · V.A. Stepanov · J.S. Kim**

Abstract Point-contact Andreev-reflection (PCAR) spectroscopy measurements have been performed in the Fe-based superconductor LaFeAsO$_{1-x}$F$_x$ in order to investigate the energy gaps. The Andreev spectra show clear and reproducible features that could be related to two nodeless gaps. Their values, as determined by fitting the conductance curves measured in junctions with local $T_c = 27.3$–28.6 K within the two-band BTK model, are $\Delta_1 = 2.75$–3.8 meV for the small gap and $\Delta_2 = 7.9$–10.2 meV for the larger one, respectively. The absence of zero-bias conductance peaks and considerations regarding the nonperfectly directional current injection in PCAR experiments and the polycrystalline nature of the samples rule out the possibility of nodal gaps in the superconductor. Moreover, the conductance curves show pseudogap-like features coexisting, at low temperature, with superconductivity and disappearing close to the Néel temperature of the parent compound, $T_N \approx 140$ K.

Keywords Fe-based superconductors · Point-contact Andreev-reflection spectroscopy · Energy gaps · Iron pnictides

M. Tortello · D. Daghero · G.A. Ummarino · R.S. Gonnelli (✉)
Dipartimento di Fisica and CNISM, Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Turin (TO), Italy
e-mail: renato.gonnelli@polito.it

V.A. Stepanov
P.N. Lebedev Physical Institute, Russian Academy of Sciences,
Leninskii Prospekt 53, 119991 Moscow, Russia

J.S. Kim
Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart,
Germany

1 Introduction

The report by Kamihara et al. that F-doped LaFeAsO oxypnictide becomes superconducting at ≈ 26 K [1] opened the way to the discovery of the new class of high T_c Fe-based superconductors with T_c up to ≈ 56 K [2–6]. Now, approximately one year after this first report, a huge research activity has been carried out by the scientific community (for a review, see [7]). The main reasons for this interest most probably rely on the relatively high T_c that these new compounds show and on some similarities (although important differences exist) with the well-known but still not fully understood high T_c cuprates. Up to now, the most intensively studied Fe-based superconductors belong to two main "families," according to their formula unit, i.e., 1111 compounds (REFeAsO$_{1-x}$F$_x$, where RE = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Y) and 122 ones (doped AFe$_2$As$_2$, where A = Ba, Sr, Ca, Eu).

As in cuprate superconductors, superconductivity occurs upon charge doping a magnetic parent compound, which, in this case and unlike cuprates, is semimetallic and shows an antiferromagnetic (AFM) spin-density-wave (SDW) order and a tetragonal to orthorhombic structural transition below a certain temperature (≈ 140 K for LaFeAsO) [8]. Charge doping breaks the long-range magnetic order, and superconductivity appears. Another difference with respect to cuprates is the multi-band character of the Fermi surface [9], which is similar in the two families and features, as revealed by nonmagnetic first-principle DFT calculations, two or more hole-like Fermi sheets near the Γ point and two electron-like sheets near the M point [10]. While DFT calculations (also in this case performed assuming a nonmagnetic ground state) revealed that the electron–phonon coupling is not sufficient to reproduce the observed experimental T_c [11], the electronic structure looks favorable to

a spin-fluctuation mediated superconducting pairing mechanism, which leads to an extended s-wave symmetry with an interband sign reversal of the order parameter, called $s_{\pm}$ symmetry [12]. It is worth noticing that, although the knowledge of the magnetic properties in these compounds still needs much improvement (especially concerning whether the theory has to be based on localized quantum magnetism or on itinerant paramagnons), the proposed $s_{\pm}$ symmetry is obtained in both cases [10].

In this regard, in order to understand the microscopic mechanism responsible for superconductivity in Fe-based superconductors, the knowledge of the number, amplitude, and symmetry of the superconducting gaps is a fundamental step.

Angle-resolved photoemission spectroscopy (ARPES), scanning tunneling (STM), and PCAR spectroscopy are certainly among the most powerful experimental techniques for the determination of the energy gaps. Many experiments using these techniques have been already performed; however, results often disagree with each other, and the actual picture concerning the gaps is far from being conclusive.

