Disorder effects in pnictides: a tunneling spectroscopy study

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Abstract
We present the synthesis and the tunneling spectroscopy study of superconducting FeSe₀.₅Te₀.₅ (T_c = 14 K), SmFeAsO₀.₈₅ (T_c = 54 K) and SmFeAsO₀.₉F₀.₁ (T_c = 45 K). The samples were characterized by Rietveld refinement of x-ray diffraction patterns and transport as well as temperature-dependent magnetic measurements. Tunneling experiments on FeSe₀.₅Te₀.₅ revealed a single superconducting gap ~1 meV in BCS-like tunneling conductance spectra. In SmFeAsO₀.₈₅ and SmFeAsO₀.₉F₀.₁, however, more complex spectra were observed, characterized by two gap-like structures at ~4 and ~10 meV. These spectra are qualitatively understood assuming a two-band superconductor with a ‘s±’ order parameter. We show that, depending on the sign relation between the pairing amplitudes in the two bands, the interband quasiparticle scattering has a crucial effect on the shape of the tunneling spectra. On the other hand, single-gap spectra found in FeSe₀.₅Te₀.₅ are more compatible with a disorder-induced ‘s’-wave gap, due to the Se–Te substitution.

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

Introduction

In 2008, i.e. 22 years after Bednorz and Muller’s discovery of superconductivity in cuprates [1], the exciting finding of superconductivity in LaFeAsO₁₋ₓFx (T_c = 26 K, reaching T_c = 43 K under pressure) [2, 3] gave rise to a completely new family of high-Tc superconductors, with the critical temperature culminating at T_c = 55 K in SmFeAsO₀.₉F₀.₁ [4]. Understanding these materials is of fundamental importance, as one could expect a ‘new’ and unconventional type of superconductivity to occur there.

As in the cuprates (see the review [5] and references therein), the iron pnictides have a layered structure and are close to a magnetic transition. The parent compound exhibits magnetism which is destroyed by electron/hole doping and the SC state ensues. Another analogy with the cuprates is the possible role of strong electronic correlations. However, the parent compound for oxypnictides seems to be a correlated metal rather than an antiferromagnetic Mott insulator. Superconductivity is obtained in this system by charge doping either outside of the FeAs blocks (by O deficiency or F substitution on the O site in the LaFeAsO compound) or directly in the active FeAs planes (by Co substitution for Fe in BaFe₂As₂, see, for example, Sefat et al [6]). In addition, superconductivity can be induced by mechanical pressure in such systems [7–11], i.e. without introducing chemical disorder.

There is thus a number of questions to be answered. Is the SC state in these compounds unconventional? If yes, what is the SC gap symmetry and the underlying pairing mechanism? Are the iron pnictides an example of superconductivity mediated by magnetism? What is the nature of the normal state? Does a pseudogap exist in the normal state, i.e. just above T_c, and in the vortex core?
In this paper we describe the fabrication of SmFeAsO$_{1−x}$F$_x$ ($T^{\text{onset}}_{c} = 54$ K) and SmFeAsO$_{1−x}$F$_{0.1}$ ($T^{\text{onset}}_{c} = 52$ K) oxypnictide crystals and FeSe-based SC FeSe$_{0.5}$Te$_{0.5}$ ($T^{\text{onset}}_{c} = 14$ K) materials (see the footnote$^4$ for the midpoint values of $T_c$). The samples were characterized by temperature-dependent magnetic and resistivity measurements and Rietveld refinement of x-ray diffraction patterns and finally studied by tunneling spectroscopy (TS) at 4.2 K. While the signature of a single ‘BCS-like’ gap was observed in tunneling spectra of FeSe$_{0.5}$Te$_{0.5}$, two ‘gap-like’ structures, at $T > 3$ and $\sim 10$ meV, were revealed in the tunneling conductance spectra of SmFeAsO$_{1−x}$ and SmFeAsO$_{0.5}$F$_{0.1}$. These structures are interpreted as two SC gaps. Moreover, some local tunneling conductance spectra showed a well-pronounced zero-bias peak that was associated with a change of sign of the order parameter (OP) similarly as in the $d$-wave high-$T_c$ cuprates. In order to give a qualitative understanding of these results, we numerically studied the two-band superconductor in the framework of the Schopohl and Scharnberg model [12] and discuss the possibility of a pairing via a magnetic coupling ($s\pm$ model [13]).

1. Pnictides and iron chalcogenides: structure, doping and superconductivity

When the SC state is obtained by charge doping of the active FeAs planes, the rare-earth element–oxygen (RE–O) plane acts as a charge reservoir, controlling the carrier concentration in the FeAs planes via the substitution of oxygen by fluorine or via oxygen vacancies. Remarkably, spin fluctuations were observed in SmFeAsO$_{1−x}$F$_{x}$ (with $x = 0.18$ and 0.3) near the SC transition [14] and magnetic resonance was reported in FeSe$_x$Te$_{1−x}$ [15]. The superconducting OP was shown to be coupled to a magnetic resonance in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ [16]. These experiments suggest that, in possible analogy to the oxypnictide crystals and FeSe-based SC FeSe$_{0.5}$Te$_{0.5}$, two ‘gap-like’ structures, at $T > 3$ and $\sim 10$ meV, were revealed in the tunneling conductance spectra of SmFeAsO$_{1−x}$ and SmFeAsO$_{0.5}$F$_{0.1}$. These structures are interpreted as two SC gaps. Moreover, some local tunneling conductance spectra showed a well-pronounced zero-bias peak that was associated with a change of sign of the order parameter (OP) similarly as in the $d$-wave high-$T_c$ cuprates. In order to give a qualitative understanding of these results, we numerically studied the two-band superconductor in the framework of the Schopohl and Scharnberg model [12] and discuss the possibility of a pairing via a magnetic coupling ($s\pm$ model [13]).

