Scanning tunneling spectroscopy of $SmFeAsO_{0.85}$: Possible evidence for *d*-wave order-parameter symmetry

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We report a scanning tunneling spectroscopy investigation of polycrystalline $SmFeAsO_{0.85}$ having a superconducting transition at 52 K. On large regions of the sample surface the tunneling spectra exhibited V-shaped gap structures with no coherence peaks, indicating degraded surface properties. In some regions, however, the coherence peaks were clearly observed and the V-shaped gaps could be fitted to the theory of tunneling into a *d*-wave superconductor, yielding gap values between 8 and 8.5 meV corresponding to the ratio $2\Delta/K_BT_C \sim 3.55-3.8$, which is slightly above the BCS weak-coupling prediction. In other regions the spectra exhibited zero-bias conductance peaks consistent with a *d*-wave order-parameter symmetry.

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Among the main fundamental questions that naturally arose after the discovery of high-temperature superconductivity (HTSC) in the oxypnictides family of layered Fe-based $R\mathrm{FeAs}(\mathrm{O}_{1-x},\mathrm{F}_x)$ (R=rare earth) materials[1,2] were the symmetry of the order parameter, the concomitant gap structure, and the value of the energy gap. In spite of the considerable experimental and theoretical efforts directed to resolve these issues, they are not yet fully established. While there are reports that present experimental evidence for a double-gap structure[3] consistent with some theoretical predictions,[4] others show a single-gap structure.[5] The resemblance between the oxypnictides system and the HTSC cuprates (e.g., the layered structure, the superconducting dome structure vs doping, and the existence of spin fluctuations) makes the *d*-wave order-parameter scenario rather appealing. Indeed, various theoretical predictions for *d*-wave superconductivity were published,[6,7] while others support an unconventional *s*-wave pairing.[8,9] On the experimental side, various spectroscopic techniques, such as point-contact spectroscopy, high-resolution and angular-resolved photoemission spectroscopies, infrared reflectance spectroscopy, and nuclear magnetic resonance, were applied in studies of different oxypnictides materials, yielding diverse results regarding both the symmetry of the order parameter and the value (or values) of the energy gap(s). A conventional isotropic *s*-wave order parameter was reported in Ref. 5, but more commonly the measurements suggested nodal *p*-wave or *d*-wave symmetries,[10–13] in some cases also along with a double-gap structure.[3] The $2\Delta/K_BT_C$ ratio, indicative of the coupling strength, also varied considerably between the different reports from close to (and in some cases even somewhat lower than) the BCS weak-coupling value of 3.52 (Refs. 10, 14, and 15) through an "intermediate-coupling" regime of ~4 (Ref. 11) up to a value as high as ~8.[16] It is thus obvious that further experimental effort is needed in order to clarify the picture.

Tunneling and Andreev-reflection spectroscopies are very suitable techniques for measuring the superconductor gap and determining the symmetry of the order parameter.[17] Until now, only point-contact spectroscopy results acquired mainly in the Andreev-reflection regime [namely, with highly transparent junctions having low-Z (<1) values in the Blonder-Klapwijk-Tinkham (BTK) model[18] and its extension to *d*-wave superconductors by Tanaka and Kashiwaya[19]] were reported for the family of FeAs-based superconductors. In some cases larger tunneling resistances (Z ~ 2) were also used, but there is not any report yet on *bone-fide* tunneling spectra acquired with Z ~ 5 tunnel junctions. It is important to note that tunneling spectroscopy may provide different information on the superconductor properties than Andreev-reflection spectroscopy.[17,20] The tunneling spectra monitor the quasiparticle excitation energy gap and thus yield information on the pairing scale. The energy scale determined by Andreev reflection is associated, on the other hand, with the coherence energy range of the superconducting macroscopic quantum-condensate state. While in conventional BCS superconductors these two energy scales coincide, there is ample evidence that the former energy scale exceeds the latter in underdoped high-temperature superconductor cuprates.[20,21] Due to the aforementioned possible resemblance between the cuprates and the oxypnictides, tunneling spectroscopy measurements are essential and could provide important complementary information on Andreev spectroscopy. A scanning tunneling spectroscopy (STS) investigation of *in situ* cleaved $(\mathrm{Sr}_{1-x}\mathrm{K}_x)\mathrm{Fe}_2\mathrm{As}_2$ single crystals, a compound belonging to the related Sr-122 family of superconductors, inferred unconventional order-parameter symmetry.[22] In this Brief Report we present STS data on polycrystalline (oxygen deficient) $SmFeAsO_{0.85}$. Our tunneling spectra suggest, in spite of the degraded surface quality whose effect cannot be ignored, that $SmFeAsO_{0.85}$ is a *d*-wave superconductor in the weak-coupling limit.

