Experimental study of the intrinsic multiple Andreev reflections effect in GdO(F)FeAs superconductor array junctions

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Abstract – We report the first observation of the intrinsic multiple Andreev reflections effect (IMARE) in S-n-S-n-S arrays (S=superconductor, n=normal metal) formed by a “break-junction" technique in the GdO(F)FeAs superconductor ($T_C = (48–53)$K). We show that superconducting gap peculiarities in $dI/dV$ spectra sharpen dramatically in the arrays as compared with that in the single-contact spectra; this enables to improve significantly the accuracy of the bulk superconducting parameters determination. By using IMARE, we determined the large- and the small-gap values $\Delta_L = 11.0 \pm 1.1\,\text{meV}$ and $\Delta_S = 2.6 \pm 0.4\,\text{meV}$. The BCS ratio $2\Delta_L/k_B T_{\text{C,local}} = 5.0–5.9 > 3.52$ ($T_{\text{C,local}}$ is the contact area critical temperature) evidences a strong electron-boson coupling. The results obtained agree well with our previous data by Andreev spectroscopy for single SnS contacts.

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Among all newly discovered iron-based pnictide superconductors [1], ReOFAs (Re = rare earth metals), or “1111-system”, shows the highest critical temperature, up to $T_C \approx 56\,\text{K}$ [2]. Like high-temperature superconducting cuprates, oxypnictides have a quasi-two-dimensional crystal structure that contains superconducting FeAs planes alternating along the c-direction with insulating ReO layers. The stoichiometric 1111 compounds are antiferromagnetic metals with a spin density wave ground state, whereas electron or hole doping turns the system into superconductivity [3,4].

Band structure calculations [5,6] showed four bands crossing the Fermi level in the normal state, forming two concentric cylinder-like hole Fermi surface sheets at the $\Gamma$-point of the first Brillouin zone and two quasi-2D electron sheets at the $M$-points. These sheets may be considered as two effective quasi-2D bands [7], where two distinct superconducting condensates arise at $T < T_C$ [8]. The total density of states at the Fermi level is formed mainly by Fe 3$d$-states [9,10], suggesting these electrons to play a key role in superconducting pairing. The interest in studying these compounds is related with the still unknown and debatable paring mechanism and symmetry of the order parameter.

The unambiguous determination of the superconducting gap, $\Delta$, remains a challenging issue for 1111-systems. The existing experimental results diverse significantly, including the ones measured by point-contact Andreev reflection (PCAR) spectroscopy (for a review see [11], and table 1 in [12]). As for GdO(F)FeAs, no other data on $\Delta$ values are available until now apart from that reported in our previous works [12,13]. Lack of experimental information on $\Delta$ values for Gd-1111 evidently calls for their independent determination by other techniques. Here we report the first observation of the intrinsic multiple Andreev reflections effect (IMARE) in Gd-based oxypnictides with natural S-n-S-n-Andreev arrays (S = superconductor, n = thin normal metal layer (ballistic limit) [14]). By using the spectroscopy based on the IMARE technique we determined accurately two superconducting gap values, $\Delta_L$ and $\Delta_S$, and the corresponding BCS ratios $2\Delta_{L,S}/k_B T_C$. We present also
a comparison of our new IMARE spectroscopy data with earlier results of the SnS-Andreev spectroscopy [12].

The two sets of polycrystalline samples were used: fluorine-doped GdO$_{1-x}$F$_x$FeAs with concentrations $x = 0.09–0.21$ and $T_{C}^{bulk} = 48–53$ K (EL- and KHL-series), and oxygen-deficient GdO$_{0.88}$FeAs with $T_{C}^{bulk} = 52 ± 2$ K. The polycrystalline samples were prepared by high-pressure synthesis detailed in [13,15]. The chips of Gd and As (99.9%) were placed in an evacuated quartz ampoule and held at $T = 1050^\circ$C during 24 hours to produce GdAs powder. Then high-purity single-phase GdAs, Fe$_2$O$_3$, FeF$_3$ and Fe powders were mixed together in a nominal stoichiometric ratio and pressed into pellets of $3 \times 3 \times 3$ mm$^3$. Afterwards, the pellets were placed in a boron nitride crucible and synthesized under the pressure $50$ kb and the temperature $1350^\circ$C during $60$ min. The resulting polycrystalline samples characterization by X-ray diffraction showed the presence of a prevailing superconducting phase with an admixture of FeAs (about 19%) and Gd$_2$O$_3$ (about 19%); measurements of the resistance and AC susceptibility temperature dependences showed rather sharp superconducting transitions width about $(1.5–4.5)$ K [12,13,15]. Since the incidental phases are nonsuperconducting, it is possible to probe the properties of the true majority phase.