Arsenic high toxicity has motivated the search for other materials with similar structural properties. This led to the discovery of superconductivity in the relatively simple compound FeSe [17] with a critical temperature $T_c = 8$ K, but posing the additional question of chemical disorder. With their similar layered structures, the comparison of the FeAs and FeSe families should be fruitful. As mentioned above, SmFeAsO$_{1−x}$ can be doped either by O deficiency or by F substitution and leaving the FeAs planes pristine. In contrast, in the FeSe system, where the SC is induced by Se deficiency or by substitution of Se by Te atoms, two different effects are obtained: in the first case, the additional Fe atoms are intercalated between the FeSe planes which thus remain intact upon substitution. The critical temperature reaches 37 K [18–20] or a slightly lower value [21–23] under applied pressure. In the second case, when doping by substitution, the Te atoms are introduced within the FeSe planes and the critical temperature is much lower: $\sim 14$ K.

To address, at least partially, the question of the SC OP in iron pnictides, we performed tunneling spectroscopy (TS) in the scanning tunneling microscope (STM) geometry. This powerful technique allows local measurements of the OP excitation spectra of superconductors (for a review of STS in cuprates, see [24] and references therein). Indeed, if one of the electrodes is a normal metal (with a constant density of states $N_s(E) \approx$ const) and the second one is a superconducting material characterized by an excitation spectrum $N_s(E)$, the derivative of the NIS junction tunneling current $I(V)$ as a function of bias voltage $V$ is

$$dI(V)/dV \propto \int N_s(E + eV)g(E)\,dE$$

(1)

where $g(E)$ is the derivative of the Fermi–Dirac function $f(E)$: $g(E) = -\delta f(E)/\delta E$, which is a bell-shaped function of width $\sim 3.5kT$. The spectroscopic resolution of the TS is therefore mainly limited by the temperature of the experiment. The above commonly used expression for the tunneling conductance $dI(V)/dV$ neglects the $k$ dependence of the tunneling transmission, though the tunneling towards materials with complex band structures may result in different tunneling probabilities for different parts/sheets of the Fermi surface. The measured tunneling conductance spectra thus probe different portions of the Fermi surface with different spectral weights. This effect, first observed in cuprates [25], was crucial in understanding the two-band superconductivity in MgB$_2$ [26], but also in CaCu$_6$ [27] and recently in Ba$_2$Si$_6$ [28]. Thus, the tunneling density of states (DOS) may significantly differ from the QP excitation spectrum of the bulk material.

Among the few comprehensive TS studies of FeAs-and FeSe-based superconductors, the case of FeTe ($T_c \approx 8$ K) is maybe the clearer. Indeed, two scanning tunneling spectroscopy studies showed a $s$-wave-like single-gap superconducting density of states in this material [29, 30]. In their scanning tunneling spectroscopy study of cleaved surfaces of single crystals of the iron chalcogenides Fe$_{10.5}$Se$_{0.15}$Te$_{0.85}$, Kato et al [29] found a simple BCS $s$-wave OP, relatively homogeneous, on a spatially inhomogeneous spectral background. Similarly, Hanaguri et al [30] found a clear $s$-wave-like density of state in FeSe, FeTe. Nevertheless, based on quasiparticle interference patterns studies, the authors claim to have shown $s\pm$ superconductivity in FeSe, FeTe.

The situation is more complex for FeAs-based materials where more complex signatures were observed. Millo et al [31] studied polycrystalline samples of SmFeAsO$_{1−x}$ and, in some regions, observed a gap $\sim 8$ meV with clear OP peaks; the shape of the tunneling spectra was found compatible with $d$-wave symmetry of the SC OP. In other regions of the sample, a zero-bias peak in the conductance spectra was observed. Although the authors suggested a possible $d$-wave OP, they also remarked that, on a large part of the surface ($\sim 70\%$), TS spectra with a characteristic ‘V’-shaped