The polycrystalline $SmFeAsO_{0.85}$ samples, in which doping is achieved via oxygen deficiency rather than by fluorine doping, were prepared by high-pressure synthesis.[2] SmAs (presintered), Fe, and Fe_2O_3 were mixed together according to the nominal composition, then ground and pressed into pellets that were sealed in a BN crucible and sintered under 6 GPa at 1250 °C for two hours. The purity and the tetragonal [space group $P4/nmm$] structure (a=3.897(6) Å and

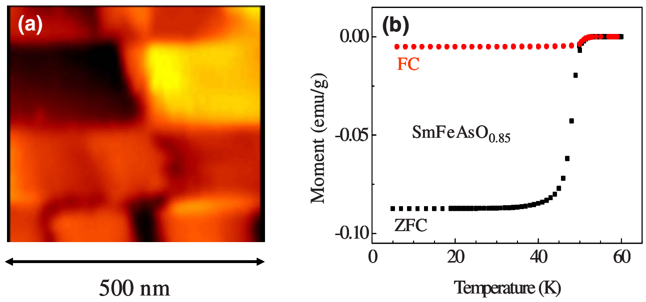

FIG. 1. (Color online) (a) STM topographic image of a polycrystalline $SmFeAsO_{0.85}$ sample showing crystallites. (b) Zero-field-cooled (ZFC) and field-cooled (FC) temperature-dependent magnetization curves measured on the sample at 5 Oe.

$c=8.407(1)$ Å) were verified by powder x-ray diffraction (XRD) using a MXP18A-HF-type diffractometer. Previous ^{57}Fe Mössbauer measurements showed an existence of magnetic order along with superconductivity, which can be attributed to the magnetic FeAs as an extra phase ($T_M=77$ K) not disclosed by the XRD data.[23] The sample surface was polished just before mounting inside our homemade scanning tunneling microscope (STM) and cooling down to 4.2 K at which all data were acquired. Two samples were measured, yielding similar spectral and topographical features, for a wide range of tunnel junction resistances ranging between 100 MΩ and 1 GΩ. The surface morphology of the sample, featuring elongated crystallites, is depicted by the STM image in Fig. 1(a). The temperature-dependent magnetization curves in Fig. 1(b) [measured in a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer] manifest a rather sharp superconductor transition onset at 52 K.

We now turn to discuss the typical energy-gap features presented in Fig. 2. On most of the sample surface (about 70% of the surface area) the tunneling spectra exhibited V-shaped gaps with no coherence peaks but with clear gap-edge features at ±7 meV as shown in Fig. 2(b). These structures resemble proximity gaps observed on the normal side of HTSC/normal-metal junctions,[24,25] suggesting that superconductivity is suppressed on the sample surface and that the corresponding bulk superconductor gap is larger than 7 meV. These proximity-like gap features may also be due to the extra magnetic phase of FeAs found via Mössbauer spectroscopy as discussed above.[23] In other regions, however, V-shaped gaps with clear coherence peaks were found similar to tunneling spectra obtained on the (001) surface (c axis) of the HTSC cuprates [Fig. 2(a)]. It is important to note here that the gap structures, both with and without coherence peaks, were not observed in tunneling spectra measured above T_c. Moreover, we have verified that the gap structures did not change significantly upon changing the STM settings (in the range corresponding to tunneling resistances between 1×10^8 and 1×10^9 Ω), and thus they cannot be associated with the Coulomb blockade effect. The energy-gap values, Δ, were determined by fitting our spectra to the Tanaka and Kashiwaya model[19] for tunneling into a d-wave superconductor (using a relatively small Dynes broadening parameter[26] $\Gamma\sim0.1\Delta$). The extracted gaps ranged between 8 and 8.5 meV [red curve in Fig. 2(a)]. The corresponding $2\Delta/K_BT_C$ ratios are in the range of 3.55–3.8, close to that reported in the majority but not all (e.g., Ref. 15) spectroscopic works on the oxypnictides. We note that these values are slightly above the BCS weak-coupling value and smaller than those typically found for the cuprate HTSCs for which $2\Delta/K_BT_C\sim4.3$ in the weak-coupling limit (although in many cases larger values are found). It should be emphasized that we also tried fitting our data to the conventional s-wave BCS tunneling model. In this case, the V-shaped gaps such as that presented in Fig. 2(a) could be reproduced only when using

