Possible two-gap superconductivity in NdFeAsO$_{0.9}$F$_{0.1}$ probed by point-contact Andreev-reflection spectroscopy

P Samuely$^1$, P Szabó$^1$, Z Pribulová$^1$, M E Tillman$^2$, S L Bud’ko$^2$ and P C Canfield$^2$

$^1$ Centre of Low Temperature Physics, IEP Slovak Academy of Sciences and P J Šafárik University, Watsonova 47, SK-04001 Košice, Slovakia
$^2$ Ames Laboratory and Iowa State University, Ames, IA 50011, USA

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Abstract

Systematic studies of the NdFeAsOF superconducting energy gap using point-contact Andreev-reflection (PCAR) spectroscopy are presented. At low temperatures the PCAR conductance spectra show a pair of gap-like peaks at about ±(4–7) mV and in most cases also a pair of humps at around ±10 mV. Fits to the s-wave two-gap model of the PCAR conductance allowed to determine two superconducting energy gaps in the system. However, the energy-gap features disappear at $T^* = 15$–20 K, much below the particular $T_c$ of the junction under study. At $T^*$ a zero-bias conductance (ZBC) peak emerges, which at higher temperatures usually overwhelms the spectrum with an intensity significantly higher than the conductance signal at lower temperatures. Possible causes of this unexpected temperature effect are discussed. In some cases the conductance spectra show just a reduced conductance around the zero-bias voltage, the effect persisting well above the bulk transition temperature. This indicates the presence of a pseudogap in the system.

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

1. Introduction

As the field of superconductivity nears its 100th anniversary, the discovery of high temperature superconducting iron-based pnictides is a significant breakthrough [1]. REFeAsO(F) systems with various rare earth (RE) elements bring a new class of layered high-$T_c$ materials having numerous similarities to high-$T_c$ cuprates, from antiferromagnetism in parent compounds (albeit metallic), through electron and hole doping as a route leading to superconductivity, to a possible unconventional pairing mechanism. NdFeAsO$_{0.9}$F$_{0.1}$, with $T_c$ above 51 K [2], together with the Sm and Pr compounds reveal the highest transition temperature at ambient pressure among all pnictides. One of the most fundamental issues for unveiling the superconducting mechanism of these multiband systems concerns the symmetry of the superconducting order parameter(s). There are numerous theoretical predictions on this topic and a body of experimental studies is also emerging. Band structure calculations have shown disconnected sheets of the Fermi surface with possibly different superconducting energy gaps. A minimal model has to include two bands: the hole band around the $\Gamma$ point and the electron one around the $M$ point [3]. In contrast to the multiband but conventional s-wave scenario in MgB$_2$ [4], here the extended s-wave pairing with a sign reversal of the order parameter between different Fermi surface sheets has been proposed by Mazin et al [5]. The iron pnictides would be the first example of a multigap superconductor with a discontinuous sign change of the order parameter phase between bands. Li and Wang [6] have proposed that the pairing occurs in the d-wave channel where, by lowering the temperature, the system enters first the $d_{x^2-y^2}$ superconducting phase and then the time-reversal symmetry-broken $d_{x^2+y^2} + id_{x'y'}$ superconducting phase.

Early experimental results are starting to provide some insight as well. The $H_{c1}$ magnetization measurements on F-doped LaFeAsO [7] suggest a nodal gap function showing a clear linear temperature behavior at low temperatures. Matano et al [8] in their NMR studies on PrFeAsOF found two superconducting energy gaps, but in contrast to the case of MgB$_2$ here with nodes. Penetration depth studies provided the
nodeless superconducting energy gap in NdFeAsO$_{0.9}$F$_{0.1}$ with remarkably small coupling $2\Delta/k_BT_c \approx 2$ [9].

Point-contact Andreev-reflection (PCAR) spectroscopy has been a very powerful technique in investigating the superconducting order parameter even in the case of multiple gaps like in MgB$_2$ [4]. The PCAR spectroscopy data for pnictides so far have brought conflicting results. Shan et al [10] found a very pronounced zero-bias conductance peak ascribed to the Andreev bound states (d- or p-wave pairing) accompanied by weak signatures of the superconducting energy gap indicating weak coupling with $2\Delta/k_BT_c$ equal to about 3.5. Chen et al [11] have presented a surprisingly conventional superconducting energy gap with a medium coupling equal to $2\Delta/k_BT_c \approx 3.7$. The recent data of Yates et al [12] obtained on 45 K NdFeAsO$_{0.85}$ also show an indication of the superconducting energy gap with $2\Delta/k_BT_c = 3.6$.