$^4$ The critical temperature depends on the definition, $T^{\text{mid}}_{c}$ is defined at half of the resistive superconducting transition, whereas $T^{\text{onset}}_{c}$ is the value at which the resistivity starts to decrease. With these definitions: for SmFeAsO$_{0.5}$F$_{0.1}$, $T^{\text{mid}}_{c} = 52$ K, $T^{\text{onset}}_{c} = 54$ K; for SmFeAsO$_{0.5}$F$_{0.1}$, $T^{\text{mid}}_{c} = 45$ K, $T^{\text{onset}}_{c} = 52$ K; for FeSe$_{0.5}$Te$_{0.5}$, $T^{\text{mid}}_{c} = 12$ K, $T^{\text{onset}}_{c} = 14$ K.
Multigap superconductivity has been suggested for FeAs-based superconductors as a possible explanation of some of the reported experimental results. Pan et al [34] studied NdFeAsO$_{0.85}$F$_{0.15}$ and found two characteristic gaps in spatially separated locations of the sample: a small gap of $\sim$9 meV with a BCS-like shape and temperature dependence, and a larger one $\sim$18 meV having a non-BCS shape. Both gaps were found to close at $T_c$ of the bulk material. In addition, Pan et al identified a ‘pseudogap’ opening just above $T_c$. Wang et al [39] explained in the same way the point contact spectroscopy data obtained in SmFeAsO$_{1-x}$F$_x$ for $x = 0.1$ and by Daghero et al [40] for $x = 0.2$ and 0.09. Indeed, Wang et al [39] found two gaps, a small one $\Delta_1 = 3.7$ meV and a large gap $\Delta_2 = 10.5$ meV while Daghero et al [40] found $\Delta_1 = 6.15$ meV and $\Delta_2 = 18$ meV for $x = 0.2$, and $\Delta_1 = 4.9$ meV and $\Delta_2 = 15$ meV for $x = 0.09$ (the typical gap uncertainties being $\sim$10%). Multigap superconductivity was also suggested in the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ family by different means such as angle-resolved photoemission [41] or muon spin rotation [42]. Both studies found a small gap $\Delta_1 \approx 1$ meV and a large gap $\Delta_2 \approx 7$ meV.

Thus, most experiments on SmFeAsO compounds suggest a two-band superconductivity scenario. (See [43] for a compilation of the various experiments showing a single gap or multigaps in various compounds of the FeAs family.)

2. Comparative crystal structure

As previously mentioned, the pnictide SC state is associated with the FeAs plane, a structure found in the natural mineral mackinawite [46] (figure 1(a)). A vast series of compounds can be designed by different stacking of this plane with other structural units [47] (figure 1(b)). In the case of oxypnictides, such as SmFeAsO$_{0.85}$ and SmFeAs(O$_{0.9}$F$_{0.1}$), the carrier doping in the FeAs plane comes from the off-stoichiometry or fluorine substitution in the RE-O plane. In the first case, RE–FeAsO$_{1-x}$, the effective doping is 26 electrons per Fe atom, whereas in the last case RE–FeAs(O$_{1-x}$F$_x$), it corresponds to $\delta$ electrons. In the latter case, one should note that the defect is located outside the SC plane and intuitively acts as an additional electrostatic potential. Defects within the SC plane can be induced in this family by the substitution of iron atoms by cobalt atoms [48–50].

Concerning the Fe$_{1+\delta}$Se$_{1-\delta}$Te$_{x}$ family (figure 1(c)), despite a simpler chemical composition, the crystal chemistry of these materials is rather complex and one should carefully consider the off-stoichiometry when discussing the SC properties [51]. In a perfect stoichiometric compound all Fe atoms, designated Fe(1), are in the tetrahedral sites of the planes. When Fe is present in excess ($y > 0$), it occupies the sites between the Fe(Se, Te) planes, designated as Fe(2). Superconductivity was first discovered in the nominal FeSe$_{0.88}$ Se-deficient compound [17]. It was then demonstrated to correspond to a nearly stoichiometric compound [52], with a $T_c$ of 8 K, and then raised to 34–37 K by applying hydrostatic pressure [18, 21, 19, 20]. The substitution of selenium by tellurium was then examined, allowing an enhancement of $T_c$ to 14 K at ambient pressure [53]. The general tendency throughout the isovalent substitution of selenium by tellurium is the further occupation of the Fe(2) sites between the planes [54]. In this system, the $T_c$ first increases with tellurium substitution with a maximum onset value corresponding to 14 K for the composition FeSe$_{0.5}$Te$_{0.5}$ [55] and then decreases for larger concentrations. The tellurium compound Fe$_{1.09}$Te is non-superconducting [56].
At this stage, one should note important differences between the oxy pnictides and iron chalcogenides. First, due to the absence of charge reservoir planes in the latter case, the inter-plane distance is smaller (the inter-plane distance, measured with respect to iron atoms, is around 8 Å in the case of oxy pnictides versus 5 Å in the case of iron chalcogenides) and the three-dimensional character is more pronounced. Second, the Se/Te substitution occurs within the SC plane and one could expect strong consequences on the SC properties. The Se/Te disorder may cause an important QP scattering that, in the case of a magnetic fluctuation-mediated superconductivity, may induce a disorder in the exchange integrals between the iron atoms and, consequently, in the scattering by spin density waves. Moreover, the additional inter-plane atom Fe(2) is believed to have a magnetic moment, and its influence on the SC state could be more complex than a simple electrostatic potential [57]. Finally, we have chosen for this study single crystals of the composition FeSe0.5Te0.5, which correspond to both the highest $T_c$ at ambient pressure ($T_c^{onset} = 14$ K), a nearly zero occupation of Fe(2) sites and a maximum Se/Te mixing.

