Observation of Multi-Gap Superconductivity in GdO(F)FeAs by Andreev Spectroscopy

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We have studied current-voltage characteristics of Andreev contacts in polycrystalline GdO$_{0.88}$F$_{0.12}$FeAs samples with bulk critical temperature $T_c = (52.5 \pm 1)$ K using break-junctions technique. The data obtained cannot be described within the single-gap approach and suggests the existence of a multi-gap superconductivity in this compound. The large and small superconducting gap values estimated at $T = 4.2$K are $\Delta_L = 10.5 \pm 2$ meV and $\Delta_S = 2.3 \pm 0.4$ meV, respectively.

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Novel superconducting compounds of 1111 family based on rare-earth oxypnictides REOFeAs (RE = La, Sm, Gd etc.) are currently in the focus of research interest. Some of their features such as layered structure and spatial separation of the carrier reservoir layers and the superconducting pairing layers are similar to those of cuprates. However, many other properties differ substantially and promise new interesting physics. At present, the key issues under investigations are the effect of various types of doping, pairing mechanism, symmetry of the order parameter, quasiparticle energy spectrum, and the superconducting energy gap(s).

The stoichiometric compounds of the 1111-family are antiferromagnetic metals with spin density wave ground state. Partial deficiency of oxygen or fluorine substitution for oxygen induces superconductivity in the FeAs layers. Replacement of rare-earth elements also affects the superconducting critical temperature, $T_c$. In particular, $T_c$ of Gd-based oxypnictides may be lowered by partial replacement of Y for Gd or gained up by introducing Th instead of Gd. $T_c=56$ K found in Gd$_{0.8}$Th$_{0.2}$OFeAs compound is today the highest one for iron-based superconductors.

According to band structure calculations, the total density of states at the Fermi level $N(0)$ is formed mainly by Fe 3d-states. As shown in Ref. 10, the $T_c$ values for different iron-based superconductors correlate with $N(0)$, thus giving support to the BCS-like coupling in these compounds.

The theoretically calculated Fermi surface for 1111-system consists of quasi-two-dimensional (2D) hole sheets centered at the $\Gamma$ point and two electron sheets at the $M$ points of the first Brillouin zone. Within the so called minimal two-band model, these four bands may be considered as two effective 2D bands.

Correspondingly, many of the available theoretical and experimental data indicate that iron-based layered materials are multiband superconductors with s-type symmetry of the order parameter. Knight shift measurements in 1111-class compounds have proven unambiguously the spin-singlet type pairing in these materials. Several data were reported in favor of $s^\pm$ or $s^{++}$ order parameter symmetry, making the experimental situation regarding 1111-compounds uncertain.

The magnitude and structure of the superconducting gap $\Delta$ is intimately related to the pairing mechanism. ARPES measurements are not sensitive enough to resolve unambiguously such fine details as $\Delta$, on the scale of a few meV, that makes this parameter accessible nearly exclusively from point contact spectroscopy, such as scanning tunneling spectroscopy (STS), tunneling- and point-contact Andreev reflection (PCAR) spectroscopy (the latter in the regime of SN-, or symmetrical SNS-junctions). The available experimental reports are however rather inconsistent for 1111-class compounds (the latter in the regime of SN-, or symmetrical SNS-junctions). The available experimental reports are however rather inconsistent for 1111-class compounds, even for the most intensively studied SmO(F)FeAs. Various types of conclusions have been reported including d-wave like, single gap-like, and multi-gap behavior.

