Topical Review

Progress in nonmagnetic impurity doping studies on Fe-based superconductors

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Abstract
We review the progress of nonmagnetic impurity doping studies on Fe-based superconductors. On the theoretical side, two highly promising candidates for the pairing symmetry order parameter, i.e. the multi-gap $s_{++}$ and $s_{±}$ wave models, have been proposed but continuously debated. The debate arises because of the complex gap structure and exceptional magnetic and metallic behaviors of Fe-based superconductors, which may vary the influence of nonmagnetic defects in the chemical potential, impurity disorder, inter- and intra-band scattering strength, and electron localization. This creates difficulties in directly obtaining the most important information for understanding the symmetry order parameter. Experimentally, nonmagnetic impurity substitution studies have been widely carried out, which have provided very useful insights. We review herein the various nonmagnetic impurity doping experiments, including the controlled defects within the superconducting Fe$_2$X$_2$ planes through sample quality improvement, single impurity effects on the electronic state and local moment, the magnetic response of the Fe$_2$X$_2$ planes both on the macroscopic scale as the antiferromagnetic state and the local scale of moment, as well as the significant effect of modifying the transport properties. The experiments enable us to qualitatively analyze the nonmagnetic impurity effects on the superconducting state for many Fe-based superconductors. We also propose herein some strategies for nonmagnetic impurity doping study. As an important model for explaining the nonmagnetic impurity doping effects, the pair-breaking model is compared with various theoretical approaches via analysis of the pair-breaking rates of various Fe-superconductors.

Keywords: Fe-based superconductor, nonmagnetic impurity, order parameter, pair-breaking
1. Introduction

In 2006, Kamihara et al discovered superconductivity with a critical temperature ($T_c$) of 5 K in LaFePO$_{1−δ}$F$_{δ}$, which has a layered ZrCuSiAs-type (1111-type) tetragonal structure [1]. Adopting the same strategy by substituting fluorine for oxygen in an analog LaFeAsO, a much higher $T_c$ of 26 K was achieved in early 2008 [2]. The exciting discovery created a peak in superconductivity research in which it was announced that a new high-$T_c$ superconductor family, the so-called Fe-based superconductor (FBS), was born. The FBS family has attracted a lot of attention and the studies have advanced rather rapidly [1–7]. This is not only due to the fact that the FBS is a second class of high-$T_c$ superconductor after the cuprate superconductors, but also because it is highly promising for understanding the superconducting (SC) mechanism of high-$T_c$ by comparing the two families.

To date, one of the remaining key issues is to elucidate the pair symmetry of the FBS, for which several possible models were proposed just after the discovery [8–17]. Among the various models, the multi-gapped $s$-wave is generally acceptable but has still been debated between the $s_0$ [8, 9] and $s_{++}$ wave models [10, 11]. In both models, the Fermi surface has the same hole-type pockets but the electron-type pockets within the $s_{++}$ wave model have opposite signs, i.e. a sign-reversal $s$-wave model, whilst having the same sign within the $s_0$ wave model. Additionally, the $d$-wave model with opposite signs for the nearest-neighbor electron pockets remains competitive, provided that there are nodes on the hole pockets or even on both the electron and hole pockets [10, 15, 16]. The various experimental results can barely reach a consensus on the symmetry model. More recent results even suggested that different systems in the iron-pnictide family may represent different pairing symmetries, as do superconductors with different doping levels [12, 12, 17]. The divergences require further investigation to provide solid evidence. Among the various strategies, the impurity substitution, especially the nonmagnetic impurity substitution for Fe, is one of the most promising approaches to address this issue.

The SC Fe$_2$X$_2$ ($X = \text{As, P or Se}$) plane, which is similar to the SC CuO$_2$ layer in cuprate superconductors, is a common feature shared by the various iron-pnictide superconductors. The substitution of point defects for the Fe-site has been proposed for understanding the physical properties, which has been demonstrated to be an effective way and has been intensively undertaken in cuprate superconductors. According to Anderson’s theorem [18], nonmagnetic impurity (NMI) cannot break Cooper pairs in an isotropic SC gap but can for an anisotropic gap, while the pair-breaking effect of the magnetic impurities is independent of gap type. Thus, the introduction of nonmagnetic point defects is crucial for probing the information of the gap. The zinc ion (Zn$^{2+}$) with a tightly closed $d$-shell is considered an ideal NMI [19–27]. The study of Zn-substitution effects for Cu on the cuprate family such as YBa$_2$Cu$_3$O$_{7−δ}$ [19–21], (La,Sr)$_2$CuO$_4$ [19, 22–24] and Bi$_2$Sr$_2$CaCu$_2$O$_8$ [19, 25–27] has been carried out over the last two decades. Only a few at.% of Zn which acts as a strong scattering center can remarkably depress SC due to the $d$-wave anisotropic gap [19]. Since doped Zn often plays a crucial role in pairing symmetry judgment demonstrated by the investigations on many superconductors, it is expected to work in the FBS as well.

In this article we review both theoretical and experimental studies of the NMI effects on the superconductivity of FBS. We start with an introduction of the potential gap symmetries of FBS and recent theoretical studies on the defect impurities in section 2, and then overview the NMI substitution methods in section 3, including both chemical doping and irradiation inducing defects. The effects of NMI on the various properties of the host superconductors are reviewed by introducing the various experiments in section 4: (i) the sample quality will be discussed for the controlled impurities within the SC Fe$_2$X$_2$ planes in section 4.1. (ii) In section 4.2, a single impurity effects on the electronic state and local moment are introduced. (iii) The magnetic response of the Fe$_2$X$_2$ planes to NMI on both the macroscopic scale as the antiferromagnetic state and the local scale of moment will be reviewed in section 4.3. (iv) Significant modifications of the transport properties of the superconductors are discussed in detail in section 4.4. (v) Some potential experiments for the introduction of NMI are also proposed in section 4.5. (vi) Finally, the most prominent qualitative feature from the impurity doping, the effects on the SC state, are discussed in section 4.5, which covers many systems of superconductors. As a summary, the pair-breaking rates in different systems will be reviewed in section 5 by comparison with various theoretical approaches.

