IRON PNICTIDES - NEW HIGH TEMPERATURE SUPERCONDUCTORS. POINT CONTACT ANDREEV REFLECTION SPECTROSCOPY STUDIES

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ABSTRACT

In 2008, 22 years after discovery of cuprates, the first high temperature superconductors, a new family of high temperature superconductors - the iron pnictides appeared. In many aspects the new systems are similar but in others very different from the cuprates. Juxtaposition of these two classes of materials represent a real challenge in the recent condensed matter physics. These studies can shed light on one of the most intriguing physical problems - high temperature superconductivity. One of the important questions in any new superconductor concerns the superconducting order parameter. In this paper a brief overview of the experimental studies of the order parameter of iron pnictides is given.

Keywords: *high temperature superconductors, cuprates, iron pnictides, superconducting energy gaps*

1. INTRODUCTION

Large scale applications of superconductivity in many possible areas of industry, from transportation of electric energy, superconducting engines, levitating trains to the superfast computers and various IT elements and devices, have been complicated by the fact that the phenomenon of superconductivity is limited to low temperatures. Keeping low temperatures near absolute zero is indeed very costly and technically complicated. That is why a discovery of the superconductors with high transition temperature T_c in cuprates in 1986 by Mueller and Bednorz [1] triggered enormous interest not only in scientific community. Recent record transition temperature $T_c \approx 130$ K in $HgBa_2Ca_2Cu_3O_8$ at ambient pressure and about 165 K at high pressure is promising. But technological problems to be overcome in cuprates are enormous and yet no definite explanation of the superconducting mechanisms is available. An unexpected discovery of a brand new family of high-T_c superconductors in semimetal compounds of iron in 2008 [2] brings a new hope.

Discovery of superconductivity in compounds containing iron was very surprising since magnetism and superconductivity are contradicting physical phenomena. Iron, the archetypal ferromagnet, with locally polarized spins pointing to one direction, was supposed to break apart any Cooper pairs, the basic constituent of superconductors. Studies of superconducting iron pnictides, where iron is always placed together with one of two pnictogens (phosphorus or arsenic) are just at the beginning. In many aspects the new systems are similar but in others very different from the cuprates. Indeed a juxtaposition of two big classes of high-T_c materials can be very helpful for finding solutions in both systems.

Similarly to the high-T_c cuprates the superconductivity in iron pnictides is enabled by chemical doping of the antiferromagnetic parental compounds. As a consequence a complicated phase diagram *Transition temperature versus doping* arises with underdoped, optimally doped (with the highest T_c) and overdoped superconducting samples revealing different properties. But in contrast to the cuprates where the parent, undoped compounds are insulators, in the case of iron pnictides these are (semi)metallic. The highest transition temperature (up to 56 K) among different iron pnicitides has been achieved in the optimally doped REFeAsO(F), so-called 1111 group with Gd, Nd, or Sm [3] standing for a rare earth element RE where doping is performed by fluorin partly replacing oxygen. Considerable interest has also been attracted by another class of iron pnictide superconductors based on AFe_2As_2 with A = Ba, Sr and Ca, referred to as the 122-type group. The 122-type compounds are chemically and structurally simpler and less anisotropic than the 1111 ones. The maximum T_c of 38 K is obtained in the optimally hole doped $Ba_{0.6}K_{0.4}Fe_2As_2$ system [4] but also the electron doped $Ba(Fe_{1-x}Co_x)_2As_2$ crystals with T_c about 25 K are available [5]. In contrast to the 1111 systems the 122-type parent compounds show magnetic (from paramagnetic to SDW antiferromagnetic phase) and structural transition (from tetragonal to orthorhombic phase) at the same temperature of about 140 K. This transition is gradually suppressed by chemical doping but the phase diagram *Temperature versus doping* shows an overlap between the SDW/orthorhombic and superconducting phases for x=0.2 to 0.4 in $Ba_{1-x}K_xFe_2As_2$ [6].