Microcontacts were formed in the bulk of the studied samples by a “break-junction” technique [16,17]. The samples of typical dimensions about $2 \times 1 \times 0.1$ mm$^3$ were attached to a springy sample holder by four-contact pads made of a liquid (at room temperature) In-Ga alloy; this set-up enables 4-contact measurements. The sample holder with the sample was further cooled down to $T = 4.2$ K. Gentle mechanical bending of the sample holder at $4.2$ K generates a microcrack in the bulk of the sample; the resulting junction is equivalent to the superconductor-constriction-superconductor (ScS; c = normal metal or insulator) contact. To operate in a superconductor-metal-superconductor (SnS) regime, the microcrack was precisely tuned until we achieved the desired Andreev-mode characteristic. As was shown in [18], the product of the bulk resistivity $\rho_n$ and quasiparticle mean free path $l$ is about $10^{-10} \Omega \cdot$cm$^2$, therefore, taking the value $\rho_n \approx 25 \mu\Omega \cdot$cm for our samples, we estimate $l \approx 40$ nm. Then, using the Sharvin formula [14] for ballistic contact $R = 4\rho_n \cdot l/(3\pi a^2)$ (where $a$ is the contact diameter), and the typical resistance for our ScS contact $R = (6–60) \Omega$, we immediately obtain $a \approx (8–26)$ nm. The value estimated appears to be less than the mean free path ($a < l$), which provides elementary S-c-S junctions to form ballistic contacts [14]. Location of the microcrack deep in the bulk of the sample prevents both cryogenic clefs degradation and overheating of the contact area by the bias current.

The electron microscope photos showed $4–7\%$ crystallites cleaved after the microcrack formation (fig. 1(a)). The layered material (such as Gd-1111) most likely exfoliates along the $ab$-plane, therefore in our setup a bias current flows along the $c$-direction. In case of a layered superconductor, exfoliation of the sample generates “steps-and-terraces” and thus may form not only single ScS junctions but also S-c-S-c-...-S-type arrays (fig. 1(b)). The latter represents several consequently connected single ScS contacts. Importantly, the “break-junction” technique enables to readjust mechanically the contact, promoting observation of several tens of various SnS contacts during one and the same experiment (fig. 1(b)). This allows us to deal with several tens of ScS arrays with different number $N$ of junctions, usually up to 20. The experimental observation of such natural mesostructures (figs. 2, 3) unambiguously proves that the studied contacts do locate in the splitted crystallites, because a grain-grain contact can provide a single ScS junction solely. When the applied bias current of order of $1$ mA flowing through the constriction exceeds the critical current, it turns the constriction into the normal state. On the other hand, weak superconducting areas $S'$ with a gap $\Delta'$, surrounded by areas with $\Delta \gg \Delta'$, would cause Andreev reflections as normal metal (p. 4004, paragraph 3 in [19]). The latter facts ensure observation of SnS arrays in 1111. Since the estimated $a$ is much less than the typical crystallite diameter $10 \mu$m (fig. 1(a)), this fact allows to apply the “break-junction” technique to polycrystalline samples as well as to single crystals.

Kümmel et al. showed [19] that the multiple Andreev reflections effect [20] in symmetric SnS contact manifests itself as an excess current in the low-bias region at the

Fig. 1: (a) Electron microscope photo of the cryogenic cleft. Black arrows point layered crystallites splitted along $ab$-planes. (b) Plausible scheme of steps-and-terraces in the splitted crystallite with a 6-junctions array formation. The gray arrow indicates a bias current through the array. The dotted line shows the contact transformation into a 5-junctions array on the neighbour terrace under a mechanical readjustment.
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Fig. 2: Normalized dynamic conductance for a single SnS junction (■: EL1 sample, contact #d6 (or, briefly, EL1d6), data from [12]), and for Andreev arrays of 2 junctions in the stack (●: KHL3c, 6 junctions (▲: KHL9d7, ■: KHL8d3, oxygen-deficient sample), and 9 junctions (●: KHL12c). Curves are shifted vertically for clarity. The subharmonic gap structure for the large gap $\Delta_L \approx 11$ meV is marked by vertical stripes (the width reflects a 10% uncertainty) and $n_L$ labels; for the small gap $\Delta_S \approx 2.6$ meV by dash-dotted lines and $n_S$ labels.