The ambiguity of the experimental information is partly due to an inevitable inhomogeneity of the 1111-type polycrystalline samples and lack of large size 1111-type single-crystals suitable for these measurements. Another cause for the divergency of the point contact spectroscopy data is inherent in those experimental techniques, where the sample surface is not cleaved in high vacuum or cryogenic environment. In order to resolve the experimental ambiguity, evidently, novel sets of comprehensive experimental data are needed, which would comprise self-consistency check, substantial statistics and provide local probing at various points of the in-situ...
Here we report the superconducting gap measurements in nearly optimally doped GdO$_{0.88}$Fe$_{0.12}$As samples by SNS Andreev spectroscopy using the break-junction technique [24]. Until now these measurements have not been done for Gd-1111, an analogue to Sm-1111 with approximately the same $T_c \approx 53$K. The break junction technique opens a nice opportunity to prepare in helium atmosphere, at liquid $^4$He temperatures, clean surfaces forming Andreev contact. Another advantage is a possibility of fine mechanical readjusting the contact during experiment, that enables to collect multiple data from different local areas of the same sample. Using this method we have unambiguously detected the presence of two superconducting gaps, whose best fit values averaged over about 30 spectra are $\Delta_L = 10.5 \pm 2$meV and $\Delta_S = 2.3 \pm 0.4$meV at $T = 4.2$K.

Polycrystalline samples GdO(F)FeAs were prepared by high pressure synthesis [23]. The chips of high purity Fe, and powders of single-phase FeF$_3$, Fe$_2$O$_3$, and GdAs were mixed together in the nominal ratio and pressed into pellets of 3mm diameter and 3mm height. The pellets were placed in boron nitride crucible and synthesized at pressure of 50 kb and temperature 1350°C during 60 min. The X-ray diffraction pattern averaged over the sample area showed a polycrystalline compound with a dominating desired 1111-phase (with lattice parameters $a = 3.902(2)$Å, $c = 8.414(5)$Å ) and an admixture of incidental FeAs and Gd$_2$O$_3$ phases. The subsequent local EDS analysis (JSM-7001FA) has revealed that the incidental phases are concentrated in grains of about 1μm size which are scattered in the bulk majority phase. This fact opens a possibility to probe properties of the true majority phase using local techniques, such as PCAR. Superconducting properties of the samples were tested by measurements of temperature dependence of ac-magnetic susceptibility and resistivity $R(T)$. Both showed a sharp superconducting transition in our polycrystalline samples with $T_c \approx 52.5$K (the latter value was defined at a maximum of $dR(T)/dT$-curve). Figure 1 shows typical temperature dependence of resistance and its derivative.

For point-contact spectroscopy we used two methods: (i) multiple Andreev reflections spectroscopy of individual superconductor-constriction-superconductor Sharvin-type contacts [26, 28] and (ii) intrinsic Andreev spectroscopy of stack contacts that usually exist due to the presence of steps and terraces on clean cryogenic cleaves in layered crystals.

Thin plates of about $2 \times 1 \times 0.12$ mm$^3$ in size were cut from the synthesized pellets. At room temperature, the plate-like sample was mounted onto an elastic bronze holder and the two current and two potential leads were attached to the sample by liquid In-Ga alloy. The holder with the sample was placed in the measuring cell and cooled down to 4.2 K. A microcrack in the sample was generated by precise bending the sample holder at $T = 4.2$K using a micrometric screw.

Current-voltage dependence, $I(V)$, and its derivative, $dI(V)/dV$, were measured automatically using the 16-bit AT-MIO-16X (National Instruments) digital board. The amplitude of a low-level 820 Hz modulation voltage at potential leads of a sample was maintained stable using a lock-in nanovoltmeter (operated as null- detector) and a computer controlled digital bridge with a proportional-integral-derivative feedback signal. As a result, the differential conductance of a contact was proportional to the amplitude of the ac feedback current through the contact.

Figure 2 represents $I(V)$, $dI(V)/dV$ and $d^2I(V)/dV^2$ characteristics for individual Andreev (SNS) break-junction in polycrystalline GdO$_{0.88}$Fe$_{0.12}$As sample measured prior a microcrack formation (dots). The bulk $T_c = (52.5 \pm 1)$K was determined at a maximum in $dR(T)/dT$-curve (solid line).