### 3. Fabrication and characterization of the samples

SmFeAsO0.85 and SmFeAs(O0.5F0.1) samples (Sm-1111) were prepared under high pressure–high temperature using a "belt"-type high pressure cell. Sm, Fe, Fe2O3, As and SmF3 (in the case of the fluorine-doped sample) powders were mixed together and pressed in the form of cylindrical pellets. They were introduced in a home-made boron nitride crucible which together and pressed in the form of cylindrical pellets. They were introduced in a pyrophyllite gasket. The whole assembly was placed in a pyrophyllite gasket. The case of the fluorine-doped sample) powders were mixed mechanically; the XRD spectrum (figure 2(b)) shows that the major phase is the one expected, Sm-1111 with small impurities: FeAs, SmAs and Sm2O3, as illustrated in one single phase. Their resistance and its Rietveld refinement which indicates the presence of the oxypnictides versus 5 Å in the case of iron chalcogenides. First, due to the absence of charge reservoir planes in the latter case, the inter-plane distance is smaller (the inter-plane distance, measured with respect to iron atoms, is around 8 Å in the case of oxy pnictides versus 5 Å in the case of iron chalcogenides) and the three-dimensional character is more pronounced. Second, the Se/Te substitution occurs within the SC plane and one could expect strong consequences on the SC properties. The Se/Te disorder may cause an important QP scattering that, in the case of a magnetic fluctuation-mediated superconductivity, may induce a disorder in the exchange integrals between the iron atoms and, consequently, in the scattering by spin density waves. Moreover, the additional inter-plane atom Fe(2) is believed to have a magnetic moment, and its influence on the SC state could be more complex than a simple electrostatic potential [57]. Finally, we have chosen for this study single crystals of the composition FeSe0.5Te0.5, which correspond to both the highest $T_c$ at ambient pressure ($T_c^{onset} = 14$ K), a nearly zero occupation of Fe(2) sites and a maximum Se/Te mixing.

![Figure 2: Rietveld refinement of Fe1+x(Se0.5Te0.5) and SmFeAsO0.85F0.1 (λ = 1.5406 Å). For both, a difference curve is plotted at the bottom (observed minus calculated intensities). Tick marks correspond to Bragg peaks of chalcogenide phase (first panel) and oxyarsenide phase (first row of second panel) and impurities (last three second rows): FeAs, SmAs and Sm2O3.](image_url)

3. Tunneling spectroscopy

We now focus on the TS experiments which were performed in the inverted junction geometry [34, 26]. It is well known that the surface of iron-based pnictides is very reactive and immediately contaminated in air. Hence, in order to limit contamination effects, the samples were broken in UHV. In our experiments, small pnictide crystals were glued to the apex of Pt–Ir STM tips (as illustrated in the inset of figure 4) with conducting silver glue and introduced in the UHV chamber containing the STM unit. The crystals were then broken under ultra-high vacuum conditions. A pure gold surface was used as the counter electrode. For each composition, a large number of samples have been studied.

Typical tunneling conductance spectra of FeSe0.5Te0.5 are presented in the inset of figure 4. The spectra clearly show a
Figure 3. (a) Resistance versus temperature dependence of polycrystalline SmFeAsO$_{0.85}$ sample (measured by the four-terminal method). (b) Left axis: resistance versus temperature dependence of a Fe(Se$_{0.5}$Te$_{0.5}$) single crystal (measured by the four-point method). Right axis: partial magnetization versus temperature curve $M(T)$ measured with an applied magnetic field $H = 10$ Oe. Inset: full magnetization curve measured down to $T = 2$ K at $H = 10$ Oe.

Figure 4. Circles: background-corrected tunneling conductance spectrum observed in FeSe$_{0.5}$Te$_{0.5}$ at $T = 4.2$ K, tunneling resistance $R_T = 12.5$ M$\Omega$. Solid line: BCS fit using the Dynes formula [58] gives $\Delta = 0.95$ meV; $\gamma = 0.22$ meV. Inset (left): geometry of the tunneling experiment: small SC crystals were glued on a Pt–Ir tip (and broken in ultra-high vacuum before the experiment in order to get a clean surface). A gold crystal was used as the counter electrode. Inset (right): tunneling spectra observed in other studied samples.

The tunneling conductance data observed in SmFeAsO$_{0.85}$ (figure 5 (left panel)) and SmFeAsO$_{0.9}$F$_{0.1}$ (figure 6 (left panel)) are very different from the simple BCS-like case of FeSe$_{0.5}$Te$_{0.5}$. A large number of spectra exhibit two 'gap-like' structures at respectively $\sim 3–4$ meV and $\sim 10$ meV. The largest gap is defined by a kink around $\sim 10 \pm 3$ meV (dashed bands in figures 5 and 6 (left panel)) while the low energy gap is directly seen in the spectra near zero bias, surrounded by two peaks at $\sim 4 \pm 1$ meV (dashed line in figures 5 and 6 (left panel)). Both spectroscopic features are observed on a ‘V’-shaped background varying from one sample to other. Such a background could be related to the electronic surface states resulting from dangling bonds or to the existence of a correlated metal. A few spectra exhibit a zero-bias peak (figures 5 and 6 (right panel)). All spectroscopic features we observed—two gaps, the ‘V’-shaped background and the presence of a zero-bias peak—are in complete agreement with the findings of Millo et al [31].
Figure 5. Tunneling spectra of SmFeAsO$_{0.85}$ acquired at $T = 4.2$ and at tunneling resistance $R_T = 12.5$ M$\Omega$. Left panel: two gap-like structures at respectively $\sim 10$ mV and $\sim 3$ mV superimposed on a ‘V’-shaped background are clearly visible. Dashed lines are put at characteristic bias values. Right panel: selected spectra exhibiting a zero-bias peak.