Up to now, the clearest result comes probably from ARPES measurements performed in a 122 compound with $T_c \approx 37$ K [13], which showed the presence of a multi-gap scenario where different gaps opens on different Fermi surface sheets and whose values cluster around 6 and 12 meV. Many other results are present which point towards a multigap picture in Fe-based superconductors [14–22]. As for PCAR spectroscopy, results up to now are still quite contradictory and presenting both a single [23–25] and a multi-gap [15–18] picture whether in the d-wave symmetry [22, 24] or with nodeless gaps [15–18, 23, 25].

Here we report PCAR spectroscopy measurements in the La-1111 Fe-based superconductor that clearly show the presence of two-nodeless gaps with ratios $2\Delta_1/k_B T_c = 2.2$–3.2 and $2\Delta_2/k_B T_c = 6.4$–8.7 for the small and the larger one, respectively. Furthermore, the absence of zero-bias conductance peaks (ZBCPs) and the comparison of the obtained PCAR spectra with the model for Andreev-reflection in d-wave symmetry allow us to rule out the presence of nodal gaps in LaFeAsO$_{1-x}$F$_x$.

2 Experimental

The LaFeAsO$_{1-x}$F$_x$ polycrystalline samples were prepared at the Max-Planck-Institut für Festkörperforschung, Stuttgart, starting from LaAs, FeO$_3$, Fe, and LaF$_3$, and were grown by solid state reaction with nominal composition of $x = 0.1$ (see [26]). The obtained samples, which show a resistive onset transition at $T_c^{on} = 27$ K, consist of different crystallites in a more disordered matrix: the F content is homogenous within each crystallite but can vary from one crystallite to another. Micro EDX (energy-dispersive X-ray spectroscopy) revealed that the variation of the F content is within $\Delta x = 0.02$ in the same sample.

The measurements have been performed by using, instead of the standard point-contact technique where a sharp metallic tip is pressed on the material under study, the "soft" one [27]. In this setup, the point contact is obtained by means of a small drop of Ag conductive paste. As a consequence, no pressure is applied on the sample (this fact is probably important in these compounds [23, 25]), the contact is very stable with temperature, and we could measure in a wide range of temperatures, 1.8–200 K, a task that is much more difficult with the standard technique.

In an N/S junction, when electrons are injected into the superconductor through a small orifice whose size is much smaller (or of the order of) the electron mean free path, ℓ of the superconductor, i.e., through a ballistic contact, then the Andreev reflection phenomenon occurs. Since the value of ℓ is still not accessible in this compound, the clear Andreev features we obtained, the absence of dips [28] and of heating effects, assure that the contacts are in the ballistic limit and that good spectroscopic information can be obtained from the measured conductance curves. The differential conductance curves obtained through ballistic point contacts contain precious information concerning the gap(s) value and symmetry. In order to compare the experimental curves with a model, it is first necessary to normalize the conductance curves by referring them to their normal state value. Since the upper critical field H_{c2} in these compounds is very high, it is not possible to access the low-temperature normal-state conductance. Furthermore, the measured conductance curves show a pseudogap-like feature—already present in the superconducting state and coexisting with the Andreev reflection—which gradually fills until it completely flattens around the Néel temperature $T_N \approx 140$ K of the parent compound [16]. This means that also the normal state curve measured at T_c might not be the most correct one for the normalization. Therefore, as shown in [16], the conductance curves were normalized by means of a B-spline curve which interpolates the "tails" of the conductance at high energies and is connected to a suitable point at zero bias that simulates the dip due to the pseudogap-like features. This method appears as the best solution, and, as reported in more details in [16], it can be shown that, if the normalization procedure is performed by using the normal-state curve measured just above T_c, the variation on the obtained gap values is within 10% for the large gap and 1.5% for the small one, indicating that the choice of the normalization is not crucial for the results.