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The dips labeled on Fig. 2 as \( n_L = 1 \) and 2 on SGS reflect the large gap; they are marked with vertical solid lines. The singularities shown by vertical dashed lines cannot be attributed to the large gap and, therefore, may reflect the existence of a small gap \( \Delta_S \approx 2.5 \text{ meV} \). Comparing the result for the large gap (Fig. 2) with Eq. (1) one can easily obtain \( \Delta_L \approx 11 \text{ meV} \).

By readjusting the contact, we could observe clear sets of dips on \( dI(V)/dV \) curve due to either large- or small-gaps, or even to both (as shown in Fig. 2). Figure 3 expands the small bias range, where the subharmonics of the small gap are clearly seen in \( d^2I(V)/dV^2 \) curves for a single SNS-contact EL3D01. For clarity, the smoothly varying background is subtracted. Using expression (1), from the set of differential conductance dips on the \( dI(V)/dV \) curve we determined the energy of the small superconducting gap \( \Delta_S \approx 2.15 \text{ meV} \). In Fig. 3, one can also see two extra features at \( \approx 3 \text{ mV} \) and \( 3.7 \text{ mV} \), which can not be attributed to either large or small gap subharmonics.

The peculiarities in the \( dI(V)/dV \) and \( d^2I(V)/dV^2 \)-characteristics shown in Figs. 2 and 3 clearly manifest the existence of two gaps in our GdO(F)FeAs samples. This behavior is similar to that observed earlier in the multi-band superconductor Mg_{1-x}Al_xB_2 [30] and in LaO_{0.9}F_{0.1}FeAs [31] (an analog to our Gd-1111 sample with somewhat lower \( T_c \approx 28 \text{K} \)). The sharpest SGS (like those in Figure 3) may be usually observed only on \( dI(V)/dV \)-characteristics of Andreev contacts of the high quality and of small size, comparable to the quasiparticles mean free path (ballistic limit) \[ 28 \]. For such a case, a number of the observable gap peculiarities (up to 4 in some samples) facilitates interpretation of the multigap subharmonic structure.

Our experimental data are summarized in Figure 4 where the normalized to a single junction bias voltages \( V_{n_L,S} \) for four microcontacts are plotted versus \( 1/n_{L,S} \). According to expression (1), such dependences have to fall onto straight lines passing through zero. This is in-

They may be caused by excitation of collective modes and require additional studies.

**FIG. 2.** Fig. 2. \( I(V) \), \( dI(V)/dV \) and \( d^2I(V)/dV^2 \)-curves for a single SNS-contact 1D06 at \( T = 4.2 \text{K} \). Background (a polynomial function) is subtracted. The set of dips in the differential conductance at bias voltages \( V_{n_L} = 2\Delta_L/en \) (vertical solid lines) determines the energy of the large superconducting gap, \( \Delta_L \approx 11 \text{meV} \). Peculiarities on the \( dI(V)/dV \) and \( d^2I(V)/dV^2 \)-curves, marked by dashed lines, indicate the presence of small superconducting gap, \( \Delta_S \approx 2.5 \text{ meV} \).

**FIG. 3.** Fig. 3. Differential conductance of the SNS contact 3D01 in GdO_{0.88}F_{0.12}FeAs sample at \( T = 4.2 \text{K} \). Background is subtracted. Two differential conductance dips define the energy of the small superconducting gap \( \Delta_S \approx 2.15 \text{ meV} \). The anticipated bias voltages \( V_{n_S} = 2\Delta_S/en \) are depicted by vertical dashed lines.
2Δs/kBTc ≈ 1.1 < 3.52 suggests that the “weak” superconductivity may be induced by interband coupling, due to k-space internal proximity effect between two condensates, where the large gap condensate plays the “driving” role. In particular, similar situation is believed to be realized in MgB2 [30] and LaO0.8F0.2FeAs [31].

![Diagram](image)

FIG. 4: Fig. 4. Normalized bias voltages Vn = 2ΔLS/cn versus 1/nL,S for the studied SNS-arrays. The averaged values of the superconducting gaps are ΔL = (10.5 ± 2)meV and ΔS = (2.3 ± 0.4)meV. Solid lines are guides to the eye.

