Point-contact study of ReFeAsO$_{1-x}$F$_x$ (Re = La, Sm) superconducting films

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Abstract

Point-contact (PC) Andreev-reflection (AR) measurements of the superconducting gap in iron-oxypnictide ReFeAsO$_{1-x}$F$_x$ (Re = La, Sm) films have been carried out. The value of the gap is distributed in the range $2\Delta \simeq 5$–10 meV (for Re = Sm) with a maximum in the distribution around 6 meV. The temperature dependence of the gap $\Delta(T)$ can be fitted well by a BCS curve giving a reduced gap ratio $2\Delta/kT_c \simeq 3.5$ (here $T_c$ is the critical temperature from the BCS fit). At the same time, an expected second larger gap feature was difficult to resolve distinctly on the AR spectra, making the reliability of determination of the second gap questionable. Possible reasons for this, and the origin of other features like clear-cut asymmetry in the AR spectra and current regime in PCs, are discussed.

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

1. Introduction

The discovery a few years ago of a new family of iron based superconductors gave rise both to intensive investigation of the fundamental properties of these materials (see reviews [1–4] and references therein) and to a search for potential applications. The fabrication of high-quality thin films is of great importance for potential applications of these new materials in superconducting devices as well as for a deeper fundamental study of their superconducting properties. Numerous experiments were undertaken to study the superconducting state of iron based superconductors; however less attention was paid to the investigation of films, due to the more complicated nature of their preparation.

In this paper we present the first point-contact Andreev-reflection (PCAR) spectroscopy investigation of LaFeAsO$_{1-x}$F$_x$ and SmFeAsO$_{1-x}$F$_x$ films. The main goal was to measure the superconducting gap(s) and its temperature dependence for the mentioned films to compare these data with existing similar measurements on bulk samples [5–7] and to clarify some issues about the presence of multiband structure in PCAR spectra and PCAR spectra asymmetry.

2. Experimental details

ReFeAsO$_{1-x}$F$_x$ (Re = La, Sm) films with superconductivity onset below 34 K were fabricated using pulsed laser deposition. The successful growth of high-quality ReFeAsO$_{1-x}$F$_x$ thin films [8–11] enables the investigation of fundamental properties. Details of the preparation of LaFeAsO$_{1-x}$F$_x$ films are described in [9]. The same parameters were also used for SmFeAsO$_{1-x}$F$_x$ film growth. The temperature dependence of the resistance of the Re = Sm film used in our experiments is shown in figure 1. The onset of the superconducting transition at about 34 K is well below the maximal transition temperature for optimally doped SmFeAsO$_{1-x}$F$_x$ crystals, probably due to severe fluorine loss during film preparation. Also the superconducting transition broadens sufficiently in a magnetic field, which could be due to nonuniform fluorine doping through the film thickness. The Re = La film was of lower quality with a much broader superconducting transition. Therefore, in this study we mainly concentrated on measurements of the Re = Sm film.

The point contacts (PCs) were established by the standard ‘needle-anvil’ method [12], touching of the film surface by a sharpened thin Cu wire. The differential resistance $dV/dI(V)$
was recorded by sweeping the dc current $I$ on which a small ac current $i$ was superimposed using the standard lock-in technique. The measurements of PCAR spectra were performed in the temperature range between 3 and 33 K applying a magnetic field up to 7 T perpendicular to the film surface.