2. Theoretical background

2.1. Gap symmetry of Fe-based superconductors

Theorists have proposed four models as candidates for the SC energy gap symmetry of FBS as shown in figure 1 [6]. Figure 1(a) illustrates the order parameter (OP) for the conventional Bardeen–Cooper–Schrieffer (BCS) superconductors [28], in which the electrons pairing by gaining energy from the electron–phonon interactions and the SC OP is the same for all electrons, namely, an ‘$s$-wave’ model. The $s$-wave SC is associated with an isotropic energy gap for the Cooper pairs, being completely symmetric along all directions. The electron–electron magnetic interaction [29–33] dominates another type of SC gap with the ‘$d$-wave’ OP as shown in figure 1(b), where the sign variation of the OP has direction dependence, e.g. cos$2\theta$, which can result in an anisotropic gap symmetry. The OP of the cuprate superconductors is generally of the $d$-wave symmetry. Additionally, the multi-gap model ($s_{++}$ wave) is also proposed, as shown in figure 1(c) [34]. It is believed that the SC mechanism for MgB$_2$ is of the BCS-type with the $s_{++}$ symmetry, whereby the Fermi surface comprises two small hole pockets around the $\Gamma = (0, 0)$ point and two electron pockets around the $\mathbf{M} = (\pi, \pi)$ point in the 2-Fe Brillouin zone. The OP is positive for all bands but has different magnitudes for
different bands, belonging to an isotropic symmetry. After the discovery of FBS, another type of multi-gap model, the so-called 's± wave’ model (see figure 1(d)) was proposed to interpret the OP. In the s± wave model, the Fermi surface also consists of two small hole pockets and two electron pockets, whereas the OP in some band(s) has a positive sign but in the other band(s) has a negative sign. Within such a framework, the s± wave gap structure possesses a strongly anisotropic symmetry.

For FBS, the conventionally simple s-wave model has already been eliminated by various studies and the multi-gapped s-wave models, i.e. the s± [8, 9] and the s++ wave [10–12], are currently promising candidates, where the former likely has a magnetic fluctuation origin while the latter probably has a charge fluctuation origin. Both models have positive OPs for the hole Fermi pockets, while having opposite signs for the electron pockets, thus the s± wave is sometimes called a sign-reversal s-wave, and the s++ state a non-sign-reversal. As a competing candidate, the d-wave model with nodes on the hole pockets or even on both the electron and hole pockets remains possible for the OP of FBS [10, 15, 16].

Various experiments have been performed to investigate the OP symmetry of FBS, including angle-resolved photoemission spectroscopy, quantum oscillation, London penetration depth, Josephson tunneling effect and so on. However, the issue remains inclusive because of the rather contrary results derived from these experiments. Here, we will review the NMI doping study on this issue.

2.2. Nonmagnetic impurity doping effect on superconductivity

In this section, we focus on theoretical studies of the effect of impurity atoms or the atomic defects. The pair-breaking effect by magnetic and NMI will be introduced. As mentioned above, magnetic impurity suppresses SC independently of the gap symmetry while the NMI effect depends strongly on it. The NMI, for instance Zn, will suppress $T_c$ according to the Abrikosov–Gor’kov (AG) formula [35–37]

$$\ln \left( \frac{T_c}{T_0} \right) = \Omega \left[ \varphi \left( \frac{1}{2} + \frac{\mu}{2} \right) - \varphi \left( \frac{1}{2} \right) \right],$$

(1)

where $\varphi(x)$ is the digamma function. In mathematics, the digamma function is defined as the logarithmic derivative of the gamma function [36]

$$\varphi(x) = \frac{d}{dx} \ln \Gamma(x) = \frac{\Gamma'(x)}{\Gamma(x)},$$

(2)

It also has an integral representation as

$$\varphi(x) = \int_0^\infty \left( e^{-t} - \frac{e^{-xt}}{1-e^{-t}} \right) dt.$$

(3)

The $\mu$ in equation (1) is defined by

$$\mu = \frac{\hbar}{2\pi k_B T_0 \tau},$$

(4)

where $\tau$ is the relaxation time of NMI scattering. $\Omega$ in equation (1) is the gap anisotropy defined as

$$\Omega \equiv 1 - \frac{\langle \Delta(k) \rangle^2}{\langle \Delta(k) \rangle^2}.$$  

(5)

For an isotropic SC gap, for instance the isotropic s-wave, $\Omega = 0$, while $\Omega$ is 1 for an anisotropic gap-like d-wave and anisotropic s-wave.

As we can see from equation (1), the introduction of NMI does not break paired electrons for an isotropic SC gap but for an anisotropic gap [37]. However, $T_c$ also depends on the
Debye frequency $\omega_D$ and the density of states $D(E_f)$ according to the BCS theory in a form

$$T_c \approx \frac{1.14\hbar\omega_D}{k_B} \exp \left( \frac{-1}{D(E_f)V} \right),$$

where $V$ is the electron–phonon interaction strength. If the introduction of NMI affects $D(E_f)$ (due to the carrier doping) or $\omega_D$, $T_c$ will consequently vary even in the isotropic $s$-wave superconductors. Except for (6) the effect on $D(E_f)$ and $\omega_D$, NMI can also break the Cooper pairs in anisotropic superconductors due to $\Omega \neq 0$, as given by the following equation derived from equation (1)

$$\frac{T_c}{T_0} = 1 - \frac{\hbar}{8k_B} \frac{1}{\tau_c}.$$  

It is clear from equation (7) that the suppression of $T_c$ is proportional to the impurity scattering strength and the last part is defined as pairing-breaking rate

$$\alpha = \frac{\pi^2 \hbar}{8k_B} \frac{1}{\tau_c},$$

where $1/\tau_c$, which is defined as the critical scattering rate where SC is completely suppressed, can be expressed as

$$\frac{1}{\tau_c} = \frac{8k_B}{\pi^2 \hbar}.$$  

We will strengthen the discussions on this critical parameter in sections 3 and 4.