The intrinsic multiple Andreev reflections effect, observed first in [23], takes place in Andreev arrays in layered superconductors, and is similar to the intrinsic Josephson effect in S-I-S-I-S contact [24,25] (I = insulator). Since the Andreev array is a stack of single SnS junctions, its CVC and dynamic conductance spectra scale by a factor of $N$ (where $N$ is the number of contacts in the array); the SGS dips should occur at bias voltages,

$$|V_n| = \frac{2\Delta}{en} .$$

Hence, by measuring the $dI(V)/dV$ characteristics of Andreev arrays for different $N$ and by normalizing them to a single SnS contact dynamic conductance, it is easy to calculate the corresponding numbers $N$ and the resulting superconducting gap value(s).

For the above reasons, and in order to check self-consistency of the measured superconducting gap values, we used both methods: Andreev spectroscopy of single symmetrical SnS contacts and IMARE spectroscopy of Andreev arrays. In general, the surface defects contribution to the dynamic conductance for an $N$-junctions array should be $N$ times less than that for a single junction. In contrast to dynamic conductance peculiarities related to the bulk properties of a superconductor, the positions of surface-related gap peculiarities (if any) do not scale with $N$. Thus, IMARE spectroscopy provides a high-precision determination of the true bulk gaps.

Figure 2 shows a comparison between dynamic conductance for Andreev arrays obtained in this work and for current-voltage characteristic (CVC) and a subharmonic gap structure (SGS) at the $dI/dV$ spectrum. For temperatures $T < T_C$ and for the ballistic limit [14], the SGS represents series of dynamic conductance dips at certain bias voltages,

$$|V_n| = \frac{2\Delta}{en},$$

where $\Delta$ is the superconducting gap, $n = 1, 2, \ldots$ the subharmonic order. The relative amplitude of these dips decreases as $n$ and one should expect the two such SGSs, corresponding to the large $\Delta_L$ and the small $\Delta_S$ gaps [21]. Generally speaking, in the case of $\Delta_L/\Delta_S \geq 3$ the large-gap SGS minima should not be visible in the range of $\pm 2\Delta_S/e$, therefore, only peculiarities caused by $\Delta_S$ are usually observed at the small bias voltages.

The dynamic conductance spectra shown in figs. 2, 3, and the excess-current CVCs (see fig. 3) are typical for clean classical SnS contacts [19]; for these reasons, the theory by Kümmler et al. is applicable to the results presented below. The main advantage of the Andreev spectroscopy with symmetric SnS junctions is that superconducting gap value(s) can be determined directly, using eq. (1), from the $dI/dV$ spectra measured up to $T_C$, with no fitting parameters [19], in contrast to the case of asymmetric Andreev NS contact [22]. The presence of several Andreev conductance dips in the $dI/dV$ spectra (various $n$ in eq. (1)) facilitates the precise determination of superconducting gaps.
Remarkably, the amplitude of the SGS minima for the large gap \( \Delta_L \approx 11 \text{ meV} \). The next peculiarity position around \( \pm 5 \text{ mV} \) is not related to the expected third harmonic position \( V_3 \approx \pm 7 \text{ mV} \) for the large gap; for this reason we attribute it to the onset of the SGS defined by the small gap \( \Delta_S \approx 2.5 \text{ meV} \).

Other dynamic conductance curves presented in fig. 2 correspond to a 2-junctions array (KHL3 sample, contact \#c, marked by a rhomb; further, for brevity, we write KHL3c), 6-junctions arrays (KHL9_d7, left triangle; KHL8_d3 in oxygen-deficient sample, right triangle), and 9-junctions array (KHL12_c, hexagon). Remarkably, the Andreev dips in the \( d^2V/dV^2 \) characteristics for various arrays, coincide well with each other when the \( V \) axis scaled down by factors of 2, 6, 6, and 9, correspondingly. One can see a good agreement between the large- and the small-gap values obtained by SnS Andreev and IMARE spectroscopies. The coincidence of the values obtained by both methods leaves no doubt in the bulk gap nature of the observed SGS dips. Indeed, only for peculiarities caused by bulk effects the characteristic voltage may scale with a number of junctions \( N \) in an array, thus proving the bulk origin of the SGS dips.