### 3. Characteristic lengths

In PCAR spectroscopy some conditions must be fulfilled, namely the contact diameter $d$ has to be smaller than the inelastic electron mean free path $l_i$ and also smaller than the superconducting coherence length $\xi$. The latter is anisotropic in the ReFeAsO$_{1−x}$F$_x$ family and does not exceed a few nanometers [4]. The contact size can be estimated from its resistance $R_{PC}$ above $T_c$ using a modified Wexler formula [12] for the case of heterocontact with a metal, where its resistivity is negligible compared with that of ReFeAsO$_{1−x}$F$_x$:

$$R_{PC} \simeq (1 + Z^2) \frac{16\rho l}{3\pi d^2} + \frac{\rho}{2d}.$$  

(1)

Here, $Z$ is the so-called barrier strength [13]. We estimated the product $\rho l$ using the upper limit for the electron carrier concentration $n_e \lesssim 10^{21}$ cm$^{-3}$ as inferred from Hall data$^3$ for Re = La just above $T_c$ [17]. Making use of the Drude free electron model we calculated $\rho l \simeq 1.3 \times 10^5 n_e^{-2/3} = 1.3 \times 10^{-10}$ $\Omega$ cm$^2$. The residual resistivity $\rho_0$ of ReFeAsO$_{1−x}$F$_x$ compounds, estimated by extrapolation $\rho(T \rightarrow 0)$, has a value of about 100 $\mu\Omega$ cm for Re = La, whereas $\rho_0$ is higher for other ReFeAsO$_{1−x}$F$_x$ compounds$^4$. Using the calculated value of $\rho l$ and the mentioned resistivity $\rho_0$, we find 10 nm as the upper limit for the elastic electron mean free path $l_e$ for ReFeAsO$_{1−x}$F$_x$ compounds.

In table 1, we present estimations of the PC diameter, according to equation (1), for PCs with three different resistances using both the lower limit of $\rho_0 = 100 \mu\Omega$ cm (for high-quality samples) and the higher value $\rho_0 = 1$ m$\Omega$ cm, taken from the literature for ReFeAsO$_{1−x}$F$_x$. Thus, in order to fulfill the condition that the dimension of the PC has to be smaller than the elastic mean free path of electrons and/or the coherence length the PC resistance must be well above a few hundred ohms, which is not the case for the PCs investigated in this paper and in existing PCAR studies cited in [6]. Therefore all PCAR measurements have been done at least in the diffusive regime when the elastic mean free path is small, i.e. $d \gg l_e$. Although the diffusive regime does not prevent PCAR spectroscopy, it favors the shortening of the diffusive inelastic mean free path $\Delta$ $\simeq (l_i l_e)^{1/2}$ of electrons so that a transition to the thermal regime $d \gg \min(l_i, \Lambda)$ [12, 16] with increasing of applied voltage is getting more probable. Taking into account that the resistivity in all ReFeAsO$_{1−x}$F$_x$ has a remarkable slope (increase) just above $T_c$, e.g. for Re = La, $\rho(T)$ behaves like $T^2$ below $\sim 200$ K [17], the inelastic, likely electron–electron, scattering in ReFeAsO$_{1−x}$F$_x$ is starting already at very low temperatures, shortening an inelastic mean free path $l_i$ and $\Lambda$.

On the other hand, the coherence length $\xi$ is also much smaller than the contact size, which can result in a distribution of superconducting properties (e.g. critical temperature, gap value) within the PC and in a suppression of superconductivity in some part of the PC with current increase. Thereby, regardless of the PC resistance (of course the higher the resistance the higher probability of being in the spectral regime), each $dV/dI(V)$ curve should be critically analyzed to see if it is suitable for spectroscopy of the superconducting gap.

### 4. PCAR spectroscopy of the superconducting energy gap in SmFeAsO$_{1−x}$F$_x$

For the above mentioned reasons, it was difficult to get ‘clean’ PCAR $dV/dI$ spectra having no humps, spikes or other irregularities, which are connected with deviations from the spectral regime in PC. Figure 2 shows one of the best series of $dV/dI$ curves, which demonstrate clear Andreev-reflection (gap) structure, namely pronounced minima at $\Delta \simeq \pm 3$ mV at $T \ll T_c$ which are to a great extent free from unwanted features. To get the superconducting gap value $\Delta$ and other parameters from the PCAR spectra the Blonder–Tinkham–Klapwijk (BTK) theory [13] including the so-called