The both cuprates and iron pnictides are layered and anisotropic systems. The cuprate superconductors are basically single-band compounds, where the conduction band is formed from the Cu 3*d* orbitals. The single superconducting energy gap has a non-trivial $d_{x^2-y^2}$-wave symmetry. Band structure calculations on iron pnictides [7] have shown that the multiple Fe *3d* bands located near the Fermi energy are responsible for the appearance of multiple Fermi surface (FS) sheets. The multiband/multigap superconductivity with interband interactions leading to an exotic *s*-wave pairing with a sign reversal of the order parameter between different FS sheets [8] stands among the hot candidates to explain the high-T_c superconductivity in iron pnictides. Since the superconductivity appears when a doping suppresses the magnetic order, the magnetic fluctuations are considered as a clue for the attractive superconducting interaction.

The following brief overview of some of the available

experimental data brings pieces of evidence for multiple superconducting energy gaps revealing basically two sizes of the coupling strength $2\Delta/kT_c$. The most of the data point to an *s*-wave pairing symmetry.

2. OVERVIEW OF THE SUPERCONDUCTING GAP STUDIES BY ARPES

High resolution angle resolved photoemission spectroscopy (ARPES) has become extremely effective tool for studies of the FS sheets and superconducting energy gaps in a momentum space. Ding et al. [9] observed three FS sheets in $Ba_{0.6}K_{0.4}Fe_2As_2$ crystals with T_c of 37 K: an inner hole-like FS pocket, an outer hole-like Fermi surface sheet, both centered at the Brillouin zone center and a small electron-like FS at the M point. A large superconducting energy gap (Δ_L = 12 meV) was detected on the two small hole-like and electron-like FS sheets while a small gap (Δ_S = 6 meV) was found on the large hole-like FS. The gaps closing at the same T_c are isotropic. Two small FS sheets with a very strong coupling strength $2\Delta_L/kT_c \sim 8$ are connected by the (π,0) SDW vector in the parent compound indicating an importance of the interband interaction between these two nested FS sheets also for superconductivity. Nakayama et al. [10] reported on the observation of the fourth FS sheet in $Ba_{0.6}K_{0.4}Fe_2As_2$. It is another, outer electron pocket centered around the M point with the superconducting energy gap comparable ($\sim$ 11 meV) to the gap on the inner electron and hole pockets. Important finding has been reported by Terashima et al. [11] on ARPES measurements on $Ba(Fe_{1-x}Co_x)_2As_2$ crystals. In the sample with x=0.15 and T_c of 25 K due to the electron doping the inner hole-like FS sheets is absent and the nesting conditions are switched from the inner hole FS sheet to the outer one which is connected to the electron FS sheets by the (π,0) SDW vector. Strong coupling strengths $2\Delta/kT_c \sim 6$ and $2\Delta/kT_c \sim 4.5$ are found on the hole and electron FS's, respectively. In heavy Co doped samples only the electron-like FS sheets remain and no superconductivity is present. All this is supporting the inter-FS superconductivity in iron pnictides.