5. Interpretation of the results

The two gap-like structures in the spectra of SmFeAsO$_{0.85}$ and SmFeAsO$_{0.9}$F$_{0.1}$ strongly suggest the existence of two SC gaps in these materials. Mazin et al [13] have proposed that a magnetic coupling could be the ‘glue’ for superconductivity, which would make the pnictides very different from other multigap superconductors such as, for instance, the double-gap SC state in MgB$_2$. In order to distinguish between the two situations, it is helpful to reconsider the problem of two-gap superconductivity and, specifically, the QP interband scattering effects.

5.1. Two-gap model of Suhl

As shown by Suhl, Matthias and Walker (SMW) [59], the one-band isotropic BCS model can be extended to the case of two energy bands. In their description, a Cooper pair can absorb a phonon and be scattered either in the same band or in the other band. The Hamiltonian is the sum of the kinetic energy $H_K = \sum_{kk'} \epsilon_k c_{k\sigma}^\dagger c_{k'\sigma} + \epsilon_{k'} d_{k'\sigma}^\dagger d_{k\sigma}$ and of the partial Hamiltonians describing the intraband pair scattering in each band, $H_{11}$ and $H_{22}$, and the interband pair scattering $H_{12}$:

$$H_{11} = V_{11} \sum_{kk'} c_{k\uparrow}^\dagger c_{-k'\downarrow} c_{-k'\uparrow} c_{k\downarrow}^\dagger$$

$$H_{22} = V_{22} \sum_{kk'} d_{k\downarrow}^\dagger d_{-k'\uparrow} d_{-k'\downarrow} d_{k\uparrow}^\dagger$$

$$H_{12} = V_{12} \sum_{kk'} c_{k\uparrow}^\dagger c_{-k'\downarrow} d_{-k'\uparrow} c_{k\downarrow}^\dagger + d_{k\downarrow}^\dagger d_{-k'\uparrow} c_{-k'\downarrow} c_{k\uparrow}^\dagger$$

where $c^\dagger$, $c$, $d^\dagger$, $d$ are the corresponding creation and annihilation operators in each band, $V_{11}$ and $V_{22}$ are the intraband coupling potential corresponding to absorption or emission of a phonon with a pair scattering in the same band, $V_{12}$ is the interband pair coupling corresponding to the scattering of a Cooper pair from one band to the other.

This model gives rise to two gaps in the excitation spectrum, $\Delta_1$ and $\Delta_2$, which are defined by two coupled equations:

$$\Delta_1 [1 - V_{11} N_1 F(\Delta_1)] = \Delta_2 V_{12} N_2 F(\Delta_2)$$

$$\Delta_2 [1 - V_{22} N_2 F(\Delta_2)] = \Delta_1 V_{12} N_1 F(\Delta_1)$$

(2)

where $N_i = N_i(E_F)$, $i = 1, 2$, is the normal state DOS at the Fermi level in each band. $F(\Delta_i)$ ($i = 1, 2$) is a function depending on the temperature $T$, $\omega_0$ is the cutoff frequency for the mechanism responsible for the coupling (i.e. the Debye frequency in the case of a phonon coupling):

$$F(\Delta) = \int_0^{\Delta_0} \text{Re} \left\{ d \tanh \left[ \sqrt{\Delta^2 + \Delta^2} / 2k_B T \right] / \sqrt{\Delta^2 + \Delta^2} \right\}.$$ (3)

If the interband pair coupling parameter term $V_{12}$ is neglected, one obtains a superposition of two SC condensates with two critical temperatures and a DOS which is the sum of two BCS-type DOS. Otherwise ($V_{12} \neq 0$), one gets two gaps which...
Figure 6. Tunneling spectra of SmFeAsO$_{0.9}$F$_{0.1}$ acquired at $T = 4.2$ and at tunneling resistance $R_T = 12.5$ M$\Omega$. Left panel: two gap-like structures at respectively $\sim 11$ mV and $\sim 4$ mV superimposed on a ‘V’-shaped background are clearly visible. Dashed lines are put at characteristic bias values. Right panel: selected spectra exhibiting a zero-bias peak.

close at the same critical temperature depending on different parameters of the model. This is the situation suggested for MgB$_2$ [44]. However, to account for the observed SC behavior of this material [45], the Cooper pair scattering is not enough and the QP scattering effects must be additionally considered [12].

5.2. Two-gap superconductor with sign reversal

Mazin et al [13] considered a more odd situation where the pairing originates from a magnetic coupling and the interband pair scattering parameter $V_{12}$ becomes negative. Consequently, the two components of the SC OP, characterized by two gaps in the excitation spectrum, have opposite signs. Mazin et al proposed that such a situation could exist in the pnictides. When the intraband coupling can be neglected compared to the interband coupling, i.e. when $V_{11}, V_{22} \ll |V_{12}|$, then the SMW equations (2) for the two gaps simplify. At zero temperature, and assuming that the cutoff frequency of the coupling mechanism is much larger than the gap amplitude $\omega_0 \gg \Delta_{1,2}$, one obtains

$$
\Delta_1 = \Delta_2 V_{12} N_2 \ln \left( \frac{2h\omega}{\Delta_1} \right),
$$

$$
\Delta_2 = \Delta_1 V_{12} N_1 \ln \left( \frac{2h\omega}{\Delta_2} \right).
$$

(4)

Therefore, it appears that in such a situation the gap in the first band is determined mainly by the DOS in the other band. The gap ratio at zero temperature is approximately given by $(\Delta_1/\Delta_2)^2 \sim N_2/N_1$.