### 2.3. Pair-breaking

To study the pair-breaking effect from magnetic and NMI on FBS, one of the most direct ways is to quantify the relation between $T_c$ suppression and the doping level $n_{\text{imp}}$. Onari and Kontani [11] first analyzed the effect of local impurity on iron pnictides, based on the five-orbital model. Figure 2 shows the calculation results for $T_c$ suppression as a function of doping level for both $s_\pm$ and $s_{i+}$ wave models. They suggested that in the $s_\pm$ wave state, the inter-band impurity scattering is promoted by the $d$-orbital degree of freedom. Consequently, the $s_{i+}$ wave state should be very fragile against impurities, regardless of magnetic or nonmagnetic impurities. $T_c$ was estimated to vanish with $n_{\text{imp}}$ of 0.01, 0.02 and 0.066 for $I = 1$ eV, $\infty$ and $-1$ eV, respectively, thus giving rise to the reduction rate of $T_c$ ($dT_c/dn_{\text{imp}}$) caused by the impurity is $\sim 50\zeta$ $K/\text{at.}\%$ [11], where $\zeta$ is the renormalization factor ($=m/m'$; $m$ and $m'$ are the band mass and the effective mass, respectively). Since the effective mass was estimated to be between $2m_n$ and $4m_c$ in the 122-type superconductors from angle-resolved photoemission spectroscopy (ARPES) measurements [38–40], one can obtain $dT_c/dn_{\text{imp}} = 25 K$ at $1.\%$ $(17 K$ at $1.\%$) for $\zeta = 0.5$ ($\zeta = 0.33$). As a contrast, the non-super $s_{i+}$ wave state is strongly against the NMI. It doesn’t seem too complicated to judge which order parameter symmetry is the nature of these superconductors, once we can quantify the relation of $T_c$ versus $n_{\text{imp}}$. Nevertheless, direct accurate determination of the real scattering rate is hardly achieved, which is generally further complicated by some other important factors that can also result in obvious $T_c$ suppression.

The impurity disorder can also affect the SC due to the fact that the SC mostly originates from doping. Efremov et al [14] analyzed the effect from disorder on two-band gap symmetry, namely, intra- and inter-band impurity scattering for which the $T_c$ suppression rate $\Gamma_{ab}$ is given by

$$\Gamma_{ab} = \Gamma_{a(b)} \frac{1}{\sigma(1-\sigma)\eta(N_a + N_b)^2/N_aN_b + \left(\frac{\sigma}{\eta}-1\right)^2}.$$  

Here, $\eta$ is the parameter as the ratio of intra- and inter-band scattering as $\eta = v^2/u^2$. $N_a$ and $N_b$ are the density of states for each band $(a, b)$ at the Fermi level, and $\sigma$ and $\Gamma_{a(b)}$ are the generalized cross-section normal state scattering rate parameters given as follows:

$$\sigma = \left(\frac{\pi^2 N_a N_b u^2}{1 + \pi^2 N_a N_b u^2}\right),$$

and

$$\Gamma_{a(b)} = n_{\text{imp}}\pi N_a u^2 \left(1 - \sigma\right).$$

In the weak scattering (Born) limit, one can get $\sigma \to 0$, while in the unitary limit (strong scattering) $\sigma \to 1$. On the other hand, for the strong scattering case, $\Gamma_{ab}$ $\to 0$, hence $T_c$ is independent of NMI. Figure 3 gives the calculation results for the effective inter-band scattering rate $\Gamma_{ab}$ dependent $T_c$ suppression in various $\sigma$ and $\eta$. The slopes of $T_c$ collapse onto one of three ‘universal’ curves, depending on the average pairing strength parameter $\langle \delta \rangle$ as positive, zero and negative. Here the sign of $\langle \delta \rangle$ depends on the coupling constant $\langle \lambda \rangle$ of the two-band superconductor as given by

$$\langle \lambda \rangle \equiv \left(\lambda_{aa} + \lambda_{ab}\right)N_a N^{-1} + \left(\lambda_{ba} + \lambda_{bb}\right)N_b N^{-1},$$

where $N = N_a + N_b$. The results indicate that a universal behavior of $T_c$ suppression is controlled by a single parameter $\langle \lambda \rangle$. As a result, the $s_{i+}$ wave SC can be suppressed by NMI for $\langle \lambda \rangle \leq 0$, but also demonstrates robustness against...
Impurities once \( \langle \lambda \rangle > 0 \). Typically, the critical value of the scattering rate \( \Gamma_{\text{crit}} \) defined by \( T_c(\Gamma_{\text{crit}}) = 0 \) is given by
\[
\frac{\Gamma_{\text{crit}}}{T_c} = \pi/2\gamma \approx 1.12
\] (14)
within the AG theory. In addition, as disorder increases, the \( s_+ \) wave may change to a fully-gapped symmetry, \( s_+ \) wave, which was suggested to be manifested by thermodynamic and transport properties.

On the other hand, Wang et al [41] and Efremov et al [42] also suggested that measurements of \( T_c \) suppression relative to the amount of chemical potential and disorder can hardly determine the gap structure in multiband systems. To improve the situation, one first needs to find a way to create points like potential scattering centers, so as to create disordered systems. From an experimental point of view, we need more accurate measurements on residual resistivity \( \rho_0 \) from high-quality NMI-doped single crystals. Here, \( \rho_0 \) corresponds to the change in the extrapolated \( T \rightarrow 0 \) value of the resistivity with disorder. Compared with the \( n_{\text{imp}} \) dependent \( T_c \), the observation of \( \rho_0 \) is the more accurate way to explore the pair-breaking effect from impurity scattering. Wang et al [41] calculated the relation between \( T_c \) suppression and the change of \( \rho_0 \) and showed how these results change for various types of gap structures and assumptions regarding the impurity scattering. Figure 4 shows the calculation results for \( T_c \) suppression versus the corresponding change in \( \rho_0 \) for the isotropic \( s_+ \) wave model and an anisotropic one with various values of the inter- to intra-band scattering ratio \( \alpha \equiv u/v \). Note that the \( s_+ \) gap can be anisotropic with nodes on the electron pockets, whose gap function \( \Delta_x \) can be given as
\[
\Delta_x = \Delta_0 (1 + r \cos 2\phi),
\] (15)
where \( \Delta_0 \) is angle-independent part of the gap function, \( r \) is the anisotropic factor, and \( \phi \) corresponds to the angle around the electron pocket. For a fully isotropic \( s \) wave gap, \( r = 0 \), hence the \( T_c \) is independent of NMI doping. In the respect that a gap which has nodes on the electron pockets, for instance set \( r = 1.3 \), the results exhibit a wide variety of initial slopes of \( T_c/\rho_0 \), which strongly depend on the scattering character of the impurity, but not just the doping level itself. Namely, the \( T_c \) may be suppressed weakly or sharply by the change of \( \rho_0 \) for instance, the pair-breaking residual resistivity \( \Delta_0 \) can be up to 1000 \( \mu \Omega \) cm once the \( \alpha \) is less than 0.2, and even without any suppression for \( \alpha = 0 \). Previous calculation results also showed \( \alpha \)-dependent suppression rate [41].