3. POINT CONTACT ANDREEV REFLECTION SPECTROSCOPY ON 122-TYPE IRON PNICTIDES

Point contact Andreev reflection (PCAR) spectra measured on the ballistic microconstriction between a normal metal and a superconductor consists of pure Andreev reflection and tunneling contributions, respectively [12]. First contribution makes the conductance inside the voltage region $|V| < \Delta/e$ twice as large as in the normal state or as what is at large bias where the coupling via the gap is inefficient. Tunneling contribution reduces the conductance at the zero bias and two symmetrically located peaks rise at the gap energy. PCAR conductance can be compared with the Blonder-Tinkham-Klapwijk (BTK) model using as input parameters the energy gap, the parameter z (measure for the strength of the interface barrier) and a parameter for the spectral broadening. For a multiband/multigap superconductor the point contact conductance dI/dV can be expressed as a weighted sum of partial BTK conductances. PCAR spectroscopy has proved to be very powerful in the investigation of the two gap superconductor MgB_2 [13]. In MgB_2 the total PCAR conductance consists of two parallel contributions, the first originated from a three dimensional π band with a small gap Δ_S and a weight α and the second from a quasi two dimensional σ band with a large gap Δ_L and a weight (1-α) respectively. In that case, the parameter α varied between 0.7 and 0.99, depending on angle between the point contact current and orientation of MgB_2 crystal. Also different values of z for each band were necessary in the fitting procedure. Spectral characteristics as the superconducting energy gaps or electron-phonon interaction features can be read from the point contact data only if the junction is in a ballistic or diffusive regime, where heating effects are avoided. There, both the elastic l_e as well as inelastic l_i mean free paths should be larger than the diameter d of the junction or a diffusion length $(l_e.l_i)1/2 > d$. These requirements should be satisfied in the normal as well as in the superconducting part of the junction. MgB_2 was quite an exceptional example where the PCAR spectroscopy worked extremely well but the situation in iron pnictides is far more complicated. The latter systems are highly resistive materials where reaching of ballistic regime is quite challenging. Point contacts (PC) made on a highly resistive material as $Ba_{1-x}K_xFe_2As_2$ have resistances between tens and hundreds of ohms which corresponds to the contact diameter of tens of nanometers. Indeed, the electron mean free path can also be on the same order, here. Then, precautions should be made to avoid the junctions with heating effects. In our work on iron pnictides only the junctions without the conductance dips and irreversibilities in voltage dependences are presented. Moreover to preserve the spectroscopic conditions we focus on PC junctions having a finite barrier strength parameter z with a tunneling component in the spectrum.

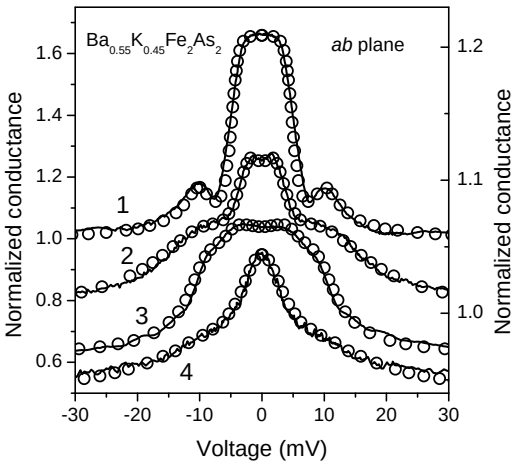

Fig. 1 Typical PCAR spectra on $Ba_{0.55}K_{0.45}Fe_2As_2$ (lines) measured at 4.4 K with the PC current mostly within the *ab* plane of the sample. Spectra are normalized to their respective normal state and fitted to the two gap BTK model (symbols). For curves 2 and 4 right *y* axis applies. Spectra 2, 3 and 4 are vertically shifted.

In the following we review our point contact spectroscopy study on the $Ba_{0.55}K_{0.45}Fe_2As_2$ single crystals recently published in Ref. [14]. The crystals were grown out of a Sn flux. The resistive measurements showed the onset of the superconducting transitions below 30 K and the zero resistance at 27 K. Rather broad transitions in some of the crystals with multiple steps are attributed to a possible different amount of potassium in different layers or different crystals. A local transition temperature measured by the point-contact technique showed superconducting T_c's between 23 and 27 K. The specific heat as well as the resistivity measurements on these crystals showed features at about 85 K [15]. Although reduced they are found at the same temperature as on the undoped $BaFe_2As_2$ samples where the tetragonal-to-orthorhombic structural phase transition takes place. This transition is revealed here at a lower temperature as compared with 140 K found in Ref. [4]. The decreased structural transition temperature is due to the amounts of Sn up to 1% incorporated into the bulk. A presence of tin does not significantly affect the high-temperature superconducting phase transition in $Ba_{0.55}K_{0.45}Fe_2As_2$. Before point contact measurements the crystals were cleaved to reveal fresh surface. For the measurements in the *c* direction the fresh shiny surface was obtained by detaching the degraded surface layers by a scotch tape. The microconstrictions were prepared in situ by pressing a metallic tip (platinum wire formed either mechanically or by electrochemical etching) on a fresh surface of the superconductor. For the measurements with the point contact current in the *ab* plane a reversed tip-sample configuration was used. The freshly cleaved edge of the single crystal jetting out in *ab* direction was pressed on a piece of chemically etched copper. A special PC approaching system allowed for lateral as well as vertical movements of the PC tip by a differential screw mechanism. Details of the technique can be found elsewhere [13]. Figure 1 shows typical PCAR spectra obtained on $Ba_{0.55}K_{0.45}Fe_2As_2$ with the PC current preferably within the *ab* plane. The spectra present double enhanced conductances, the typical features of the Andreev reflection of quasiparticles coupled via two superconducting energy gaps. The first enhancement starts below 20 mV with the gap-like humps at about 10 mV while the second one is located below $\sim$ 5-7 mV. On the spectra 2 and 3 also two symmetrical maxima at 2-3 mV are displayed. Majority of the spectra measured in the *ab* direction revealed a heavily broadened enhanced conductance near the zero bias as indicated by the spectrum 4. This is most probably caused by the sample inhomogeneities on the nanoscale.