The presence of the large superconducting gap characterized by 2ΔL/kBTc > 3.52 in the 1111-family compounds REOFa (RE = La, Sm, Nd) was confirmed by tunneling spectroscopy using break-junction technique [20, 22, 35–40], scanning tunneling spectroscopy [21, 33], and angle-resolved photoemission spectroscopy (ARPES) [34] (see Table 1). To the best of our knowledge, there is no other available data for Gd-1111. Therefore, we compare in Table 1 our data for Gd-1111 with other data available for Sm-, Nd- and Tb-1111 superconductors with similar Tc. We emphasize rather good agreement between 2ΔL/kBTc values determined from our study and those from STS [21], break-junction measurements [33], and some PCAR-measurements [22, 38, 40].

As to the small gap, there is evidently a sizeable spread in its value (2−5)meV observed in different experiments. We can not also exclude that the spread may be caused by the existence of three-gap superconductivity in 1111-system with multiple-sheet Fermi surface [13, 41]; for the smallest gap, we estimate 2Δs/kBTc ≈ 0.5.

In conclusion, we have studied the J(V)- and dI(V)/dv-characteristics at T = 4.2K for various SNS Andreev break-junctions in polycrystalline GdFeAs sample. The reproducibility of two SGSs detected at dI(V)/dv-characteristics of various Andreev arrays, formed by the break-junction technique support this conclusion. In some cases we observed extra features in dI/dv-curves signalling the existence of the 3rd, smaller gap, ΔSS ≈ 1 meV.

Using the determined gap energies and bulk Tc = (52.5 ± 1)K, one can estimate 2Δ/kBTc ratio. For the large gap, our experimental data lead to 2ΔL/kBTc = (4.8 ± 1.0) that exceeds the standard BCS value, 3.52, for single-gap superconductors in the weak coupling limit. This fact together with rather conventional exponent value for Fe isotope effect [32] resembles the BCS - model behavior with strong electron-phonon coupling. At the same time, the 2Δ/kBTc ratio for the small gap

| RE | Tc (K) | method | 2ΔL | 2ΔS | ref. |
|----|-------|--------|-----|-----|-----|
| Gd | 53    | BJ     | 10.5±2 | 2.3±0.4 | this work |
| Sm | 53    | ARPES  | 15±1.5 | no | 34 |
| Sm | 52    | PCAR  | 18±3 | 6.15±0.45 | 35 |
| Sm | 52    | PCAR  | 19 | 5.7 | 36 |
| Sm | 52    | STS   | 8–8.5 | no | 21 |
| Sm | 51.5  | PCAR  | 20 | 6.6 | 36 |
| Sm | 51    | PCAR  | 10 | 4 | 22 |
| Nd | 51    | PCAR  | 14±1 | 6 ±1 | 37 |
| Nd | 51    | PCAR  | 12.5±0.5 | 6.3±0.3 | 38 |
| Nd | 48    | BJ,STS| 7–10 | no | 33 |
| Tb | 45    | PCAR  | 8.8 | 5 | 39 |
| Sm | 45    | PCAR  | 11±2 | 5 ±1 | 40 |
| Sm | 42    | PCAR  | 15±1 | 4.9±0.5 | 35 |
| Sm | 42    | PCAR  | 6.7±0.1 | no | 22 |

TABLE I: Table 1. Summary of the Δ values (in meV) measured for 1111-family REOFa compounds by point contact Andreev reflection (PCAR), break-junction Andreev reflection (BJ), scanning tunneling spectroscopy technique (STS), and ARPES.
observed independent subharmonic gap structures point at the existence of two distinct superconducting gaps, $\Delta_1 = (10.5 \pm 2)\text{meV}$ and $\Delta_2 = (2.3 \pm 0.4)\text{meV}$ determined at $T = 4.2\text{K}$. The estimated $2\Delta_1/k_BT_c$ ratio exceeds the standard BCS value, 3.52, for single-gap superconductors and weak-coupling limit while for the small gap the $2\Delta_2/k_BT_c \ll 3.52$.

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