In the following we present systematic PCAR studies on the NdFeAsO$_{0.9}$F$_{0.1}$ polycrystals, indicating a two-gap s-wave superconductivity in the system. In the conductance spectra the smaller gap is pronounced in the form of two peaks positioned symmetrically at $\pm (4-7)\text{ mV}$, while the large gap is revealed at the humps at about $\pm 10\text{ mV}$. In some cases the point-contact spectra show no signature of enhanced conductance due to the Andreev reflection of quasiparticles on the superconducting energy gap. In this case just a reduced conductance near the zero-bias voltage is observed, persisting well above the bulk transition temperature. This indicates the presence of a pseudogap in the system. Surprisingly, the gap features disappear from the spectra at $T^* = 15-20\text{ K}$, much below the particular $T_c$ of the junction under study. At $T^*$ the spectrum is reduced to a zero-bias peak with an intensity sometimes significantly higher than the conductance signal at lower temperatures. Possible reasons for this temperature behavior are discussed.

2. Experiment

Samples with a nominal composition NdFeAsO$_{0.9}$F$_{0.1}$ have been prepared by high pressure synthesis in a cubic, multi-anvil apparatus, with an edge length of 19 mm (Rockland Research Corporation). Stoichiometric amounts of NdFe$_2$As$_3$, Nd$_2$O$_3$, NdF$_3$ and Nd were pressed into a pellet with mass of approximately 0.5 g and placed inside a BN crucible with an inner diameter of 5.5 mm. The synthesis was carried out at about 3.3 GPa. The temperature was increased over a period of 1 h to 1350–1400°C and held for 8 h before being quenched to room temperature. The pressure was then released and the sample removed mechanically. More details of the synthesis and characterization will be found elsewhere [13]. The value of 10% F substitution is nominal, based on the initial stoichiometry of the pellet. The synthesis yields polycrystalline NdFeAsO$_{0.9}$F$_{0.1}$ samples that contain what appears to be plate-like single crystals as large as 300 $\mu$m [14]. Whereas extraction of these crystallites is difficult, we could measure the properties of individual crystals by using a local point-contact probe with a metallic tip.

The PCAR measurements were realized via the standard lock-in technique in a special point-contact approaching system with lateral and vertical movements of the PC tip by a differential screw mechanism. The microconstrictions were prepared in situ by pressing different metallic tips (copper and platinum formed either mechanically or by electrochemical etching) on different parts of the freshly polished surface of the superconductor. The typical dimension of the microconstriction formed by such a method is usually of the order of tens of nanometers. $T_c$'s have been determined from the resistive transitions and also from the temperature dependences of the point-contact spectra. While onset of the transition to the zero-resistance state was at 51 K, the transition temperatures found by the point-contact technique varied between 45 and 51 K.

The point-contact spectrum measured on the ballistic microconstriction between a normal metal (N) and a superconductor (S) consist of the Andreev-reflection (AR) contribution and the tunneling contribution [15]. Charge transfer through a barrierless metallic point contact is realized via the Andreev reflection of carriers. Consequently at $T = 0$ the PC current as well as the PC conductance inside the gap voltage ($V < \Delta/e$) is twice as high as the respective values at higher energies ($V \gg \Delta/e$). The presence of the tunneling barrier reduces the conductance at zero bias and two symmetrically located peaks arise at the gap energy. The evolution of the point-contact spectra between the pure Andreev-reflection and the Giaever-like tunneling has been described by the Blonder–Tinkham–Klapwijk (BTK) theory [15] for the case of s-wave superconductors. The point-contact conductance data can be compared with this theory using as input parameters the energy gap $\Delta$, the parameter $\Gamma$ (measure of the strength of the interface barrier) and a parameter $\Gamma$ for the spectral broadening [16]. In any case the voltage dependence of the N/S point-contact conductance gives direct spectroscopic information on the superconducting order parameter $\Delta$. For a multiband/multigap superconductor the point-contact conductance $G = dI/dV$ can be expressed as a weighted sum of partial BTK conductances. As shown in our previous work [4], in the case of MgB$_2$ the total PCAR conductance could be simply summarized from two contributions of band 1 and 2 (the 3D $\pi$-band with a small gap $\Delta_1$ and the quasi-two-dimensional $\sigma$-band with a large gap $\Delta_2$, respectively)

$$G = \alpha G_1 + (1 - \alpha) G_2$$

where $\alpha$ is the weight factor for the $\pi$-band contribution [4]. Tanaka et al [17] have also extended the BTK formulation for unconventional pairing (d-wave or p-wave).