The presented spectra are normalized to their respective normal state and fitted to the two gap BTK model (symbols). The resulting values of energy gaps are spread in the range of 2-5 meV and 9-10 meV for the small and large gap, respectively. The values of smearing parameters were 10, 60, 30, and 100% of each energy gap value for curves 1, 2, 3, and 4, respectively. For each presented fit different values of z for the two bands were also necessary. Typically, z_L for the band with a large gap was about 0.4 - 0.8, while z_S was twice smaller. Although the *s*-wave two gap BTK formula has been successfully used to fit our PCAR data a possibility of unconventional pairing symmetry cannot be completely ruled out. Obviously, rather strongly broadened spectra as presented here could be in principle fitted also by model taking into account anisotropic or nodal gaps, if an appropriate current injecting angle was selected [16].

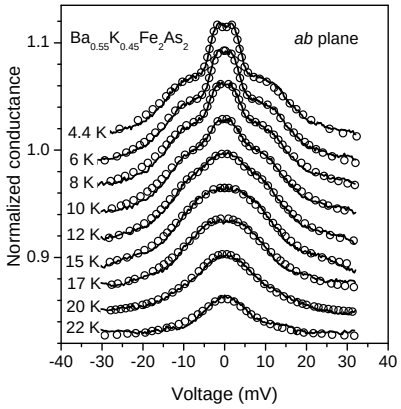

Fig. 2 Temperature evolution of spectrum 2 from Fig.1 (lines). Fits to the BTK model are indicated by symbols.

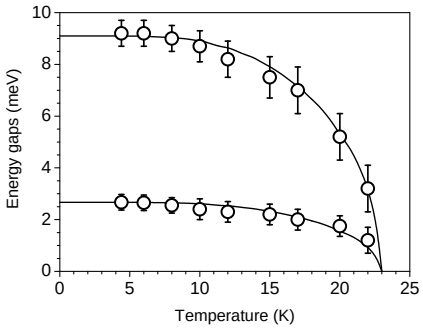

Fig. 3 Values of the energy gaps obtained from fitting procedure for distinct temperatures. Lines represent the BCS type temperature dependences of energy gaps.

In Fig. 2 temperature evolution of the second spectrum from previous figure is presented. All the spectra (lines) were normalized to the conductance measured at 27 K and fitted to the BTK model with a proper temperature smearing involved. Obviously, the spectrum at the lowest temperature reminds the two gap spectrum of MgB_2 for a highly transparent junction with conductance enhancements due to Andreev reflection of quasiparticles. As the temperature is increased the double enhanced point contact conductance corresponding to two energy gaps is gradually smeared out and spectrum intensity decreases. Indeed, the spectra could be well fitted to the two gap BTK formula. The best fit for each temperature is shown by open circles. The extracted values of the gaps at different temperatures are shown in Fig. 3 (symbols) following nicely a BCS prediction (lines) rescaled to the size of the respective gap. The values of the energy gaps at lowest temperature are for the small $\Delta_S \sim 2.7$

meV and the large one $\Delta_L \sim 9.2$ meV, which corresponds to the coupling strengths $2\Delta_S/kT_c \sim 2.7$ and $2\Delta_L/kT_c \sim 9$ for T_c = 23 K. The smearing parameters (about 60% of the respective gap values), the barrier strengths $z \sim 0.3$ and 0.6 as well as the weight factor $\alpha \sim 0.5$ obtained at 4.4 K were kept constant at higher temperatures. From the data obtained on more junctions we observe that the gaps are scattered as $2\Delta_S/kT_c \sim$ 2.5-4 and $2\Delta_L/kT_c \sim$ 9-10.