![Figure 1. Superconducting transition of a SmFeAsO$_{1−x}$F$_x$ thin film at zero field and at 9 T. Arrow shows $T_{c\text{ onset}}$ $\simeq$ 34 K. Inset: temperature dependence of the resistance of the film up to room temperatures.](image-url)
the normal state curve used for normalization can be slightly different for biases respectively. Normalized line represents the BCS-like gap behavior. Inset: symmetrized and theoretical model and are described in more detail in the appendix of [14]. The possible reasons are connected with deviation of the PC structure from the $S$ experimental measurement in a magnetic field, see, e.g., [11]. This means that so-called $T_\text{c}$ even at low temperatures and also below $T_{\text{c}}$ (see figure 2) from the fitting within the BTK theory. We tried to keep constant such fitting parameters as $\Gamma$, the barrier $Z$ and the scaling $S$. Here, the parameter $S$ corresponds to the ratio of the experimental $dV/dI$ intensity to the calculated one$^5$.

It is seen from figure 2 that $\Delta(T)$ is in line with the BCS curve (solid line); however, the resulting critical temperature of $T_{\text{c}}\approx 21.6$ K obtained by extrapolating

5 Parameter $S$ is intended to equalize the intensities of experimental and theoretical curves. Theoretically $S = 1$, but $S < 1$ happens very often too. The possible reasons are connected with deviation of the PC structure from the theoretical model and are described in more detail in the appendix of [14].

6 Resistivity of Sm and La pnictides has pronounced temperature dependence even at low temperatures and also below $T_{\text{c}}$, as it follows from the measurement in a magnetic field, see, e.g., [11]. This means that so-called the normal state curve used for normalization can be slightly different for different temperatures. Therefore we have used for normalization of each $dV/dI(V)$ a weak parabolic-like curve which fitted the same $dV/dI(V)$ at biases $|V| > 10$ mV, i.e. above the gap minima.

the BCS curve to $\Delta = 0$ is significantly lower than $T_{\text{c}}$ determined from the temperature dependence of the resistivity of the SmFeAsO$_1$–F$_x$ film (see figure 1). At the same time, the superconducting main minimum in $dV/dI$ for the investigated PC disappears close to 30 K, as shown in figure 2 which approximately corresponds to the midpoint ($T_{50\%}$) of the superconducting transition in figure 1. However, by approaching this temperature, the shape of the $dV/dI$ minimum already starts to deviate from the theoretically expected behavior above 20 K, as shown in figure 2. This is probably due to inhomogeneities of the superconducting state in the PC region in the case of its size $d$ being larger than the coherence length $\xi$. Also with increasing temperature inelastic scattering increases, favoring the transition to the thermal regime. This hinders a determination of the gap in this temperature range. Therefore, the determination of the gap of the PC shown in figure 2 is restricted to temperatures below 20 K.

Investigating a dozen PCs with clear double minima AR structure around $\pm 3$ mV (see figure 3) we nevertheless could not observe or detect reproducible structures at a higher voltage, which were found, e.g., in the representative two-band superconductor MgB$_2$ [18]. Also, second gap features about three times larger reported for bulk SmFeAsO$_1$–F$_x$ samples [6] could not be unambiguously resolved for the investigated PCs of the SmFeAsO$_1$–F$_x$ film. Instead, for increasing bias a peaked structure or other irregularities usually

Figure 2. Upper panel: $dV/dI$ curves of a SmFeAsO$_1$–F$_x$–Cu contact ($R = 26$ $\Omega$) for varying temperature. Bottom panel: temperature dependences of the fitting parameters: superconducting gap $\Delta$ (triangles), barrier parameter $Z$ (diamonds), scaling parameter $S$ (squares), position of minima in $dV/dI$ (stars) for the PC from the upper panel. The broadening parameter $\Gamma$ is equal to zero. The solid line represents the BCS-like gap behavior. Inset: symmetrized and calculated according to the generalized BTK theory: dashed (blue) and solid (red) lines—fit with curves calculated according to the generalized BTK theory: dashed (blue) and solid (red) lines—fit with $\Delta = 3.35$ mV, $\Gamma = 0$, $Z = 0.38$, $S = 0.5$ and $\Delta = 3.47$ mV, $\Gamma = 0.25$ mV, $Z = 0.41$, $S = 0.58$, respectively.