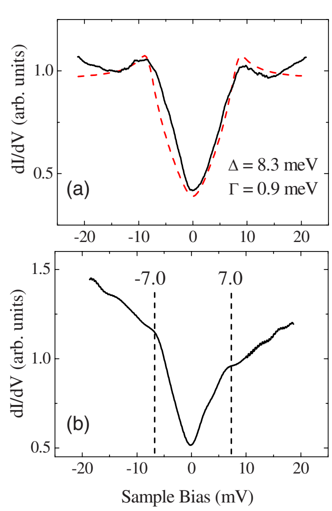

FIG. 2. (Color online) Tunneling spectra at 4.2 K taken (a) in a region where coherence peaks were observed and (b) in a region where only sharp gap edges were found. The red dashed curve in (a) is a fit to the theory of tunneling into a d-wave superconductor along the c axis using the parameters denoted in the figure.

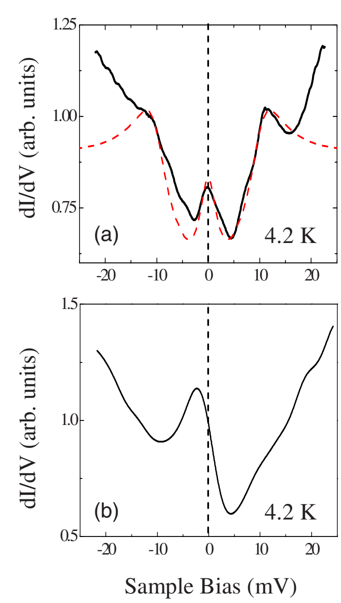

FIG. 3. (Color online) (a) A tunneling spectrum exhibiting a zero-bias conductance peak with gaplike features. (b) A tunneling spectrum showing a shifted zero-bias conductance peak. The red dashed curves are theoretical fits calculated as described in the text, and the vertical dashed lines are guides to the eyes.

unreasonably small-gap values ($\Delta \sim 5.5$ meV) and relatively large Dynes parameters ($\Gamma \sim 3$ meV; comparable to the gap value). Moreover, a simple *s*-wave model cannot account for the zero-bias conductance peaks (ZBCPs) found on some areas of our sample as described below.

The observed V-shaped gaps imply that $SmFeAsO_{0.85}$ has a nodal order-parameter symmetry, either *p* wave or *d* wave. It is well established that the latter gives rise to Andreev bound states on the nodal surface of the superconductor, which manifest themselves by the emergence of a ZBCP in tunneling spectra taken in the nodal direction and (in a less pronounced way) also in spectra acquired in other nonantinodal directions.[19] We have observed such ZBCPs within gaplike features on some locations (on less than 5% of the sample area), as exhibited by the spectrum presented in Fig. 3(a). This spectrum resembles STS spectra measured on the cuprates (e.g., see Ref. 26), and its main features can be reasonably fitted using the *d*-wave superconductor tunneling model assuming in-plane tunneling at an angle of 15° with respect to the nodal direction. However, unlike our previous investigation[27] of $YBa_2Cu_3O_{7-\delta}$, we could not find a correlation between the local surface morphology and the tunneling spectra, and in particular we did not find here *U*-shaped gaps as were previously observed by us in tunneling spectra measured on smooth (100)$YBa_2Cu_3O_{7-\delta}$ surfaces.[27,28] Moreover, the abundance of the ZBCPs was smaller compared to the case of the hole-doped cuprates in HTSCs. This may be due to surface disorder that obstructs the multi-Andreev-reflection process needed for the formation of zero-energy surface Andreev bound states,[29,30] which is an issue that was raised also by Yates *et al.*[14] in the discussion of their point-contact spectra. Another interesting feature we have occasionally observed was a shift of the peak to a finite (small) voltage as shown in Fig. 3(b). Such shifts may be related to the local magnetic order of FeAs described above,[23] which is reminiscent of our previous finding on $SrRuO_3$-$YBa_2Cu_3O_{7-\delta}$ ferromagnetic-superconducting bilayers.[31]

In summary, our scanning tunneling spectroscopy data suggest that $SmFeAsO_{0.85}$ is a weak-coupling *d*-wave superconductor. However, measurements on freshly cleaved single-crystal samples are still needed in order to further verify this conclusion.

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