5.3. Effect of quasiparticle scattering on the DOS

Schopohl and Scharnberg [12] considered, in addition to the SMW approximation, a term allowing the QPs to be scattered from one band to the other. This Schopohl–Scharnberg model (SSM) of a two-gap SC is formally equivalent to the McMillan model [60] describing the normal metal–superconductor proximity effect in real space. When taking into account the interband QP scattering, not accounted for in the SMW model (equation (2)), the energy gaps $\Delta_i(E)$ (where $i = 1, 2$) become energy-dependent and are given by two coupled equations:

- $\Delta_1(E) = \frac{\Delta_1^0 + \Gamma_{12} \Delta_2(E)}{1 + \Gamma_{12}/\sqrt{\Delta_2^2(E) - (E - i\Gamma_{21})^2}}$

- $\Delta_2(E) = \frac{\Delta_2^0 + \Gamma_{21} \Delta_1(E)}{1 + \Gamma_{21}/\sqrt{\Delta_1^2(E) - (E - i\Gamma_{12})^2}}$

(5)

where $\Gamma_{ij} = \hbar/\tau_{ij}$ and $\tau_{ij}$ represent the QP lifetimes in each band.
\(\Delta_i^0\) and \(\Delta_i^1\) are the intrinsic gaps\(^5\). The partial DOS \(N_{ij}^s(E)\) corresponding to the two different bands \(i = 1, 2\) are obtained by inserting the energy-dependent gaps \(\Delta_1(E)\) or \(\Delta_2(E)\) in the standard BCS expression for the DOS \([61]\):

\[
N_{ij}^s(E) = \text{Re} \left[ \frac{|E|}{\sqrt{E^2 - \Delta_i(E)^2}} \right].
\]

Following Mazzini et al.\([13]\), we considered that the energy gaps in each band have opposite signs \((s\pm\text{ model})\). We further developed the SSM approach to this \(s\pm\) approximation. We have then calculated the partial DOS in each band in the \(s\pm\) case, for different values of the interband QP scattering parameters \(\Gamma_{ij}\). We finally compared the effects of QP scattering on SC DOS within the \(s\)-wave two-band SSM\([62]\) and the \(s\pm\) SSM model. The results of our calculations, done for \(\Delta_1^0 = \pm 3\) meV (small initial gap) and \(\Delta_2^0 = 8\) meV (large initial gap), are presented in figure 7, for different amplitudes of the QP interband scattering \(\Gamma_{ij}\). In the \(s\)-wave two-gap SSM case (figure 7 (left panel)), the partial DOS \(N_{ij}^{s\pm}(E)\) (corresponding, respectively, to small and large gap bands 1 and 2) are relatively weakly affected by increasing the QP interband scattering. However, in the \(s\pm\) SSM case (figure 7 (right panel)) the interband QP scattering has a dramatic effect on the partial DOS. Both the small gap and the large gap partial DOS (figures 7(c) and (d), respectively) show rapid filling with the states inside the initial gaps. The effect is particularly strong for the large gap DOS, since for a high enough value of the interband QP scattering parameter \(\Gamma_{21}\), the QP peaks at the large gap energy almost disappear in the DOS (figure 7(d)). In such a case, the large gap can be hardly distinguished in the tunneling conductance spectra (figure 7(d)).

In order to compare the calculated DOS to the TS data, one has to take into account the \(k\) selectivity in the tunneling process\([25, 26]\). The simplest way is to consider that some part \(T_1\) of the tunneling electrons go into the band \(i = 1\) where the gap \(\Delta_1(E)\) (small gap) exists whereas the rest of the electrons \(T_2 = 1 - T_1\) tunnel into the band \(i = 2\) characterized by the gap \(\Delta_2(E)\) (large gap). Such an approximation gives the tunneling DOS as a weighted sum of two partial SSM DOS (equation (6)):

\[
N_{ij}^{s\pm}(E) = T_1 N_{ij}^0(E) + T_2 N_{ij}^1(E),
\]

with the condition \(T_1 + T_2 = 1\). The tunneling conductance at finite temperature is then obtained by replacing the term \(N_{ij}^0(E + eV)\) by \(N_{ij}^{s\pm}(E + eV)\) in the integral \(dI(V)/dV\) (equation (1)). The resulting curves, calculated for \(T_1 = 0.8\) and \(T_2 = 0.2\), are presented in figures 7(e) and (f), respectively, for \(s\)-wave two-gap and \(s\pm\) situations. We point out a striking difference between the two results, specifically at high enough QP scattering rates \((\Gamma_{ij} \geq 1)\), where the large gap peaks (at \(\approx \pm 8\) mV) are suppressed in the \(s\pm\) case and only some kinks remain. Remarkably, the QP peaks due to the small gap are very robust: they remain clearly visible at any studied value of \(\Gamma_{ij}\).

### 6. Discussion and perspectives

It is tempting to compare the effects of disorder in pnictides and chalcogenides to high-\(T_c\) cuprates. In cuprates, it has been shown that two main types of disorder can be distinguished, having drastically different effects: in-plane disorder in the CuO\(_2\) layer and out-of-plane disorder (see, for instance, \([63]\) and references therein). Weak disorder consists in the substitution of atoms belonging to the charge reservoir planes (out-of-plane disorder), whereas strong disorder corresponds to oxygen vacancies or copper substitution by zinc or nickel (in-plane disorder). The former is known to induce spatial inhomogeneities in the superconducting state and a pseudogap in the excitation spectrum\([64]\), whereas the latter is far more detrimental to superconductivity. As an example, a few percent of Zn decreases the critical temperature, even though it is non-magnetic\([65]\) and causes gapless SC\([66]\).