3. Results and discussion

Before evaluating the point-contact spectra, precautions have to be made that the heating effects are avoided and the junction is in a ballistic or spectroscopic regime. One way is to evaluate the contact size and check if it is smaller than the quasiparticle mean free path in the normal as well as in the superconducting electrodes and superconducting coherence length. Even if the bulk resistivities of the tip and the sample are known (which is
not the case for our NdFeAsO$_{0.9}F_{0.1}$) the local resistivity at the point-contact area can be significantly enhanced due to pressure of the tip on the sample. Then, the evaluation of the contact size and the quasiparticle mean free path becomes problematic. Moreover, very often multiple parallel contacts are formed. That is why inspection of typical heating effects is usually used to determine whether the spectroscopic regime is established in the junction. In the following we present data for which the heating effects, as sharp conductance dips and irreversibilities in the conductance curves usually observed at low voltages, are absent. Moreover, we have focused on the junctions with important tunneling component indicated by the interface barrier-strength parameter $z > 0$.

Figure 1 shows a variety of PCAR spectra obtained on the junctions made by Pt tip on the NdFeAsO$_{0.9}F_{0.1}$ polycrystalline samples at 4.3 K (solid lines). The spectra labeled as A, B, C and D have been normalized to their particular normal-state conductances measured above $T_c$. The spectrum E was just divided by its own value at 60 mV. For the sake of clarity the lower curves are vertically shifted. As can be seen, the spectra show a pair of the gap-like peaks symmetrically placed at $\sim \pm (5)$ mV (the curves A, B and C) or at $\sim \pm (7)$ mV in the case of the spectrum D. In the spectra A, B and C a reproducible shoulder near $\sim 10$ mV and some smaller structures with much less reproducibility are also revealed.

Location of the gap-like peaks/humps is indicative of the size of the related gap but precise determination of the gap is not possible in this way. For example, in the case of important spectral broadening, typically found in samples of new and in addition nonstoichiometric materials, the gap-like peaks can be pushed to significantly higher voltages than would correspond to the real size of the gap. Another uncertainty can be caused by the method of normalization of the spectra, etc. One way to partly overcome this is to compare the measured data to the appropriate model. In the following the spectra showing apparent enhanced conductance and gap-like peaks (both features indicating the Andreev reflection of quasiparticles on the superconducting energy gap) have been fitted to the BTK single-gap formula. The resulting fits, except for the curve D, were poor and unable to reproduce the measured curves. The failure concerned not only the humps at about 10 mV; the overall width of the enhanced conductance around the zero bias was also impossible to determine. Then, in the case of the spectra A, B, and C, we proceeded to the two-gap BTK model mentioned above. As can be seen from the curves indicated by the open circles in figure 1, the two-gap s-wave BTK formula represents a good fit to the data. We remark that even if the two-gap model describes our spectra measured at $T = 4.3$ K quite well, small deviations occur at higher voltages above $\Delta_2$. The following fitting parameters have been obtained: (A) $\Delta_1 = 5$ meV, $\Delta_2 = 12$ meV. (B) $\Delta_1 = 5.2$ meV, $\Delta_2 = 10$ meV. (C) $\Delta_1 = 5$ meV, $\Delta_2 = 12$ meV. The smearing parameters $\Gamma_{1,2}$ vary but they have always been in the range $\Gamma_i < 0.4\Delta_i$ of the respective gap value. The weight factor $\alpha$ for the contribution of band 1 with a smaller gap $\Delta_1$ has been scattered between 0.4 and 0.6. In the case of spectrum D, the fit by the single-gap formula was possible yielding $\Delta_1 = 4$ meV with a significant large smearing $\Gamma = 3.35$ meV. The barrier-strength parameter $z$ was found between 0.3 and 0.5 in the case of curves A, B, C and D as well as in the case of the junctions with similar gap-like spectra.

The particular transition temperature of junctions A, B, C and D was very close to 45 K. It is documented by the temperature dependence of the spectrum B displayed in figure 3(a), where the enhanced conductance around zero bias is completely gone at this temperature. Taking a value of $T_c = 45$ K the following superconducting coupling strengths are obtained from junctions A, B and C: $\Delta_1/k_B T_c = 2.6 \pm 0.1$ and $2\Delta_2/k_B T_c = 5.7 \pm 0.5$. Consequently, weak coupling below the canonical BCS single-band value is found in band 1 with the small gap and a strong coupling is characteristic for the second band. In the case of the junction D the coupling strength is even smaller, with $2\Delta_1/k_B T_c = 2.1$ indicating that the information is probably not complete.