Studying the pair-breaking effect associated with the defects is a complicated issue. Besides the pair-breaking and the scattering character of the impurity, one has to consider the separation of the exploration of impurity effects on different length scales, from lattice spacing to the coherence length to sample size, as suggested by Anderson’s theorem [18]. In addition, Sato et al [13] proposed two other mechanisms for \( T_c \) suppression from impurity substitution: (i) the electron localization with sheet resistance \( R_\parallel \) exceeding \( h/4e^2 \approx 6.45 \text{ k}\Omega \), and (ii) the disappearance (or reduction in the area) of the whole Fermi surfaces around the \( \Gamma \) point in the reciprocal space. Furthermore, considering the NMI in the isotropic \( s_{++} \) wave state, the SC suppression may be caused by the following mechanisms: (i) suppression of the orbital fluctuations, which is a possible origin of the \( s_{++} \) wave state,
because of the violation of the orbital degeneracy near the impurity atom, and (ii) the strong localization effect in which the mean-free-path is comparable to the lattice spacing.

To thoroughly probe pair-breaking behavior, the fabrication of a high-quality nonmagnetic Zn-doped compound, especially for single crystals, is the most important issue. In the next section, we will discuss recent progress on the fabrication of impurity-substituted FBS.

3. Impurity substitution methods

Substitution of impurity is considered the simplest defect to ‘tune’ the nature (magnetic and/or electronic properties) of the perturbation potential. Generally, substitution was obtained by chemical doping during the synthesis process or irradiating defects into a host crystal. Here, the substituted chemicals work as external impurities, while the irradiating defects work as intrinsic impurities. In this section, we will discuss the fabrication of chemical-doped FBS crystals using ambient and high-pressure methods, and also impurities introduced by irradiation techniques.

3.1. Chemical substitution

Compared with the host atoms, the impurities may vary in atomic size, bond valance, electron structure, magnetic state and so on. Experimental design for chemical substitution should choose at least a similar atomic size and bond valance of the impurity as the host atoms, and the atomic substitution site should also be confirmed before and after the synthesis. Taking the well-studied cuprate superconductors as an example [19–27], impurities of Zn, Ni and Co can be successfully substituted for a Cu-site owing to a similar atomic size. However, the substitution sites may occur on various Cu-sites, for instance in the multi-layered Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ superconductors the impurities may go into the CuO$_2$-planes or the chain Cu-site, where the former is believed to be the SC layer but the latter is a nonSC site and will be misleading in the impurity doping experiments. Therefore, we have to consider the structure of the FBS before doping.

Up to now, seven series have been discovered in the Fe-based family as given in figure 5 [1–8]. Similar to the cuprates, each Fe-based compound has a distinct layered structure with a key layer of FeX ($X = \text{As, P, Te, or Se}$) (see figure 6). In fact, the common FeX layer should be more accurately written as Fe$_2$X$_2$, because half of the X atoms lie above the Fe plane and the others lie below the plane [43]. For the Fe-site, however, we can consider it only one site regardless of the spin direction. Thus, it consists of a square lattice of iron atoms coordinated tetrahedrally by the X anions that form a checkerboard pattern below and above the Fe plane which can double the unit cell size. Except for the case of $X = \text{Se}$, the Fe$_2$X$_2$ layers are separated by blocking layer(s) through which carrier doping into the Fe$_2$X$_2$ layer takes place in the same manner as in the cuprates. The blocking layer provides a quasi-two-dimensional character to the crystal since it forms bonds of a more ionic nature with the Fe$_2$X$_2$ layer. The Fe$_2$X$_2$ layer itself is characterized by a combination of covalent (i.e. Fe-X) and metallic (i.e. Fe-Fe) bonding. We note that among these seven systems, the 122-system has attracted a great deal of attention owing to the availability of high-quality single crystals. To substitute the Fe-site, transition metals, including Cr, Mn, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, etc, are chosen.

Generally, the FBS was synthesized through the solid-state reaction in an inert atmosphere or vacuum. The solid-state reaction can also be implemented under a high pressure of a few tens of thousands atmospheric pressure. To distinguish between these two methods, we name them ambient-pressure and high-pressure techniques. It is worth noting that the growth of impurity-doped epitaxial thin film by pulsed-laser deposition is also a promising method, but there is no report on it yet.
were sealed in BN crucibles [46–48], then placed into a graphite heating tube and mounted into high-pressure sintering equipment for the solid-reaction process, which can be of belt-type or cubic-type with different kinds of anvils. Here, the pressure, target temperature and heat-treatment time all strongly depend on the material system and doping type. For the 1111-system [46], the pressure should be up to 6 GPa, while less than 3 GPa for the 122-system. We take the 122-system as an example [47, 48], e.g., BaFe$_2$–$_y$Zn$_2$Co$_2$As$_2$ and Ba$_1$–$_y$K$_y$Fe$_2$–$_2$M$_2$As$_2$ ($M$ = Mn, Ru, Co, Ni, Cu and Zn). The stoichiometric mixture and capsule sealing processes resemble those of the ambient-pressure technique, but here 50 wt.\% of BaAs for BaFe$_2$–$_y$Zn$_2$Co$_2$As$_2$ and 50 wt.\% of BaAs/KAs for Ba$_1$–$_y$K$_y$Fe$_2$–$_2$M$_2$As$_2$ were added as flux for single crystal growth. The capsule was compressed at 3 GPa in the belt-type high-pressure apparatus and heated at 1300 °C for 4 h, followed by a decrease to a constant temperature of 1100 °C for 1 h. Note that the pellet self-separates into sizes of around 0.3 × 0.2 × 0.11 mm$^3$ or much smaller after it was left in a vacuum for 2–3 days. Since additional BaAs and KAs were added in excess to be the flux, it can be washed away using pure ethanol. The single crystals can be cleaved along the c-axis.

3.2. Irradiation

For the heavy impurity doping level, the chemical substitutions may lead to inhomogeneity in the lattice sites, resulting in a change of local electronic density and even the Fermi-surface topology, which may mask the intrinsic impurity effects on the superconductivity. Despite the fact that Zn is similar to that of Cu in the cuprate superconductor system YBa$_2$Cu$_3$O$_6$, previous experiments demonstrated that Zn impurities cannot be substituted beyond 5\% per Cu [19, 26], or some second phases like Y$_2$BaCuO$_5$ will appear and some Zn ions will gather around the surface of grains, which will mislead the nature of SC suppression effects caused by Zn. Alternatively, particle irradiation, generally used to introduce intrinsic defects or carriers artificially for the semiconductors, is a promising method for studying the scattering centers.

