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Gap features of layered iron-selenium-tellurium compound below and above the superconducting transition temperature by break-junction spectroscopy combined with STS

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Abstract. We studied correlations between the superconducting gap features of Te-substituted FeSe observed by scanning tunnelling spectroscopy (STS) and break-junction tunnelling spectroscopy (BJTS). At bias voltages outside the superconducting gap-energy range, the broad gap structure exists, which becomes the normal-state gap above the critical temperature, $T_c$. Such behaviour is consistent with the model of the partially gapped density-wave superconductor involving both superconducting gaps and pseudogaps, which has been applied by us earlier to high-$T_c$ cuprates. The similarity suggests that the parent electronic spectrum features should have much in common for these classes of materials.

1. Introduction

From the early stages of our break-junction tunnel spectroscopy (BJTS) measurements on the superconducting FeSe$_{1-x}$Te$_x$ single crystals, the normal-state gaps were manifested in addition to the Bardeen-Cooper-Schrieffer (BCS)-type superconducting gap features [1,2]. The observed unusual electronic properties of this superconductor including the gap distributions extending to several tenth of meV are in fact intriguing in view of the possible manifestation of the local anomalously high (about 100 K [3]) superconducting critical temperature ($T_c$). On the other hand, it is reasonable to consider that the normal-state gap is a consequence of the charge- or spin-density-wave formation below the structural/magnetic phase transition, as stems from the phase diagram [4]. In particular, there has been suggested that the lower symmetry C$_2$ nematic/smectic charge ordering emerges in the iron-based superconductors [5,6]. In such states, the normal-state gap structures can be readily observed by tunnelling spectroscopy, which was proposed theoretically [7]. However, there were not enough direct tunnel measurements of such a normal-state gap.

In this paper, we report the observations of both superconducting and the normal-state gaps for the simple iron-based superconductor, FeSe$_{1-x}$Te$_x$, using the BJTS techniques as well as the scanning tunnel spectroscopy (STS). We emphasize that the gap of ± 10-20 mV observed by STS in the superconducting state below $T_c = 15$ K is larger than that revealed in the BJTS measurements [1]. The attention should be paid to the fact that these measurements constitute the most direct and precise tool among the gap-probing experimental techniques. This probe dealing with the conduction electrons themselves immediately leads to the well energy-resolved data needing no further assumptions and relatively easy in interpretation [8].
2. Experimental procedures

Single crystals of FeSe\textsubscript{x}Te\textsubscript{1-x} were synthesized by a standard procedure. The pristine samples thus obtained were annealed at 673 K for 100 hours [9]. The electron probe micro analyzer (EPMA) was employed to determine the crystal composition. The tunnelling measurements were done using the BJTS and the scanning tunnelling microscopy/spectroscopy (STM/STS). The surface Se/Te composition ratio checked by STM is consistent with the bulk EPMA [2]. In the BJTS technique, clean unaffected superconductor – insulator – superconductor (SIS) junction interface is obtained \textit{in situ} along the crack of the thin single-crystal platelet at temperature as low as \( T = 4 \) K [10]. In this case, the peak-to-peak separation, i.e., the distance between the gap edges, is \( V_{p-p} = 4\Delta/e \), twice as much as \( 2\Delta/e \) for the SIN (N=Normal metal) junction, where \( e (> 0) \) is the elementary charge. The tunnelling conductance \( dI/dV = G(V) \) of the current (I)-voltage (V) characteristics was measured using a low-frequency ac-modulation. The break-junction configuration is usually mechanically unstable, but we can obtain a stable junction, who can survive a long-time bias sweep. The STS apparatus was an Omicron LT-UHV-STM, which was upgraded to suppress external disturbances. The samples were cleaved along the layer \textit{in situ} at the temperature \( T = 4K \) in an ultra-high vacuum (UHV) chamber with the vapor pressure of \( \sim 10^{-8} \) Pa to avoid any contamination of the crystal surface. The tunnelling Pt/Ir tip was cleaned by the high-voltage field emission with the Au target prior to the measurements. The scanning measurements of \( G(V) \) were carried out at \( T = 4.9 \text{ – } 77 K \) under the UHV condition of \( \sim 10^{-8} \) Pa.