Inspecting the data obtained on numerous junctions having gap-like features has shown that the values of the small gap $\Delta_1$ vary between 4 and 6 meV and for the large one $\Delta_2$ between 9 and 13 meV.

Quite a few of the measured spectra revealed a behavior indicated at the spectrum E in figure 1. These spectra have shown neither enhanced point-contact conductance nor coherence peaks, both effects indicating the Andreev reflection of quasiparticles on the superconducting energy gap, but they have rather displayed a reduced conductance around the zero-bias voltage.

In figure 2 the effect of temperature on another junction with tunneling-like characteristics is shown. One can notice that the effect of the reduced conductance persists well above the bulk transition temperature $T_c \approx 51$ K. It is better observed from the ZBC versus temperature dependence shown in the inset of figure 2. Then, the conclusion can be made that this tunneling-like feature cannot be connected with the superconductivity in the system but reflects a reduced density of states of the normal quasiparticles or pseudogap observed in the underdoped high-$T_c$ cuprates. Since the measurements

![Figure 1](image-url)
Figure 2. Spectra showing a reduced conductance even above \( T_c \). The spectra have been normalized to their values at \(-100 \) mV. Inset: the zero-bias conductance as a function of temperature, the arrow depicts the position of the critical temperature in the system.

were done on polycrystals one can only speculate whether the tunneling-like conductance characteristics are related to a specific direction of the point-contact current with respect to the crystallographic orientation of the sample. In this line it is worth noticing that very recently we have observed this kind of characteristic in single crystals of \((\text{Ba, K})\text{Fe}_2\text{As}_2\) when the point-contact current was oriented in the \( c \) crystallographic direction, while spectra with two superconducting gaps were observed in the \( ab \) planes [18].

In figures 3(a) and (b) the temperature dependence of the spectra showing the superconducting gap-like features is shown. The presented curves are in fact the raw data just normalized to their values at voltage \( V = 40 \) mV. The lower curves are shifted for clarity. Similar to all the other numerous spectra we have measured, the spectral backgrounds reveal a small asymmetry, being higher at negative bias voltage, i.e. when the electrons are injected from the tip into the superconductor. This asymmetry is also revealed in the spectra with a tunneling-like character like those displayed in figure 2. This feature is also shown above \( T_c \), in agreement with the measurements of Chen \textit{et al} [11]. One possible explanation might be that the asymmetry is due to energy dependent DOS in the normal state.

At 4.3 K both sets of spectra in figure 3 show two symmetrically placed gap-like peaks at \( \sim 5 \) mV and humps at \( \sim 10-13 \) mV and higher voltage. The effect of temperature is very unusual. Namely, while the position of the gap-like peaks is rapidly shrinking with increasing temperature, the intensity of the conductance spectrum near the zero-bias voltage surprisingly increases. The latter effect is better presented in the insets, where the curves are not vertically shifted. Above 10 K the only visible feature of the spectrum 3(a) is the narrow ZBC peak, which at even higher temperatures loses its intensity and vanishes at the local \( T_c \), here at about 45 K. In the second set of spectra shown in figure 3(b) the ZBC peak appears at \( T = 10 \) K and coexists with the gap-like peaks up to \( T = 20 \) K. If one looks to the evolution of the spectrum from higher to lower temperatures, it seems that below \( T_c \) the peak in conductance at zero bias is evolving and at a certain transition temperature \( T^* \) a gap opens on this central conductance maximum.

We remark that the temperature \( T^* \) at which the gap-like peaks are replaced by the zero-bias maximum is not always the same but depends on the strength of the interface barrier \( \varepsilon \). The higher \( \varepsilon \), the higher temperature \( T^* \). This finding is consistent with the behavior of the point-contact junctions on SmFeAsO \(_{0.85}\)F \(_{0.15}\) as presented in figure 2 of [11]. Co-presence of the gap-like peaks and the zero-bias peak has also been found in [12]. There, in figure 1, one can moreover notice that, similar to our observations, the height of the ZBC peak at 32 K is larger than the zero-bias conductance at 5.2 K.