Figure 3 shows excess-current CVCs (thin lines) and dynamic conductance for Andreev arrays of 9 junctions (KHL7_d2, circle), 8 junctions (KHL10_c, up triangle) and 11 junctions (KHL9_d, down triangle). After normalizing all the curves to a single junction (and shifting them vertically for clarity), the minima positions nicely coincide. Gray vertical stripes depict bias voltages \( V_1 \approx \pm 21 \text{ mV} \), \( V_2 \approx \pm 10.9 \text{ mV} \) and \( V_3 \approx \pm 7 \text{ mV} \), corresponding to the first, second and third Andreev peculiarities for the large gap; the stripe width reflects a 10\% spread of the values. Dash-dotted lines and arrows depict peculiarities at \( V_1 \approx \pm 5.2 \text{ mV} \) and \( V_2 \approx \pm 2.6 \text{ mV} \) for the small gap (with 15\% uncertainty). Using eqs. (1), (2), we immediately obtain average gap values for three KHL samples: \( \Delta_L \approx 10.9 \text{ meV} \) and \( \Delta_S \approx 2.6 \text{ meV} \). The details of spectra decoding for our SnS contacts are presented further.

Equations (1), (2) imply a linear relation between the SGS minima positions \( V_n \) and their inverse subharmonic number, \( 1/n \); the respective line should also tend to the \( (0; 0) \) point. The measured \( V_n(1/n) \) dependence is presented in fig. 4, where all \( V_n \) values are normalized to a single junction. The gap peculiarity symbols in fig. 4 are the same as those for the conductance curves in figs. 2, 3. The upper and lower dash-dotted lines indicate a 10\% uncertainty interval for each gap. Clearly, the dip positions marked as \( n_L = 1, 2, 3 \) for the large gap follow the line which passes through the \( (0; 0) \) point. Therefore, we believe, the peculiarities observed do satisfy equations (1), (2).

According to the theory by Kümmel et al. [19], the intensity of the SGS minima for \( 1/a = 1.5–5 \) should decrease as the subharmonic number \( n \) increases. The amplitude dependence could also help one to distinguish between the peculiarities belonging to the large and small gaps. In order to test this theory prediction, we scale the amplitude of various peculiarities to the amplitude of the \( n_L = 1 \) dip. The procedure of amplitude determination for Andreev minima is explained in fig. 5. The characteristics plotted in panel (a) of fig. 5 are taken as typical data from figs. 2, 3. Background dynamic conductance for the large-gap SGS is shown by dotted lines in fig. 5. These linear dependences are subtracted to exclude the background and thus to simplify the amplitude determination.

The dip amplitudes for small and large gaps were normalized then to the amplitude of the first Andreev minimum (\( A_{L1} \)) of the large-gap SGS; the results are shown in panel (b) of fig. 5. In fig. 6 we plotted relative amplitudes of the conductance peculiarities \( vs. \ n \) for all spectra from figs. 2, 3.

Figure 6 with a semi-log vertical scale clearly shows the decrease of the relative amplitude of the \( \Delta_L \) dips \( (n_L = 1, 2, 3) \) with a subharmonic number rise. As the bias voltage decreases, a new sequence of peculiarities (marked as \( n_S \)) sets in with drastically enhanced \( n_S = 1 \) amplitude; in the same way, it decays to the next \( n_S = 2 \) minimum. Such nonmonotonic amplitude behavior is the unambiguous evidence that the enhanced \( n_S = 1 \) dip amplitude is the onset of the small-gap SGS. Another test of the association of the bias voltage minima with \( \Delta_L \) and \( \Delta_S \) harmonic numbers may be performed using eq. (2). The dip positions for the small gap, plotted in
The subharmonic gap structure (SGS) for the large gap $\Delta_L \approx 11\,\text{meV}$ is marked by $n_L$ labels and gray vertical stripes (their width reflects 10% spread of data due to the difference in $T^\text{local}_C$ for the contacts); for the small gap $\Delta_S$ by black vertical line and the $n_S$ label. The dotted lines reflect a background dynamic conductance for the large-gap SGS.