The particles should be light elements as electron, proton, neutron and low power $\alpha$-particle. However, most particle irradiation introduces correlated disorder and external defects as columnar and/or clusters, especially for the heavy particles like protons. Although the MeV-range electron irradiation can produce vacancy-interstitial (Frenkel) pairs as scattering centers [19], one should be extremely careful with identifying the defect types before concluding on the nature of their pair-breaking effects. Figure 7 demonstrates various particle irradiations and the corresponding defect types [84]. The profiles of the irradiation induced defects strongly depend on the irradiation particles and power. To create uniformly distributed point defects over the entire crystal, it is essential to apply long attenuation length and small recoil energy, such as electron irradiation with a small mass of electron particles.

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**Figure 6.** Structure of the Fe$_2$X$_2$ ($X$ = As, P, Te or Se) layer, where half of the $X$ atoms lie above the Fe plane, while the others lie below the plane.

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**i. Ambient-pressure technique**

Up to now, most of our present FBS were synthesized under ambient pressure which can be divided into several steps [1–3, 44, 45]: firstly, the starting materials are stoichiometrically mixed together. Secondly, the mixture was sealed into a tantalum capsule, sometimes with an $h$-BN inner to isolate the sample from the capsule, because of the toxicity and low vaporization temperature of the arsenic/phosphorus elements and the high reactivity of rare-earth, alkali and alkali-earth metals. Thirdly, the as-prepared pellets were sealed in an evacuated quartz tube and then heat-treated, where the heating conditions may vary from different material systems and different labs. Fortunately, apart from an oxygen-deficient system like AFeAsO$_{1−δ}$, of which the sample quality may be very sensitive to the synthesis procedure like the heat-treatment process and even the used furnace as those of oxygen-deficient cuprate, most of the other Fe-based systems are quite reproducible. Here, we take the 122-type (Ba,K)Fe$_2$–$_2$Zn$_2$As$_2$ as an example [44, 45]. The arsenide compounds as BaAs, KAs, FeAs and ZnAs were synthesized from the metal pieces (Ba, K, Fe, Zn, etc) and As powders at a relatively low temperature (500–700 °C), which is essential to avoid the loss of As in the following steps and also to obtain a fine powder of all the starting materials other than the metal pieces. The stoichiometric mixture of BaAs (lab made), KAs (lab made), FeAs (lab made), Fe (3N) and Zn (4N) or ZnAs (lab made) was placed in a tantalum capsule with an $h$-BN inner (preheated in advance at ~1900 °C for 1 h in nitrogen). The loaded capsule was sealed in an evacuated quartz tube under vacuum conditions. The sample was finally heated at 1000 °C for 72 h, and then slowly cooled down to room temperature at a rate of 20 °C h$^{−1}$.

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**ii. High-pressure technique**

In a high-pressure process the as-prepared pellets were sealed in BN crucibles [46–48], then placed into a graphite heating tube and mounted into high-pressure sintering equipment for the solid-reaction process, which can be of belt-type or cubic-type with different kinds of anvils. Here, the pressure, target temperature and heat-treatment time all strongly depend on the material system and doping type. For the 1111-system [46], the pressure should be up to 6 GPa, while less than 3 GPa for the 122-system. We take the 122-system as an example [47, 48], e.g., BaFe$_2$–$_y$Zn$_2$Co$_2$As$_2$ and Ba$_1$–$_y$K$_y$Fe$_2$–$_2$M$_2$As$_2$ ($M$ = Mn, Ru, Co, Ni, Cu and Zn). The stoichiometric mixture and capsule sealing processes resemble those of the ambient-pressure technique, but here 50 wt.\% of BaAs for BaFe$_2$–$_y$Zn$_2$Co$_2$As$_2$ and 50 wt.\% of BaAs/KAs for Ba$_1$–$_y$K$_y$Fe$_2$–$_2$M$_2$As$_2$ were added as flux for single crystal growth. The capsule was compressed at 3 GPa in the belt-type high-pressure apparatus and heated at 1300 °C for 4 h, followed by a decrease to a constant temperature of 1100 °C for 1 h. Note that the pellet self-separates into sizes of around 0.3 × 0.2 × 0.11 mm$^3$ or much smaller after it was left in a vacuum for 2–3 days. Since additional BaAs and KAs were added in excess to be the flux, it can be washed away using pure ethanol. The single crystals can be cleaved along the c-axis.

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**3.2. Irradiation**

For the heavy impurity doping level, the chemical substitutions may lead to inhomogeneity in the lattice sites, resulting in a change of local electronic density and even the Fermi-surface topology, which may mask the intrinsic impurity effects on the superconductivity. Despite the fact that Zn is similar to that of Cu in the cuprate superconductor system YBa$_2$Cu$_3$O$_6$, previous experiments demonstrated that Zn impurities cannot be substituted beyond 5\% per Cu [19, 26], or some second phases like Y$_2$BaCuO$_5$ will appear and some Zn ions will gather around the surface of grains, which will mislead the nature of SC suppression effects caused by Zn. Alternatively, particle irradiation, generally used to introduce intrinsic defects or carriers artificially for the semiconductors, is a promising method for studying the scattering centers.

The particles should be light elements as electron, proton, neutron and low power $\alpha$-particle. However, most particle irradiation introduces correlated disorder and external defects as columnar and/or clusters, especially for the heavy particles like protons. Although the MeV-range electron irradiation can produce vacancy-interstitial (Frenkel) pairs as scattering centers [19], one should be extremely careful with identifying the defect types before concluding on the nature of their pair-breaking effects. Figure 7 demonstrates various particle irradiations and the corresponding defect types [84]. The profiles of the irradiation induced defects strongly depend on the irradiation particles and power. To create uniformly distributed point defects over the entire crystal, it is essential to apply long attenuation length and small recoil energy, such as electron irradiation with a small mass of electron particles.
Nevertheless, the relatively large recoil energy may induce complex defects such as clusters and cascades, and even bulk defects as columnar tracks. Besides, the sample itself is also crucial for the irradiation experiments, for which the crystal structure, composition and even the sample geometry can influence the irradiation results. Therefore, the particle irradiation can hardly replace the chemical doping completely.