Figure 3. $dV/dI$ curves of several SmFeAsO$_1$–F$_x$–Cu contacts measured at 3 K. PC resistance is shown for each curve. Vertical dashed stripes mark reproducible AR minima.
appear in the $dV/dI$ characteristics testifying to the transition to the non-spectral regime. But even if features similar to the second gap are observed, e.g. shallow minima slightly above $\pm 10$ mV in the upper PC spectrum in figure 3 (see also low temperature spectra in figure 2), then this gap structure expected around $\pm (9-12)$ meV is hard to resolve for the other PC spectra (see, e.g., the bottom spectrum in figure 3). Moreover, already a weak magnetic field suppresses the mentioned structure, and no second gap features can be detected (see figure 4). The same concerns $dV/dI$ for PC with $R = 14 \, \Omega$, where a shoulder is seen above $\pm 10$ mV, often taken as a larger gap structure. The shoulder is washed out in a magnetic field of 7 T, while the small gap minima are only slightly suppressed at the same field. On the contrary, in the mentioned MgB$_2$ the small gap vanishes more quickly in a magnetic field than the larger one (see circles in figure 15 in [19]).

The above mentioned larger gap structure is also badly resolved in a recent tunneling study of SmFeAsO$_{1-\delta}$F$_x$ compounds [20]. The authors concluded that interband quasiparticle scattering has a crucial effect on the shape of the tunneling spectra, in particular smearing out a larger gap structure in the electronic DOS. Taking into account the very short elastic electron mean free path in SmFeAsO$_{1-\delta}$F$_x$ compounds the interband quasiparticle scattering is expected to be quite strong.

From other tunneling measurements [21], a distribution of gaps (conductance peaks) $\Delta_{\rho}$ between 6 and 8 meV with a mean value of 7 meV was derived, which results in a reduced gap $2\Delta_{\rho}/kT_c \simeq 3.6$. Also, no second gap structure was resolved from these tunneling spectra.

We show in figure 5 a histogram of the gap distribution measured for PCs with a pronounced double minimum AR structure. The distribution has a maximum around $\Delta = 6$ mV and a high energy tail around 10 mV. We connect this large gap value and its broad distribution to the inhomogeneities of the superconducting properties on the film surface due to fluorine loss. Supposing that the critical temperature for the PC with the gap of around 10 meV is close to the onset of superconductivity of $\geq 34$ K in figure 1, then $2\Delta/kT_c$ will be again close to the BCS value of 3.5.