3. Results and discussion

At first, we show the results of the STS measurements in the superconducting state at 4.9 K. Figure 1 shows the distribution map of the gap energy on the cleaved surface of FeSe\textsubscript{0.3}Te\textsubscript{0.7} consisting of the Fe(Se,Te)\textsubscript{4} tetrahedral network. The gap energy is determined by the bending edge in \( G(V) \) shown for several local regions. In the conductance map, the substantial inhomogeneity of the gapped regions occurs including the clusters of sizes \( \sim 1 \text{ – } 2 \text{ nm} \) or more, corresponding to regions with differing gap values from almost zero to about 40 meV. As is shown in the representative \( G(V) \) examples, the observed gap edge is substantially broadened and asymmetric with respect to zero bias. The STS gap structures of \( \sim \pm 10 \text{ – } 20 \text{ mV} \) are predominantly observed in the vicinity of the excess Fe-atom regions identified by the STM topography, which are locally clustered on the regular atomic sites of surface arrangements [11]. The gapped areas at the excess Fe regions tend to locate at the higher local-barrier-height (LBH) regions with the correlation coefficient between the LBH and the gap being \( \sim 0.3 \).

In the crystal locations where almost no gap feature exists, the tunnelling conductance exhibits the broadened tiny hump at zero bias showing the V shaped background conductance concomitant with the minima at \( \pm 10 \text{ mV} \). Such a zero-bias enhancement could be tentatively explained by the Andreev reflection from the superconductor, but it might be observed only when there is a direct point-contact between electrodes showing a low (<10 ohms) junction resistance [12]. In the STS spectra, however, the existence of the high enough junction resistance \( \sim 10 \text{ G ohms} \) is crucial for the vacuum tunnelling from the tip to occur. Therefore, this phenomenon should have another origin, which is discussed below. Since the conductance map presented here expresses the representative feature of the Te-substituted FeSe superconductors at least for our measurements, it means that nanoscale inhomogeneity of the gap energy is inherent to iron-based superconductors similar to what is observed in cuprates [6,13,14].
Figure 1. Gap distribution map on the $ab$-plane surface of FeSe$_{0.3}$Te$_{0.7}$ at 4.9 K. The STS data acquisition area of 10 nm $\times$ 10 nm is divided into 128 $\times$ 128 segments. STS conductance $G(V)$ is averaged within the indicated area.

The representative STS conductance spectra $G(V)$ in the gap regions below $T_c$ are shown in figure 2, together with the corresponding BJTS ones. The STS spectra indicated by the top three curves are taken from the single bias-sweep and are in fact largely broadened, showing the depressions near zero bias correlating with the gap edge energies. The gap energy estimated by the broad-peak positions around $\pm 10 - 20$ mV is surprisingly large as compared with the bulk $T_c = 15$ K and suggesting the weak-coupling BCS relationship between $T_c$ and the gap ($\sim 1.3$ meV). The fitting of the conductance gives the smaller gap value together with the large broadened energy feature located at the voltage corresponding to the gap itself [11]. The huge gaps found by the present STS were also observed in the superconducting monolayer FeSe film as distinct edge peaks, which disappeared at 60 – 70 K [15]. In the BJTS studies, the obtained BCS-like superconducting gap region is depicted in the left inset [1], demonstrating distinct peaks and well-depressed intra-gap region. These features completely disappear at local $T_c \sim 10$ K of the junction, which is considerably lower than the bulk $T_c = 15$ K. The BJTS also reveals the apparent gap scatter, as shown in the right inset for the larger superconducting gap. The pattern is consistent with our STS data. Since the bulk $T_c$ depends on the Se-Te composition ratio, the observed narrow STS gap distribution can be naturally attributed to the random substitution of the Se and Te atoms. From the comparison of the STM topography elucidating the atomic composition ratios and the BJTS distributed gap values, the probed area of BJ is suggested to be less than $\sim 50$ nm$^2$.

The bottom curve in figure 2 is the BJTS conductance obtained as the largest gap-like feature of the multi-gap curve with a number of peculiarities. The apparent agreement of the gap-edge positions at $\sim \pm 10$ mV in STS and BJTS data is observed, but it is misleading because the factor of two needed to adjust SIS and SIN spectra should be taken into account. Actually, the outer humps of the BJTS curve at $\pm 20$ mV are twice as large as the broad main gap peaks at $\pm 10$ mV in the STS conductance spectra. At the same time, the most inner peaks of the break-junction spectra agree with the proper scaling of
the BJTS and STS results. The inner BJTS double peaks testify the proximity character of the gap at the junction region, which approximately fits the gap-peak positions of the STS curves. Since this BJTS dependence is conspicuously broadened, the inhomogeneity is suggested to be significant for the junction.