The normalized conductance curves obtained by means of the above-mentioned procedure have been then fitted with a two-band [29, 30] modified [31] BTK model [32] generalized to take into account the angular distribution of the injection current at the N/S interface [33]. In the two-band
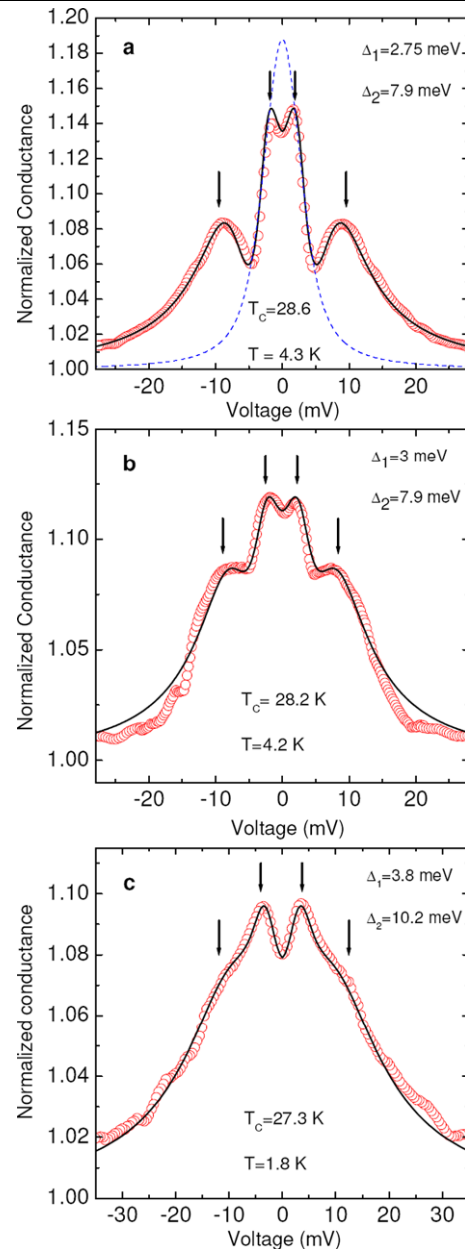
case the conductance curve is the weighed sum of the BTK conductance of each band, $G = w_1 G_1 + (1 - w_1)G_2$, and each BTK conductance G_i is defined by three parameters: the gap value Δ, the broadening parameter Γ, and the Z parameter, which accounts for the potential barrier and the mismatch of the Fermi velocities between the normal metal and the superconductor at the N/S interface.

Furthermore, as explained in more details in the next section, a comparison has been done between the experimental results and a d-wave-gap model [33] in order to consider the possible presence of a nodal gap, the possibility of which is however ruled out by our results.

The above-mentioned inhomogeneous F content, together with the size of the crystallites which is relatively small if compared to the macroscopic size of the point contact, suggests some care in interpreting the data: indeed the occurrence of multiple ballistic contacts on crystallites with different critical temperatures and gap values cannot be, in principle, excluded. This situation has been simulated by averaging over different theoretical Andreev conductances calculated by using parameters typical of our experimental data and Δ and Γ varying over the maximum range observed in our contacts: the resulting curve can be perfectly fitted by using Δ and Γ that are the averages of the starting ones. Thus, the inhomogeneity of F content in the samples does not have dramatic consequences in the determination of the energy gaps and would result, in the worst case, in an average of the gap values over a few different crystallites and in an increase of their uncertainty, especially on the larger one.

3 Results and Discussion

Figure 1 shows some examples of normalized conductance curves (symbols) obtained for different Ag/LaFeAsO$_{1-x}$F$_x$ point-contact junctions prepared as described in the previous section. In all the conductance curves it is clear the presence of two pairs of peaks/structures in the measured PCAR spectra (indicated by arrows). In particular, all spectra feature a pair of peaks around 2–4 meV, related to the small gap, and a second pair of peaks (Fig. 1a, b) or shoulders (Fig. 1c) at about 8–10 meV, related to a possible second gap. It is therefore already evident by eye that a single-gap model is not able to reproduce the whole shape of the measured conductance curves. Solid lines represent the fitting curves obtained with the two-band BTK model: the calculated curves, as can be seen, reproduce very well the experimental ones, and the extracted gap values are $\Delta_1 = 2.75$ and $\Delta_2 = 7.9$ meV for the curve of Fig. 1a, $\Delta_1 = 3$ and $\Delta_2 = 7.9$ meV for the curve of Fig. 1b, and $\Delta_1 = 3.8$ and $\Delta_2 = 10.2$ meV for the curve of Fig. 1c. The broadening parameters Γ are always smaller than the gap, and very often the ratio Γ/Δ is about 0.5. The