5. Asymmetry of $dV/dI$ curves

A characteristic feature of $dV/dI(V)$ of PCs with ReFeAsO$_{1-\delta}$F$_x$ is their pronounced asymmetry. From our study of this phenomenon we conclude that the asymmetry of $dV/dI(V)$ is present independently of the superconducting features. Figure 6 shows $dV/dI(V)$ curves for a few PCs, where clear AR double minima are observed (figure 6(a)) or the superconducting structure is superimposed on a broad maximum (figure 6(c)), or no superconducting features, but only a sharp zero-bias maximum, are present (figure 6(e)). In all cases, the antisymmetric part of $dV/dI(V)$ shows similar behavior, and even the same relative value independent of the drastic difference in $dV/dI(V)$ shape corresponding to different mechanisms of $dV/dI(V)$ formation. Such robustness of the asymmetry of $dV/dI(V)$ testifies that this phenomenon is not related to the spectroscopic PC properties, but mainly determined by the properties of the bulk material (or the film). One common and plausible reason for $dV/dI(V)$ asymmetry can be the thermoelectric (Seebeck) effect if the PC is heated up at increasing bias in the thermal regime [12]. It is known that ReFeAsO$_{1-\delta}$F$_x$ compounds have a huge Seebeck coefficient at low temperatures which reaches $-80 \, \mu V \, K^{-1}$ for Re = Sm just above $T_c$ for a sample with $T_c = 53$ K [22] and even more $(-140 \, \mu V \, K^{-1})$ for a sample with $T_c = 36$ K [26] (similar to our film). Taking thermoelectric effects in the case of heterocontacts into account, the $dV/dI(V)$ asymmetry was explained both for heavy-fermion high-resistive compounds [12, 23] and for diluted Kondo-alloys [12, 24], where the Seebeck coefficient is strongly enhanced. It seems that an equilibrium heating of the PC is not the only condition.
Figure 6. Left panels: $dV/dI$ curves of a SmFeAsO$_{1-x}$F$_x$–Cu contact measured at 3 K (solid curves) for a broader bias range. Dashed curves have been measured for the same contacts at higher temperature. PC in panel (a) is the same as shown in figure 2. Right panels: antisymmetric part $dV/dI_{as}(\%) = 100R_{PC}^{-1}dV/dI(V > 0) - dV/dI(V < 0)$ for the corresponding curves from the left panels. Voltage polarity is given for the film.

for the appearance of thermoelectric effects. The electron distribution function in ballistic and diffusive PCs is in a highly nonequilibrium state which can be represented by two Fermi spheres shifted from each other by an applied voltage $eV$ [12]. This nonequilibrium electronic state produces nonequilibrium phonons with an effective temperature $\leq eV/4$ [25] which is close to the temperature $eV/3.63$ [16] reached in the thermal regime. Therefore, we suggest that the nonequilibrium state in the PC can also cause a thermoelectric voltage in the case of heterocontacts. This results in a $dV/dI(V)$ asymmetry similar to that observed in PCs in the thermal regime [12].

We would also like to point out that asymmetry of the STM spectra, see figures 5 and 6 in [20], varies and even has different signs for spectra with a similar structure. Since STM spectra reflect in a direct way the electronic density of states (DOS), then the non-reproducible asymmetry of STM spectra point also to the non-DOS nature of the asymmetry, which strengthen our arguments.

6. PCAR spectroscopy of the superconducting energy gap in LaFeAsO$_{1-x}$F$_x$

As mentioned above, the investigated LaFeAsO$_{1-x}$F$_x$ film has a rather poor quality showing a broad superconducting transition already at zero field which is comparable with that of the SmFeAsO$_{1-x}$F$_x$ film at 9 T (see figure 1). Additionally, a downward kink appears in $\rho(T)$ at temperatures around 18 K. The inset in figure 7 shows $dV/dI$ of the LaFeAsO$_{1-x}$F$_x$–Cu PC with Andreev-reflection minima for varying temperature along with gap behavior evaluated by fitting of the $dV/dI$ curves. As in the SmFeAsO$_{1-x}$F$_x$ film, only small gap minima are found. Again, the critical temperature obtained by extrapolating the BCS curve to $\Delta = 0$ is low, i.e. about 18 K.
(close to the kink in $\rho(T)$), while superconducting features in $d\rho/dI$ are seen even at 25 K, as shown in figure 7. We attribute this behavior of varying superconducting properties in the PC region to the short coherence length and sample inhomogeneity.

7. Conclusion

We investigated the superconducting energy gap in ReFeAsO$_{1-x}$F$_x$ (Re = La, Sm) films by PCAR spectroscopy. The mean value of the reduced superconducting gap $2\Delta/kT_c^*$ is found to be close to the BCS value of 3.5, which is in agreement with the PCAR data reported in [5]. A second larger gap feature is hard to resolve on PCAR spectra. The reason could be strong interband quasiparticle scattering, larger gap feature is hard to resolve on PCAR spectra. The mean value of the reduced superconducting gap $2\Delta/kT_c^*$ is independent of the shape of the curves or whether superconducting or AR features are present or not in $d\rho/dI(V)$. Therefore, the asymmetry is not related to the spectroscopy but reflects bulk properties of ReFeAsO$_{1-x}$F$_x$. Very probably the asymmetry is caused by the thermoelectric effect.