4. Experiments on impurity effects

4.1. Controlled impurities within the Fe$_2$X$_2$ planes

Up to now, most of the previous impurity doping studies have been carried out on the polycrystalline samples synthesized under ambient pressure. Figure 8 shows a scanning electron microscopy image for the Zn-doped Ba$_{0.5}$K$_{0.5}$Fe$_{1.9}$Zn$_{0.1}$As$_2$ polycrystal from Cheng et al.[49]. The crystal was detected by energy dispersive x-ray (EDX) in several points, and the compositions of Zn in different grains were found to be close to the nominal one. However, one possibility is that the Zn may filter onto the surface of grains, which cannot be detected by EDX because the technique cannot eliminate the surface element from the real concentration of grains.

To avoid the possibility of Zn precipitating, high-quality single crystals are essential for the study. Compared with a polycrystal, a single crystal often has substantially lower defects and less strain [19]. A single crystal also has sizable and atomically ordered surfaces, which are vital for surface sensitive measurements, such as scanning tunneling microscopy (STM) [43, 50, 51] and ARPES [52–54]. As mentioned in section 3.1, most of the single crystals are from the 122-system, owing to the superior quality and stability [56]. However, it is still extremely difficult to grow high-doping level and high-quality Zn-doped Fe-based single crystals, for which the main difficulty is the low melting point (419 °C) of Zn which is far below the reaction temperature (around 800–1000 °C). On the other hand, although one can select ZnAs alloy instead of Zn metal [49], such a method has been scarcely used due to the difficulty of ZnAs preparation.

Tan et al. [56] utilized the starting material of Fe$_{2−x}$Zn$_x$Se$_2$ instead of Zn or ZnSe, and synthesized the hole-type single crystal K$_{0.8}$Fe$_{2−y}$Zn$_y$Se$_2$, as shown inside figure 9. The XRD and EDX results demonstrated that the Zn had been successfully doped into the crystal. This is an impressive method for the future growth of other single crystals under ambient pressure.

Under ambient-pressure conditions, it is generally necessary to synthesize the single crystals for a long time, for instance, 92 h for K$_{0.8}$Fe$_{2−y}$Zn$_y$Se$_2$ [56]. To shorten the time, the high-pressure method is a promising approach for synthesizing Zn-doped single crystals, owing to the virtues of...
from Cheng energy dispersive x-ray. The EDX data suggested that the \( \sim \) single crystal is given on the top of insert, from Tan typically of only a few hours. Figure 10 shows typical single high reaction temperature and the short time synthesis period single crystals with Figure 9.

Figure 8. Scanning electron microscopy image of a Zn-doped Ba\(_{0.5}K_{0.5}Fe_{1.95}Zn_{0.05}As_2\) polycrystal. Several grains with diameters of \(~1 \mu m\) were chosen randomly to carry out the measurement of energy dispersive x-ray. The EDX data suggested that the compositions of Zn were in accordance with that of normal content, from Cheng et al [49].

Figure 9. Powder x-ray diffraction patterns for K\(_{0.8}Fe_{2-x}Zn_xSe_2\) single crystals with \(x = 0-0.023\). The red curve is the single-crystal XRD pattern of a K\(_{0.8}Fe_2Se_2\). An optical photo of the as-grown single crystal is given on the top of insert, from Tan et al [56].

high reaction temperature and the short time synthesis period typically of only a few hours. Figure 10 shows typical single crystals of Zn-doped Ba\(_{0.5}K_{0.5}Fe_{1.95}Zn_{0.05}As_2\) grown by the high-pressure method. The crystals crystallize into the tetragonal ThCr\(_2\)Si\(_2\)-type structure (\(I4/mmm\)), which has a two-dimensional feature. However, the two-dimensional anisotropic factor is not as large as those of cuprates or other 2D materials, and few reports have been presented on the cleavability of the crystals, except for some studies by using special techniques like STM and ARPES. The high-pressure grown single crystals can be cleaved using Scotch tape.

Indeed, this cleaving technique is indispensable for exploring the real concentration of Zn in the crystal, and consequently for elucidating the intrinsic properties of the Zn-substitution effect on SC. In figure 10(c), a flake-like crystal was cleaved on Scotch tape. The crystal demonstrates a mirror-like surface and is free of inhomogeneous distribution or grain boundary. Such thin crystals were held on silicon substrate using epoxy as shown in figures 10(a) and (b), which were then used for the electron probe micro-analyzer (EPMA), EDX, x-ray diffraction and transport property measurements.

EPMA and EDX measurements on such cleaved single crystals showed that the real concentration of Zn is very much in accordance with the nominal one. Powder and single crystal x-ray diffraction measurements demonstrated (see figure 11) that the impurities induced a systematic change of lattice parameters. Thus, the expected difficulties of the substitution due to the high volatility of Zn and the electronic difference between Zn\(^{2+}\) and Fe\(^{3+}\) had really been overcome by using the high-pressure technique.

4.2. Single impurity in the superconducting state

Single NMI dot Zn\(^{2+}\) has a filled \(d\)-shell, and hence works as quasiparticle interference scattering and provides information on the gap structure of the superconductors [1–4]. Since any sort of impurity or defect in a crystal can be screened by the conducting electrons, this leads to the well-known Friedel oscillations of the charge and spin density around the imperfection. In real space, interference among such oscillations stemming from random impurities is currently irresolvable in these systems, but the Fourier transform of the measured electron density will reflect the structure of the charge susceptibility in reciprocal space. A natural technique to map out the electron density near the Fermi level is by STM which worked well for the study on cuprates, especially on Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) [19, 50, 51]. It is worth noting that the most crucial requirements in this experiment are doping impurity into the SC layer and such crystal should be of high quality and free of other defects. In addition, the single crystal should behave as a 2D structure so as to be mechanically cleaved to obtain atomically flat and clean surfaces.