Panel (b): dynamic conductance data from panel (a) with subtracted background. The spectra are normalized to the panel (b). dynamic conductance data from panel (a) with background dynamic conductance for the large-gap SGS.

The two averaged gap values following from fig. 4 are $\Delta_L = 11 \pm 1.1\,\text{meV}$ and $\Delta_S = 2.6 \pm 0.4\,\text{meV}$. Single-contact SnS Andreev and IMARE spectroscopies also allow measuring a local critical temperature $T^\text{local}_C$. By “local” we mean the intrinsic critical temperature which corresponds to the contact area (of the order of $20 \times 20\,\text{nm}^2$) transition to the normal state and determined from the dynamic conductance linearization [26]. $T^\text{local}_C$ can differ from the bulk $T_C$ obtained from resistance or AC susceptibility measurements. For all studied contacts $T^\text{local}_C$ varies from 48 K to 50 K. The $T^\text{bulk}_C$ value is usually greater than $T^\text{local}_C$, therefore the latter value is more appropriate for estimating the true BCS ratio. Particularly, in our previous work [12] we used the $T^\text{bulk}_C$ value and obtained, respectively, a somewhat lower BCS ratio $2\Delta_L/k_B T^\text{bulk}_C = 3.8–5.8$. Here, using the $T^\text{local}_C$ value we find for the large-gap $2\Delta_L/k_B T^\text{local}_C = 5.0–5.9$, which exceeds the weak-coupling BCS limit equal to 3.52 and points at a strong electron-boson interaction in the “leading” bands with the large superconducting gap. This result agrees well with the BCS ratio obtained by PCAR spectroscopy [27,28]. On the other hand, the BCS ratio for the small gap is much less, $2\Delta_S/k_B T^\text{local}_C = 1.0–1.4$.

Let us define the “intrinsinc” critical temperature $T^\text{local}_C$ for the band with the small gap in a hypothetic case of zero interband coupling. Being smaller than 3.52, the obtained $2\Delta_S/k_B T^\text{local}_C$ ratio indicates that the superconductivity in the second (“driven”) condensate at temperatures much higher than its $T^\text{local}_C$ is induced by the “leading” condensate. The driven band intrinsic $T^\text{local}_C$ may be evaluated by adopting the typical BCS ratio $2\Delta_S/k_B T^\text{local}_C = 3.5–6$; as a result, we get estimate $T^\text{local}_C \approx (17–10)\,\text{K}$.

Noteworthy, by analyzing the shape of the Andreev dip, one can estimate the type of the order parameter symmetry. As was shown theoretically in [29], the s-wave superconducting gap provides sharp, symmetrical SGS dips; on the contrary, in the case of a nodal gap, the dips should be smeared and strongly asymmetric. Turning to the spectra presented in fig. 5, we attribute somewhat asymmetric minima $n_L$ to the extended s-wave without nodes rather than pure s-wave symmetry type for the large gap. A similar conclusion can hardly be made for the small gap, because the corresponding $n_S$ peculiarities are observed on the strongly rising monotonic background.

In order to check whether the influence of surface defects is negligible in an array contact, we plotted in fig. 7 the relative width of the $n_{L,S} = 1$ SGS minima (for $dI(V)/dV$ from figs. 2, 3) vs. the corresponding number of junctions $N$ in the array. The relative width was calculated as its half-width divided by its bias voltage $V_1$. As expected, the relative half-width of the minima tends to decrease linearly as the number of junctions $N$ increases.
for the sample KHL8 (solidsymbols, upper panel) and the small gap (opensymbols, vs. thenumber of junctions in the stack).

Troscopy (smearing values were precisely measured by the IMARE spectroscopy) agree well with the results of experimental works [27,28]; $2\Delta_S/k_BT_{C_{local}}^S = 1.0–1.4$. These significantly different BCS ratios indicate that the large-gap condensate is in the strong-coupling regime and drives the superconductivity in the small-gap condensate for temperatures above $T_B^S \approx (10–17)$ K. The shape of the Andreev peculiarities in dI(V)/dV spectra points to an extended s-wave–type symmetry of the large order parameter. We also show that the array contacts with a large number of junctions in the stack provide suppression of the surface defects influence (in comparison with single SnS contacts); this suppression results in an essential increase of the accuracy of the gap measurements.

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