Fig. 1 Three examples of low-temperature normalized conductance curves measured in Ag/LaFeAsO$_{1-x}$F$_x$ point-contact junctions (*symbols*) together with their relevant two-band BTK fitting curves (*solid lines*). Figure 1a reports also a single-band BTK fit in d-wave symmetry (*dash line*) obtained by averaging over all $\alpha \in [0, \pi/4]$, where α is the angle between the normal to the interface and the antinodal direction
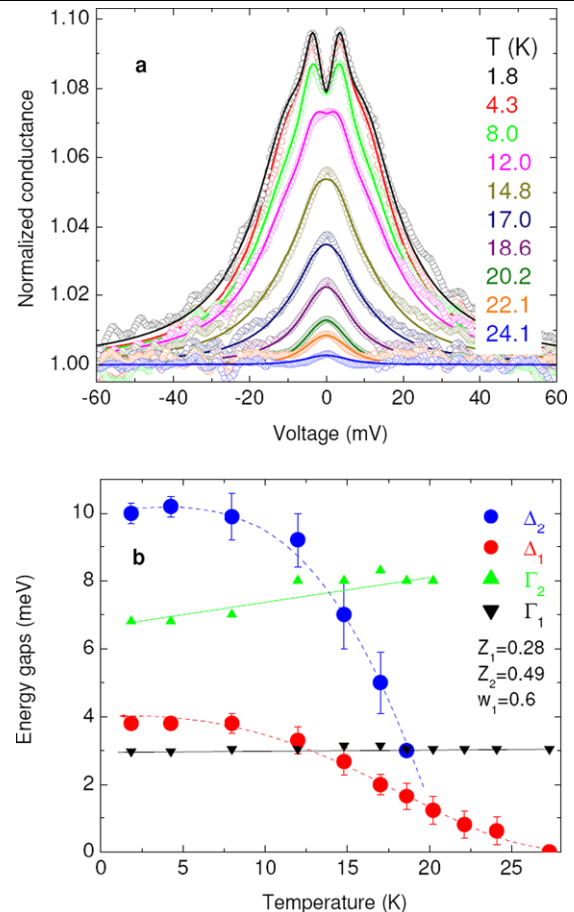
Z parameters are usually smaller in band 1 than in band 2 and are always smaller than 1.

Some PCAR measurements performed in these compounds reported a dependence of the shape of the measured spectra on the contact resistance and therefore on the pressure applied by the tip [23, 25]. This led to the appearance of additional structures in the conductance curves, which very often manifest as ZBCPs and very likely are not related to

the superconducting gaps. These features however are not present in our measurements since, in the "soft" technique, no pressure is applied to the material under study. The absence of ZBCPs in our measurements that are carried out on polycrystalline samples, where the current is randomly injected into the superconductor, allows us to exclude the presence of nodal gaps too. This conclusion can be better understood by analyzing our results within the generalized BTK model in the d-wave symmetry [33]. As a matter of fact, the d-wave symmetry would lead to ZBCPs whenever the angle α between the normal to the interface and the antinodal direction is larger than $\pi/16$. This implies that if we take the best parameters obtained by the fit of our PCAR conductance curves, i.e., $\Gamma/\Delta \approx 0.5$ and $Z \approx 0.3$–0.4, the conductance curves would feature a two-peak structure (as in our experimental results) only when $\alpha < \pi/16$. Clearly, the picture in which all the randomly oriented contacts we create on these polycrystalline samples always allow the current injection within an angle $\alpha < \pi/16$ with respect to the antinodal direction is unrealistic. As an example, Fig. 1a shows a theoretical curve (dash line) calculated with the 3D BTK model in d-wave symmetry [33] and obtained averaging over all $\alpha \in [0, \pi/4]$ compared with the experimental conductance (symbols). The calculated conductance features a pronounced ZBCP which the experimental one does not.