At first glance, the concepts developed for the cuprates can be extended to the case of iron-based superconductors. Indeed, we can define in the same spirit in-plane and out-of-plane disorder, with respect to the FeAs plane. However, making direct comparison between pnictides (LnFeAsO) and chalcogenide (FeSe) is not straightforward since, contrary to iron pnictides and cuprates, a charge reservoir plane does not exist, strictly speaking, in the iron chalcogenides family.

Based on the fact that the experimental spectra in SmFeAsO\(_{0.85}\) and SmFeAsO\(_{0.6}\)\(_\text{F}_{0.1}\) are quite similar, we first suggest that the SC properties are relatively insensitive to the nature of out-of-plane dopants. The situation is drastically different for in-plane doping. The effect of in-plane disorder is complex since, as shown in the literature, doping by substitution depends on the nature of the substituting atoms, isovalent or non-isovalent: the doping can be induced in the LnFeAsO family by non-isoelectronic substitutions of iron by cobalt and nickel in the FeAs plane. In this case, the superconducting region is dome-like with optimal \(T_c\) of 13 K for a doping level \(x_{Co} = 0.075\) in LaFe\(_{1-x}\)Co\(_x\)AsO\([50, 48]\). Hence, the superconductivity appears robust with respect to strong in-plane disorder. However, we point out that the order of magnitude of the \(T_c\) remains in the range of what is expected for conventional superconductivity. On the other hand, isovalent doping such as substitution of As by phosphorus in LaFe\(_{1-x}\)P\(_x\)O leads to superconductivity with a reduced temperature \((T_c^{\text{red}} \sim 10.8\) K for the optimally doped \(x = 0.25 - 0.3)\)\([67]\). Those different results suggest that one has to distinguish between doping effects (for non-isovalent substitution) and disorder effects (for isovalent substitution).

Our simulations show that the effect of QP scattering in the \(s\pm\) case (i.e. in the case of a magnetic coupling) is very different from the \(s\)-wave situation. Accordingly, the disorder in the FeAs (FeSe) plane should lead to destructive effects...
interferences in the $s\pm$ case, and only a remaining $s$-wave phononic superconductivity would survive. This point should be further confirmed experimentally, for example, by a decrease of the magnon frequency when the active planes are affected.

In the case of Fe(Se, Te), the substitution of Se by Te should give rise to a strong disorder, i.e. more precisely to a strong interband quasiparticle scattering that would destroy the $s\pm$ SC OP, resulting in a single BCS-like SC gap (this occurs if $V_{11}$ and $V_{22}$ are non-zero). From our full self-consistent calculations [68], we infer that even a very small amount of Te would probably be enough to suppress the $s\pm$ SC OP. This scenario is not in agreement with Hanaguri et al [30] who claim to observe $s\pm$ superconductivity in Fe(Se, Te). The fact that neutron scattering experiments show a resonance at $\sim$6 meV in the magnetic scattering at the antiferromagnetic
wavevector $Q = (0.5, 0.5)$, whose intensity increases abruptly when the sample is cooled below $T_c$ [15] is also in favor of a $s^\pm$ scenario\(^6\). In SmFeAsO\(_{0.85}\) we observed a strongly damped double gap together with frequent zero-bias peaks (figures 5 and 6), in agreement with a change of sign of the order parameter as observed in $d$-wave cuprates in the presence of non-magnetic impurities [69]. Both features are thus well explained in an $s^\pm$ scenario. On the other hand, in the case of FeSe\(_{0.5}\)Te\(_{0.5}\), a simple $s$-wave-like gap is observed and no zero-bias peaks are present; both facts point to a simple BCS mechanism. However, we cannot completely exclude a ‘MgB\(_2\)–like’ double-gap scenario, with a single gap being observed in STM as a result of a tunneling selectivity effect as in MgB\(_2\) [72] or in Ba\(_2\)Si\(_2\)O [28].

Apart from substituting Se by Te atoms, doping in FeSe is also possible with inter-plane Fe atoms, such as in Fe\(_{1+x}\)Se. Such a doping might have a different effect. In this case, FeSe planes are preserved, the doping being provided by the excess of Fe localized in between them. This hypothesis seems to be confirmed by thermal conductivity measurements by Dong et al [70] which are favorable to a nodeless multigap SC OP in Fe\(_{1+x}\)Se. The impressive increase of $T_c$ with pressure observed in Fe\(_{1+x}\)Se, which can reach 37 K [22,18–20,23,71,21], is most probably related to the evolution of the strength of the SC pairing mechanism (presumably of magnetic origin) with pressure. On the other hand, the FeSe\(_{1-x}\)Te\(_x\) saturates to $\sim 20$ K in thin films with epilayer pressure [73] and 22–23 K under mechanical pressure in the bulk [74, 75], a value compatible with a conventional phononic superconductivity. The isostructural substitution of iron by ruthenium and non-isoelectronic substitution of iron by cobalt atoms, which both induces a strong in-plane disorder, leads to a dramatic decrease of $T_c$ in NdFe\(_{1-x}\)M\(_2\)AsO\(_{0.89}\)F\(_{0.11}\) (M = Co, Ru) which drops from $\sim 48$ K for $x = 0$ to 0 K (non-superconducting phase) above $x = 0.13$ [76]. Such results strongly support our idea about the fragility of the $s^\pm$ SC OP with respect to the disorder strength.