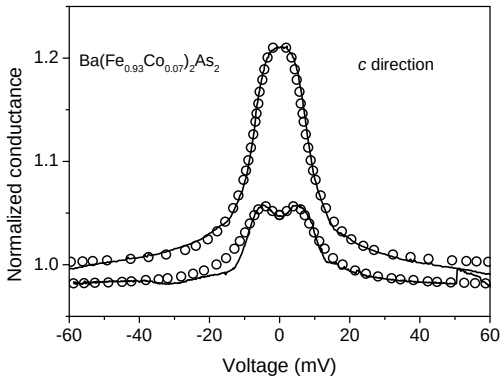

Fig. 4 Spectra of Pt-$Ba(Fe_{0.93}Co_{0.07})_2As_2$ junctions measured at 4.5 K (lines). Fits to the single gap BTK model are shown by circles.

Recently we extended our PCAR measurements to the hole doped system of the 122-type family, namely to the optimally doped $Ba(Fe_{0.93}Co_{0.07})_2As_2$ samples with T_c of approximately 23 K determined from transport and susceptibility measurements. The single crystals were grown from FeAs/CoAs flux from a starting load of Ba, FeAs and CoAs precursors. Details of the preparation resulting to large crystals of a few mm size can be found elsewhere [18]. In Fig. 4 the typical spectra of the Pt-$Ba(Fe_{0.93}Co_{0.07})_2As_2$ junctions measured at 4.5 K are presented. The spectra show enhanced differential conductances and the bottom curve reveal also a single pair of peaks at about 5 mV. In no case a double enhanced conductance spectrum indicative for two gap superconductivity was found. Indeed, the spectra on $Ba(Fe_{0.93}Co_{0.07})As_2$ can be fitted just by a single *s*-wave gap BTK formula. This is in strong contrast to the PCAR spectra of the hole doped $Ba_{0.55}K_{0.45}Fe_2As_2$. The fits on the electron doped system have yielded the superconducting energy gap of around 5-6 meV. In all spectra a significant broadening was observed which is witnessed by a large value of the parameter spreading between 50% and 100% of the respective gap value. The superconducting transition temperature at the junctions was 22 K very close to the bulk T_c determined from transport measurements. With T_c the coupling strength $2\Delta/kT_c$ between 5.3 and 6.3 can be determined. This is remarkably consistent with the above mentioned results obtained by the ARPES measurements. Although our results are only preliminary and the statistics is not yet sufficient, the data seem to prove that if there are multiple gaps in the electron doped $Ba(Fe_{0.93}Co_{0.07})_2As_2$ superconductors they are quite close to each other.

4. CONCLUSIONS

In contrast to cuprates which are single band and *d*-wave superconductors, 122-type iron pnictides seem to be proven as the multiband systems with multiple nodeless gaps. In the hole doped $Ba_{1-x}K_xFe_2As_2$ the available data point to an existence of two distinct superconducting energy gaps with the strength below and much above the single band BCS weak coupling limit, respectively. In the electron doped $Ba(Fe_{1-x}Co_x)_2As_2$ if there are two gaps present they are very close to each other having a strong coupling $2\Delta/kT_c$ between 5 and 6. Further experimental and theoretical effort is certainly needed to elucidate physics in these extremely interesting systems.

ACKNOWLEDGEMENT

This work was supported by the Slovak R&D Agency under Contracts Nos. VVCE-0058-07, APVV-0346-07, and LPP-0101-06, and by the U.S. Steel Košice. Centre of Low Temperature Physics is operated as the Centre of Excellence of the Slovak Academy of Sciences. Work at the Ames Laboratory was supported by the U.S. Department of Energy, Basic Energy Sciences, under Contract No. DE-AC02-07CH11358. Valuable discussions with I.I. Mazin, A.A. Golubov and N.L. Wang are appreciated.

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Received January 28, 2010, accepted July 9, 2010

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