What could be the explanation for the observed ZBC peak in the PCAR spectra? There is an analogy with cuprates where it is connected with the nodal superconducting energy gap or the order parameter phase sign changing along
the (110) surface. For the iron pnictides, Mazin and co-workers [5] suggested two s-wave gaps on disconnected Fermi surface sheets but with opposite sign. Recently, Choi and Bang [19] adopted this model of ‘sπ’ pairing (s-wave order parameter with sign reversal) in analogy with a behavior of the superconducting/ferromagnet (S/F) bilayers in which the order parameter sign change also happens. Their calculations show that in the case of the two-band system the superconductivity is possible only for a negative pairing interaction by generating the sign reversal between the gaps Δ1 and Δ2. One of the consequences of the sπ state is that one gap is smaller and another one larger than the BCS weak coupling value. The calculations have also shown that sπ state can produce a zero-bias peak in the local density of states at the superconducting/normal interface. This can be detected in the tunneling or PCAR spectroscopy measured on normal metal/superconductor junctions. Specific conditions enabling observations of the ZBC peak must be studied in detail to explain why this effect appears only at higher temperatures. But it is noteworthy that the ZBC peak effect is observed in all the PCAR tunneling data available so far [10–12].

On the other hand, the presence of the ZBC peak in the point-contact spectrum could be just a fingerprint of the local destruction of superconductivity, i.e. the point contact would rather be in a thermal than a spectroscopic regime. Obviously, even the point contact revealing spectroscopic features in the form of gap-like peaks at low temperatures could be driven out of the spectroscopic regime by higher temperatures and/or higher voltages. This is due to the fact that a mean free path of the quasiparticles is shortened at higher temperatures/voltages. This scenario seems to contradict the behavior seen in figure 3(b), where the ZBC peak is accompanied by the presence of gap-like peaks at 10 and 15 K. The higher voltage cannot redirect the junction back into the spectroscopic regime. This means that once the junction is in the thermal regime at voltages near zero bias it cannot show such pronounced gap-like peaks at higher voltages. But we cannot completely rule out this behavior in the case of parallel junctions where one would be very close to a thermal regime at low temperatures. In any case, the unusual development of the spectra with temperature has prevented reasonable fits of the spectra taken at higher temperatures to the BTK formalism, where the parameters Γi, zi, and α must be kept constant once obtained from the fit to the data measured at the lowest temperature.

Due to the presence of magnetism in the parent compound and/or magnetic impurities (Fe, Nd) possibly present in the sample, Kondo scattering must also be considered [20]. The conductance minimum (or resistance maximum) around zero-bias voltage can be caused in principle also by the Kondo effect. Its appearance in the spectrum can be tested by a bias voltage can be caused in principle also by the Kondo effect. Its appearance in the spectrum can be tested by a bias voltage. The unusual increasing intensity of the PCAR spectrum with increasing temperature is not necessarily connected with unconventional superconductivity in the system.

In figure 5(c) the spectrum presented in figure 3(b) at 4.3 K is reproduced after normalization to its high-voltage background (curve A). The normalized spectrum was impossible to fit with the BTK formalism. Let us consider again a parallel connection of two junctions, one with a two-gap spectrum and another with a tunneling-like character. Let junction A represent the sum of these two. In figure 5(c) the conductance of the tunneling-like junction (curve B) was subtracted with a proper weight (0.5) from the conductance of junction A. The resulting spectrum is indicated by curve C. The spectrum C could be well fitted by the two-gap BTK formula. The circles represent this fit with Δ1 = 5.5 meV, Δ2 = 11 meV, Γ1 = 1.35 meV, Γ2 = 6 meV and α = 0.5. Using this simple model we have arrived at the two superconducting

![Figure 4. PCAR spectra of the junction from figure 3(a) in magnetic fields.](image)
gaps which are consistent with those found on junctions A, B and C presented in figure 1.

Recently the concept of two-gap superconductivity in pnictides has been supported by other works such as the ARPES experiments of Ding et al. [21] on (Ba, K)Fe2As2. Also Gonnelli et al. [22] have obtained pronounced two-gap PCAR spectra and pseudogaps on the LaFeAsO1−xFx polycrystals.

4. Conclusions

Systematic studies on the NdFeAsO0.9F0.1 superconductor show evidence of two-gap superconductivity with gap values \( \Delta_1 = 5 \pm 1 \text{ meV} \) and \( \Delta_2 = 11 \pm 2 \text{ meV} \), indicating very weak coupling in the band with the small gap with \( 2\Delta_1/k_B T_c = 2.6 \pm 0.1 \) and strong coupling for the second band with \( 2\Delta_2/k_B T_c = 5.7 \pm 0.5 \). Also, an indication for a reduced DOS in the normal state or pseudogap persisting well above the bulk transition temperature is found in the system.

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