In our previous BJTS measurements, the representative superconducting gap values in FeSe$_{0.5}$Te$_{0.5}$ were obtained to be less than $2\Delta \sim 10$ meV appropriate to the junction with $T_c = 10 - 11$ K, the latter being lower than the bulk $T_c = 15$ K [1]. This is most likely due to the inevitable surface degradation of the superconductivity involving the crack of the possible non-stoichiometric area in the BJ forming process. On the other hand, when the bulk $T_c$ superconductivity region is located at the junction, the gap value showing the factor of 1.5 or more will be observed because of the optimal electronic structure. One can also suppose that the observed gap-like structures at $\pm 20$ mV in figure 2 characterize the really higher $T_c$ local break-junction sections, as was suggested previously [3,16].

**Figure 2.** Tunnelling conductances $G(V)$ of STS (upper three curves) and BJTS (the bottom curve) for FeSe$_{0.5}$Te$_{0.5}$. The insets show low-bias BJTS $G(V)$ at 4.2 K with representative gap sizes of $4\Delta/e = 5.5$ mV (left) and 12 mV (right) measured under the different junction geometries. The BJTS measurements were carried out for the same crystal piece.

**Figure 3.** BJTS conductance $G(V)$ for FeSe$_{0.5}$Te$_{0.5}$ at different temperatures up to 15 K. The inset shows the $T$ dependence of the hump position compared with the scaled BCS curve.
Figure 3 shows the $T$-evolution of the break-junction conductance. At low temperatures the BJ spectra demonstrate the giant hump at zero-bias along with the broad peaks at $\pm 13$ mV and the outer weak humps at $\pm 22 - 25$ mV. We attribute the central zero-bias peak to the well-known characteristic weak-link feature of the SIS junction. The break-junction configuration in figure 3 was almost stable mechanically against the temperature changes. The locations of the sideband peaks at $\pm 13$ mV and the broader ones at $\pm 22 - 25$ mV correlate with the characteristic gap-edge energies of the break-junction data in figure 2. The positions of the inner $\pm 13$ mV humps also almost coincide with those observed by the STS as comes about from figures 1 and 2. The spectra gradually smear with $T$. The sideband gap-related peaks are suppressed to merge into the background at about $12 - 13$ K, which is lower than the bulk $T_c$ but it is the highest $T$, where the superconducting gap remnants are observed by our BJTS in this compound. At the same time, the zero-bias hump, also originating from the superconducting gapping, survives up to at about 15 K, suggesting that the junction area includes a small patch with $T_c$ close to the bulk one. The further $T$ increase above $T_c$ leads to the disappearance of all conductance peculiarities.

The $T$ dependence of the sideband gap-peak energy is plotted in the inset of figure 3. It is readily seen that the $T$ evolution is consistent with the scaled BCS temperature dependence (reduced $s$-wave and $d$-wave dependences are very similar), demonstrating that the order parameter, detected by the gapping concerned, corresponds to the conventional mean-field second-order phase transition. Therefore, the features observed at $\pm 13$ mV in the break-junction conductance should be attributed to the superconducting gaps manifesting themselves in the SIS junction configuration.

Note, that the obtained gap values are extremely large as compared to the bulk $T_c = 15$ K if we adopt the BCS-like theory (even making allowance for the strong-coupling corrections), although the reduced $T$-dependences, as was shown above, do demonstrate the BCS behavior. Such large gap-to-$T_c$ ratios are well known, e.g., for copper oxides.

One should also indicate that the iron-based high-$T_c$ superconductor NdFeAsOF with $T_c = 48$ K possesses the gap-to-$T_c$ ratio $2\Delta/|k_B T_c|$, where $k_B$ is Boltzmann constant [17]. If we suggest that the same ratio is valid in our case, then our gap value of 13 mV should correspond to a local $T_c \approx 30$ K. Superconductivity with $T_c$ as high as this was actually found under the pressure in the FeSe superconductor [16]. Since this gap disappears quickly at lower $T \sim 12 - 13$ K, it might be a surface rather than a bulk phenomenon.