Zhu and co-workers [57] calculated the effects of a single NMI on (K,Tl)Fe\(_2\)Se\(_2\) superconductors, within both a two-band model and five-band model. Figure 12 gives the estimated density of states in the system without impurity and the local density of states at the nearest neighboring site to the NMI dot. The authors found that the impurity-induced resonance state can only exist for a \(d^{2}_{\pm}\) \(-\)wave pairing state. In addition, they also found that the bound-state peak in the local density of states occurs at a nonzero energy even in the unitary limit, indicating an opposite situation from the cuprate systems. The prediction arouses subsequent various theoretical studies [57–61]. Chen et al [58] calculated the local effect of Zn on the 122-type Ba(Fe\(_{1-x}\)Co\(_{x}\)Zn\(_y\))\(_2\)As\(_2\), and suggested quite short correlation lengths \(\xi_\Delta\) for the case of the \(s_\pm\) wave state, which is only two lattice sites, namely, \(\xi_\Delta\) is about a two-lattice distance of Fe ions. Such a short screening
length was attributed mainly to the strong local Coulomb repulsion $U$ which acts on the charge sector.

However, for the STM measurement of Zn-doped single crystals, there has been no report on FBSs up to now. The main reason lies in the technical difficulty of the growth of high-quality single crystals, as discussed in section 4.1. Moreover, to probe the local effect of the Zn ion the surface layer should be an Fe-$X$ plane, but not the barrier layer, i.e. the $A$-site ions as Ba, Sr, Ca, K, Eu, etc. However, the terminal ions often end up on either of the two cleaved Fe-$X$ surfaces, masking the profile of Zn. Previous successful observations of atomically resolved STM images are mostly on terminal $A$-ions, with few reports on the As-ion terminal, depending on the materials system and cleaving temperatures [43].

Recently, Yang and co-workers [62] studied the scattering of Cu impurities on Na(Fe$_{0.97}$-$x$Co$_{0.03}$Cu$_x$)$_2$As$_2$ via STM, instead of Zn. They considered the Cu as a NMI or weak magnetic impurity comparing with the strong magnetic host ions Fe$^{2+}$. Figure 13 shows spatial maps of the local density of states measured at different energies. The local density of states around the Cu impurity exhibits a systematic evolution with a spatial length of about 1.5–2.0 nm being about 5–7 Fe sites, which is consistent with the coherence length. Therefore, the Cu impurity was believed to result in a point disorder, leading to decay of the in-gap quasiparticle states on the scale of the coherence length. Consequently, Cu impurities induce Cooper pair-breaking in the strongly anisotropic $s_{\pm}$ pairing symmetry state.

To explain the reduction of superconducting regions by Zn impurity in the cuprate superconductor, Nachumi et al [63] proposed a two-dimensional ‘Swiss cheese’ model based on the muon spin relaxation measurements. In this model, the charge carriers are excluded from superconductivity around each Zn ion, resulting in non-superconducting regions with the diameter of characterized coherence length $\xi_\Delta$. The result was consistent with the subsequent magnetic susceptibility measurement [64].
Scattering from the nearest neighboring site, where the black line corresponds to the bare density of states, the red line to the local density of states without inter-band scattering ($\alpha = 100$ eV and $\nu = 0$) and the green line with a black line ($\alpha = 100$ eV). (b), (c) The local density of states imaging in the superconductor with (d$^1$) pairing symmetry without and with inter-band scattering, respectively, from Zhu et al [57]. Reprinted with permission from [57]. Copyright (2011) by the American Physical Society.

In the FBS, the most recent work demonstrates the local destruction of superconductivity by nonmagnetic Zn impurities in Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ by exploring phase-slip phenomena in a mesoscopic structure with a 119 × 102 nm$^2$ cross-section [65]. However, the impurity-free nanobridges demonstrated thermal stability due to a smaller number of defects. Considering the general condition for the appearance of phase-slip, the cross-sectional area should be comparable with the value of $\sqrt{2\pi}\xi$ [66–68]. However, the $\xi_{ab}$ and $\xi_c$ of Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ were estimated to be only 2.05 and 1.20 nm, respectively, two orders magnitude less than the cross-section of the nanowire. The Zn impurity was therefore proposed to suppress superconductivity in a ‘Swiss cheese’-like pattern as that of cuprate superconductors. Since the 122-type superconductors possess a weakly anisotropic layered structure, the Cooper pairs reside both in and out of the Fe$_2$As$_2$ superconducting planes, indicating a 3D ‘Swiss cheese’ model, where the order parameter can fluctuate along abundant narrow superconducting channels with both in-plane and out-of-plane directions as shown in figure 14. For a conventional superconducting gap like $s_\pm$, the nonmagnetic impurity ions work as point defects, but do not affect the Cooper pairs. As a contrast, the Zn ions can induce local destruction of superconductivity for the unconventional $s_\pm$ pairing symmetry, and consequently result in phase-slip phenomena in the Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Zn$_{0.05}$As$_2$ nanobridges. The local destruction may provide evidence for the pair-breaking effect of non-magnetic impurities and the unconventional $s_\pm$ pairing symmetry for the iron pnictide superconductors.

4.3. Magnetic properties

Since the SC mechanism for the FBS is widely considered to be of spin fluctuation origin, magnetic properties are of great importance for understanding the NMI effects on the SC [5–12]. First of all, magnetic susceptibility measurement provides a direct determination of $T_N$ owing to the Messer effect. More importantly, since the FBS demonstrates the metallic nature of the parent compounds before the carrier doping, and an antiferromagnetic (AF) order phase appears below the critical temperature of spin density wave (SDW) ordering at $T_N \approx 130$ K, as well as in the under-doped regime, substitution of spinless Zn$^{2+}$ ions will be very interesting for exploring information on the pair symmetry and even the SC mechanism [69–74]. However, compared with the transport properties, the magnetic properties of the Zn-doped FBS have been reported in very few works. In this section, we will briefly summarize some present work of the Zn effects on the AF state and local magnetic moments.

(i) Antiferromagnetic state

In the SDW state, the ordered magnetic moment is about 0.3 $\mu_B$ and the ordering vector is $Q \approx (\pi, 0)$. SC was induced by suppression of $T_N$ via carrier doping, the AF phase however generally exists within the under-doped regime. It was expected from the single-defect calculation [70–74] that the substitution of spinless Zn$^{2+}$ ($s = 0$) ions for strongly magnetic host ions of Fe$^{2+}$ ($s = 2$) may result in a strong local suppression of short-range AF order, hence the Zn may also suppress $T_N$ as what was done from the carrier doping.