Figure 2a shows an example of temperature dependence of the normalized conductance curves (symbols)—whose low-temperature behavior is shown in Fig. 1c—together with their relevant two-band BTK fitting curves (lines). The theoretical curves can reproduce well the evolution of the Andreev spectra, and the extracted gap values are reported in Fig. 2b. The behavior of the gaps as function of temperature looks rather unconventional: Δ_2 follows approximately a BCS-like curve but apparently closes below T_c or becomes (within the experimental resolution) indistinguishable from Δ_1. This small gap, already below $T_c/2$, differs from the BCS trend and closes with a sort of tail-like shape, common to all the contacts we measured. It is worth noticing that from our measurements we obtain a gap ratio $\Delta_2/\Delta_1 \approx 3$. This ratio cannot be obtained within the $s_\pm$ model by considering only two bands: at least three effective bands should play a role [10, 34], and probably some intraband contribution, maybe small, should be considered as well, depending on the gap values [10].
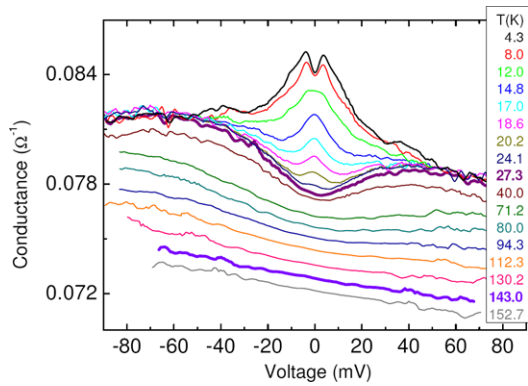
Besides the presence of two nodeless gaps, our PCAR measurements performed up to ≈ 200 K revealed another interesting feature, which can be seen, for example, in the conductance curves reported in Fig. 3: the curves are asymmetric and show pseudogap-like features with two broad humps at ≈ 50–60 meV and a depression of the conductance at zero bias. These structures, which are present also below T_c and coexist with superconductivity, gradually fill with increasing

Fig. 2 (**a**) Temperature dependence of the normalized conductance curves obtained in an Ag/LaFeAsO$_{1-x}$F$_x$ point-contact junction (*symbols*). *Solid lines* are the two-band BTK fitting curves. (**b**) Temperature dependence of the energy gaps obtained by fitting the curves shown in Fig. 1a (*symbols*). The broadening parameters Γ_1 and Γ_2 used in the fitting procedure (*down* and *up triangles*, respectively) slightly increase or remain constant. *Dash lines* are only a guide to the eye. The *legend* reports also the values of Z_1, Z_2, and w_1, which are constant with temperature

temperature until they disappear close to the Néel temperature of the parent compound $T_N \approx 140$ K while leaving the conductance still asymmetric. The shape of this pseudogap-like feature is very similar to that observed in point-contact spectroscopy measurements in URu$_2$Si$_2$ [35], a material which exhibits a long-range SDW order. This static long-range SDW order is certainly not present in the superconducting Fe-based compounds. Nevertheless: (i) the fact that these peculiar features of the PCAR conductances disappear close to TN; (ii) the sensitivity of the PCS technique to electron dynamics on a short time scale and (iii) recent theoretical results which consider the opening of a pseudogap in 2D systems in presence of local AF fluctuations [36], indicate the possible existence of spin fluctuations coexisting with superconductivity in LaFeAsO$_{1-x}$F$_x$ [16].

Fig. 3 Temperature dependence of the raw (unnormalized) conductance curves measured in an Ag/LaFeAsO$_{1-x}$F$_x$ point-contact junction up to $\approx$150 K. The *curves* show, already in the superconducting state, pseudogap-like features, which gradually fill and disappear close to the Néel temperature of the parent compound, $T_N \approx 140$ K. The *upper thick line* denotes the superconducting critical temperature of the junction, while the *lower one* denotes the temperature at which the pseudogap-like features disappear

4 Conclusions

In conclusion, we reported PCAR spectroscopy measurements in the La-1111 superconductor LaFeAsO$_{1-x}$F$_x$ which show the presence of a pair of peaks related to a small superconducting gap Δ_1 plus another pair of peaks or shoulders possibly related to a second, larger gap Δ_2. The spectra can be fitted well within a two-band BTK model with two nodeless gaps and a ratio $2\Delta_1/k_B T_c = 2.2$–3.2 has been obtained for the small gap and $2\Delta_2/k_B T_c = 6.4$–8.7 for the larger one. The temperature dependence of the two gaps, Δ_1 and Δ_2, has been obtained and shows a rather unconventional behavior, with Δ_1 featuring a sort of tail-like shape near T_c and Δ_2 apparently closing below the critical temperature of the junction.

Furthermore, by comparing experimental results with a *d*-wave gap model, it has been shown that the absence of ZBCPs in our measured conductance spectra and the polycrystalline nature of the samples and the noncompletely directional current injection in PCAR experiments rule out the possibility of a nodal gap in these compounds.

Finally, all the spectra we measured show pseudogap-like features which are present in the superconducting state and persist up to the Néel temperature of the parent compound $T_N \approx 140$ K.

These results bring important information concerning the physics of these fascinating and newly discovered superconductors while, at the same time, reveal their complexity and the important role that magnetism could play in determining many of their properties, including superconductivity.

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