7. Conclusion

In conclusion, we have synthesized iron-based superconductors FeSe\(_{0.5}\)Te\(_{0.5}\) ($T_c^{\text{onset}} = 14$ K), SmFeAsO\(_{0.85}\) ($T_c^{\text{onset}} = 54$ K) and SmFeAsO\(_{0.9}\)F\(_{0.1}\) ($T_c^{\text{onset}} = 52$ K) and performed tunneling spectroscopy of them at 4.2 K and in ultra-high vacuum. In FeSe\(_{0.5}\)Te\(_{0.5}\) crystals we observed a single ‘BCS-like’ gap while in SmFeAsO\(_{0.85}\), SmFeAsO\(_{0.9}\)F\(_{0.1}\) the tunneling spectra revealed two energy scales which we associate with a multigap superconductivity in these materials. The tunneling conductance spectra can be qualitatively understood within a $s^\pm$ two-gap model considering the sign reversal in the OP, due to a magnetic pairing. We showed that the $s^\pm$ SC DOS is dramatically affected by QP interband scattering, in contrast to the case of an $s$-wave two-gap superconductivity, which was found much more robust. One of the possible explanations of the observed single-gap DOS in FeSe\(_{0.5}\)Te\(_{0.5}\) could be the suppression of the $s^\pm$ superconductivity by strong disorder resulting from the Se–Te substitution.

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References

[1] Bednorz J G and Muller K A 1986 Z. Phys. B 64 189
[2] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[3] Takahashi H, Iwaga K, Ariiz K, Kamihara Y, Hirano M and Hosono H 2008 Nature 453 376
[4] Ren Z-A et al 2008 Chin. Phys. Lett. 25 2215
[5] Lee P A, Nagaosa N and Wen X-G 2006 Rev. Mod. Phys. 78 17
[6] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 Phys. Rev. Lett. 101 117004
[7] Torikachvili M S, Bud’ko S L, Ni N and Canfield P C 2008 Phys. Rev. Lett. 101 057006
[8] Okada H, Iwaga K, Takahashi H, Kamihara Y, Hirano M, Hosono H, Matsubayashi K and Uwatoko Y 2008 J. Phys. Soc. Japan 77 113712
[9] Alireza P L, Chris Ko Y T, Gillette J, Petrone C M, Cole J M, Lorenzach G G and Sebastian E 2009 J. Phys.: Condens. Matter 21 012208
[10] Matsubayashi K et al 2009 J. Phys. Soc. Japan 78 037306
[11] Iwaga K, Okada H, Takahashi H, Matsuishi S, Kamihara Y, Hirano M, Hosono H, Matsubayashi K and Uwatoko Y 2009 J. Phys. Soc. Japan 78 025001
[12] Schopohl N and Scharnberg K 1977 Solid State Commun. 22 371
[13] Mazin I I, Singh D J, Johannes M D and Du M H 2008 Phys. Rev. Lett. 101 057003
[14] Drew A J et al 2008 Phys. Rev. Lett. 101 097010
[15] Drew A J 2009 Nat. Mater. 8 310
[16] Qiu Y et al 2009 Phys. Rev. Lett. 103 067008
[17] Wen J et al 2010 Phys. Rev. B 81 100513(R)
[18] Christianson A D et al 2008 Nature 456 930
[19] Hsu F C et al 2008 Proc. Natl Acad. Sci. USA 105 14262
[20] Medvedev S et al 2009 Nat. Mater. 8 630
[21] Margadonna S, Takabayashi Y, Ohishi Y, Mizuguchi Y, Takano Y, Kagaaya M, Nakagawa T, Takata M and Prassides K 2009 Phys. Rev. B 80 064506
[22] Sidorenkov V A, Tszybashchenko V V and Sadykov R A 2009 J. Phys.: Condens. Matter 21 415701
[23] Garbarino G, Sow A, Lejay P, Sulpece A, Toulemonde P, Mezouar M and Núñez-Regueiro M 2009 Europhys. Lett. 86 27001
[24] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 93 152505
[25] Miyoshi K, Takeichi Y, Mutou E, Fujiiwara K and Takeuchi J 2009 J. Phys. Soc. Japan 78 093703
[26] Øystein F, Kugler M, Maggio-Aprile I, Berthold C and Renner C 2007 Rev. Mod. Phys. 79 353
[27] Mallet P, Roditchev D, Sacks W, Déroufdeau D and Klein J 1996 Phys. Rev. B 54 13324
[28] Giubileo F, Roditchev D, Sacks W, Lamy R, Thanh D X, Klein J, Miraglia S, Fruchart D, Marcuis J and Monod Ph 2001 Phys. Rev. Lett. 87 177008
[29] Berges N, Dubost V, Noat Y, Sacks W, Roditchev D, Emery N, Hérold C, Maréché J-F, Lagrange P and Loupias G 2006 Phys. Rev. Lett. 97 077003

\(^6\) Note that such a low resonance energy of 6 meV would require a very strong electron–magnon coupling if magnon exchanges were responsible for the pairing mechanism.