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**Figure 4.** STM topography (left, $V = -50$ mV, $I = 0.4$ nA) and the line profile of $G(V)$ (middle) along the line in the STM topography for FeSe$_{0.5}$Te$_{0.5}$ at $T = 15$ K. The right panel is the all-averaged $G(V)$ within the whole area of the STM topography.
Let us examine the STS spectra around $T_c$ in order to clarify the nature of the local gap features from figures 1 and 2. Figure 4 shows the STM/STS of FeSe$_{0.5}$Te$_{0.5}$ taken at 15 K, which is higher than the local surface $T_c$. The left panel indicates the STM topography, while the STS conductance line spectra and the all-averaged $G(V)$ are shown in the middle and the right panels, respectively. The STM topographic resolution is worse than that at 5 K. However, the regular atomic lattice grid arrangement is still visible at 15 K with inhomogeneous background electronic modulations [2]. The STS data indicate that there are no quasiparticle gap-like structures. Instead, the zero-bias humps are observed in the whole scanned region with minima in $G(V)$ at $\pm 10$ mV. Since these humps are similar to their counterparts in the superconducting state at 4.9 K in figure 1, they are probably not related to superconductivity, e.g., to Andreev reflection phenomenon. They might have been due to the fluctuating orbital order [18]. However, in our BJTS studies of those samples the hump structures were never observed in the normal state.

The Kondo scattering during the tunneling by the excess Fe atoms on the Pt-Ir STM tip might be another possible origin of the effect. This is supported by our STM observations of the double-periodic superlattice structure in the antiferromagnetic state of the non-superconducting FeTe, which is believed to be possible only when the tip is partially coated by the Fe excess atoms [19]. The more detailed studies of the $T$ dependence of the zero-bias hump can be of help to find its origin, because in the Kondo scenario the hump or peak should decrease logarithmically with $T$ [20]. Assuming this to be the case, the characteristic temperature in terms of the Kondo singlet formation can be estimated as $\sim 40 – 50$ K from the half-width of the hump at the half maximum.

In our previous report, the high-energy gap surviving in the normal state up to $\sim 70$ K was observed, but we did not manage to elucidate its interplay with the superconducting gap [1]. The origin of this feature is not fully clear, but it is reasonable to associate it with the density-wave condensation arising from the local nematic electron spectrum distortion [3,4]. In figure 5, we can see the gradual smearing of the central superconducting gap structure, while the outer high-energy gap remains unchanged with the increase of $T$ through the superconducting transition. The independent thermal behavior of the both gaps means that their origin is different. The broadened normal-state gap along with the cusp-like zero-bias dip, existing even when the superconducting gap disappears, argues for the partial Fermi-surface nesting of the parent quasiparticle spectrum. Such broadened gap is seen in the normal state at $\sim 20$ K, but there is no trace of it at 80 K. Such a behavior can be met in the layered conductors including high-$T_c$ cuprates and dichalcogenides. In that situation, the intrinsic disorder may play the substantial role [6].

From figure 5, the multiple gap structures revealed at 4.2 K and consisting of $\pm 10 – 20$ mV and $\pm 50$ mV peculiarities can be interpreted as being due to the Cooper pairing and the electron-hole one, respectively. These data seems to be similar to the intertwining of the superconducting and pseudogap features in the tunneling data of cuprate superconductors, whatever the pseudo-gap origin [14].

**Figure 5.** $G(V)$ of BJTS for FeSe$_{0.5}$Te$_{0.5}$ below and above $T_c$. All the curves except that taken at 4.2 K are offset for clarity.
4. Conclusion
We presented and discussed our scanning-tunneling and break-junction-tunneling data for the single crystal FeSe$_x$Te$_{1-x}$ ($x = 0.3 – 0.5$) superconductors. The characteristic large-gap of $\sim 20 – 25$ meV observed by both STS and BJTS disappears at temperatures close to but below the bulk $T_c = 15$ K for this compound. The gap-to-$T_c$ ratio, which is the characteristic of the electron pairing mechanism and its strength, appears to be similar to that for copper-oxide superconductors. Both the conductance hump around zero-bias conspicuous in the range between $-10$ mV and $+10$ mV in STS measurements and the distinct gap-like structures at $\pm 50 – 70$ mV seen in the BJTS above $T_c$ suggest the occurrence of an additional normal-state Fermi-surface instability different from that induced by the Cooper pairing. The difference between two phenomena seems reasonable because the observed features are of different scale, the normal-state-gap low temperature values being substantially larger than $T_c$ and the corresponding superconducting gaps. Moreover, the larger gaps survive far above local $T_c$. Further experiments are now in progress to elucidate the interplay between two phenomena in more detail.

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