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Note added in proof. We have made a thorough elemental analysis of one of our Re = Sm films and found a small amount of La inside. This is likely the main reason of the reduced $T_c$ (not optimal 55 K) of the films due to local disorder.

References

[1] Sadovskii M V 2008 Phys.—Usp. 51 1201
[2] Ivanonskii A L 2008 Phys.—Usp. 51 1229
[3] Izyumov Y A and Kurmaev E Z 2008 Phys.—Usp. 51 1261
[4] Ishida K, Nakai Y and Hideo H 2009 J. Phys. Soc. Japan 78 062001
[5] Chen T Y, Tesanovic Z, Liu R H, Chen X H and Chien C L 2008 Nature 453 1224
[6] Gonelli R S, Daghero D, Tortello M, Ummardo G A, Stepans V A, Kremer R K, Kim J S, Zhigadlo N D and Karipins K J Physica C 469 521
[7] Chen T Y, Huang X S, Tesanovic Z, Liu R H, Chen X H and Chien C L 2009 Physica C 469 521
[8] Bobrov N L, Kremer R K, Kim J S, Zhigadlo N D and Karipins K J Physica C 469 521
[9] Daghero D, Tortello M, Gonnelli R S, Stepans V A, Zhigadlo N D and Karipins K J Phys. Rev. B 80 060502(R)
[10] Kidszun M, Haindl S, Reich E, Hänisch J, Iida K, Schulz L and Holzapfel B 2010 Supercond. Sci. Technol. 23 022002
[11] Kidszun M, Haindl S, Thersleff T, Hänisch J, Kaufmann A, Iida K, Freundengerber J, Schulz L and Holzapfel B 2010 arXiv:1004.4185
[12] Naidyuk Yu G and Yanson I K 2004 Point Contact Spectroscopy (Springer Series in Solid-State Sciences vol 145) (New York: Springer)
[13] Blonder G E, Tinkham M and Klapwijk T M 1982 Phys. Rev. B 25 4515
[14] Bobrov N L, Chernobay N V, Naidyuk Yu G, Tyutrinina L V, Yanson I K, Naugle D G and Rathnayaka K D D 2010 JETP Lett. 90 57005
[15] Bobrov N L, Chernobay N V, Naidyuk Yu G, Tyutrinina L V, Yanson I K, Naugle D G and Rathnayaka K D D 2010 Sov. J. Low Temp. Phys. 36 990 (Engl. Transl.)
[16] Fasano Y, Maggio-Aprile I, Zhigadlo N D, Katezych S, Karlipins K and Fischer O 2010 Phys. Rev. Lett. 105 167005
[17] Matusiak M, Plackowski T, Bukowski Z, Zhigadlo N D and Karipins K 2009 Phys. Rev. B 79 212502
[18] Naidyuk Yu G and Yanson I K 1998 J. Phys.: Condens. Matter 10 8905
[19] Naidyuk Yu G, Gribov N N, Shklyarevskii O I, Jansen A G M and Yanson I K 1985 JETP. Lett. 41 1053
[20] Naidyuk Yu G, Gribov N N, Shklyarevskii O I, Jansen A G M and Yanson I K 1985 Sov. J. Low Temp. Phys. 11 580 (Engl. Transl.)
[21] Kulik I O, Yanson I K and Omelyanchouk A N 1981 JETP. Lett. 32 6
[22] Kulik I O, Yanson I K and Omelyanchouk A N 1981 Sov. J. Low Temp. Phys. 7 129 (Engl. Transl.)
[23] Tropeano M et al 2009 Supercond. Sci. Technol. 22 034004