Li and co-workers studied the Zn-doping effect on the polycrystalline LaFeAsO parent compound [75]. Figure 15 shows the temperature dependence of magnetic susceptibility ($\chi$) of LaFe$_{1-x}$Zn$_x$AsO with various doping levels of Zn. The insets show the enlarged plots for $x = 0$ and 0.02. The arrows indicate the anomaly in susceptibility related to structural and/or magnetic transitions. Slight Zn doping in LaFe$_{1-x}$Zn$_x$AsO drastically suppresses the AF in the parent compound. For instance, the $T_N$ is decreased to 137 K with 2 at.% doping of Zn, slightly less than that of the Zn-free sample (150 K). However, the SDW can barely be observed with Zn up to 5 at.%. Since the sample is polycrystalline and the SDW order is weak even for the impurity-free sample, the sample quality may dominate the SDW other than the Zn doping. Even so, the magnetic data together with their resistivity properties indicated that the SDW order was sensitive to Zn doping. Zhang and Singh [74] proposed two mechanisms for the $T_N$ suppression from Zn doping: (i) the Zn ion provides localized states and disrupts the electronic structure of the Fe sheets near the Fermi level. (ii) It introduces local moments that have the pattern of the checkerboard antiferromagnetic state mainly on the four neighboring Fe.
Local magnetic moments

The impurity ions of Zn$^{2+}$ work as spinless centers, which may induce moments of $s = 2$ on the Fe sites. However, there is still an open question for the Zn-induced local moment behavior and no direct experimental evidence can support it. For instance [57, 60, 61, 76, 77], the first question is whether a nonmagnetic site can induce a free paramagnetic moment in a metallic correlated system. It should be noted that the study of Zn suppression effects on $T_N$ should be focused on the under-doped or undoped regimes where the AF state still exists. A few candidates can be used to explore the Zn-induced local moment, such as STM, muon spin rotation, neutron scattering, specific heat, magnetic susceptibility and so on. Among these methods STM measurement is the best and most direct method as we introduced in detail in section 3. However, the STM analysis was plagued by materials problems as in section 4.2, as well as the muon spin rotation and neutron scattering measurements. Apart from the specific heat experiment as we will introduce in section 4.5, magnetic susceptibility measurement is a promising and simple method.

Theoretically, once substitution of Zn provides the local spin moment, it will enhance a Curie-like behavior in the uniform magnetic susceptibility, despite the fact that the host material represents the metallic conduction of carriers. Curie-like behavior for the characteristics of temperature dependent magnetic susceptibility $\chi(T)$ is given by [19]

$$\chi(T) = \chi_0(T) + \frac{NP_{\text{eff}}^2 \mu_B^2}{3k_B(T - \Theta)}, \quad (16)$$

where $\chi_0(T)$ corresponds to the $\chi(T)$ without Curie–Weiss background which depends on the carrier density of the impurity-free sample, $N$ is the number of magnetic ions, $\Theta$ is the Curie–Weiss temperature, and $P_{\text{eff}}$ is the effective moment in the units of the Bohr magnet $(\mu_B)$ and relates to the Zn doping. Therefore, by fitting the temperature dependent magnetic susceptibility $\chi(T)$ for different doping levels of Zn, one can systematically obtain the $P_{\text{eff}}$. Although initial susceptibility data on Zn-substituted Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ polycrystals did suggest yielding of moments from 0.482 $\mu_B$/Fe to 0.362 $\mu_B$/(Fe + Zn) [49], the nature of the impurity contribution to the magnetic susceptibility can only be determined in carefully impurity-controlled samples, as discussed in section 4.1. Future comprehensive study on the Curie–Weiss behavior of Zn-doped single crystals is essential.

In addition, nuclear magnetic resonance (NMR) can probe nuclei coupled to the SC Fe$_2$X$_2$ planes which are capable of yielding insights into the local magnetic structure.

![Figure 13](image)

**Figure 13.** Local density of state mapping of the first nearest neighboring site of the Cu site in Na(Fe$_{0.97-x}$,Co$_{0.03}$Cu$_x$)$_2$As superconductors. (a) The topographic image of a Cu impurity, where the scale bar is 1 nm. (b)-(f) The mapping of the local density of states measured at bias voltages of $-5, -0.6, 0.6, 1.8$ and $5$ mV, respectively. The spatial influence of a Cu impurity is about 20 Å, being about 5–7 Fe sites as the corresponding coherence length, from Yang et al [62]. Reprinted by permission from Macmillan Publishers Ltd: Nat. Commun. [62], copyright 2013.
Using a variety of nuclei, NMR can develop a fairly clear picture of how a nominal NMI provides a cloud of local staggered polarization on nearby Fe-sites, and can characterize the response as a function of doping and temperature, for different materials. Kitagawa and co-workers [76] studied the Zn-substituted LaFeAsO$_{0.85}$ polycrystal using $^{75}$As and $^{139}$La NMR and nuclear quadrupole resonance (NQR) (see figure 16). Although SC in LaFeAsO$_{0.85}$ disappears by 3% Zn substitution as we will introduce in section 4.6.1 [46], it was found that NMR/NQR spectra and NMR physical quantities in the normal state had hardly changed, indicating that the crystal structure, electronic states and magnetic moments are not modified by Zn substitution. The results suggest that the suppression of SC by Zn substitution is not due to the change of the normal-state properties, but the strong nonmagnetic pair-breaking effects.

4.4. Transport properties

Transport property measurements can probe the impurity or defect effects on various SC properties, including the carrier, coupling between charges, spin degrees of freedom and so on [19]. All of these parameters are correlated with the induced suppression of $T_c$, and more importantly with the pair-breaking from impurities. In this section, we will first discuss the in-plane transport properties in both high-temperature and low-temperature (around $T_c$) regions. Although transport properties of the 2D FBS are slightly anisotropic along the c-axis and ab-plane, we will focus on the in-plane properties where the impurity scattering occurs within the SC Fe$_2$X$_2$ planes.

(i) In-plane transport properties

Studying the normal state in-plane resistivity is the most common way to explore the impurities’ influence. Apart from a few systems, like hole-doped systems (e.g. Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and K$_{1-x}$Fe$_{2-y}$Se$_2$ [47, 78]), most of the FBSs behave with a typically metallic nature, especially for the optimally doped crystals. The in-plane resistivity ($\rho_{ab}$) decreases linearly with temperature above $T_c$ as

$$\rho_{ab} = \rho_0 + kT,$$

Figure 14. (a) Transport measurement scheme along a nanobridge. The current flows along the ab-plane. (b) High angle annular dark field scanning transmission electron microscopy image of a Ba$_{0.5}$K$_{0.5}$Fe$_{1.94}$Zn$_{0.06}$As$_2$ flake, where the crystal was detected along the c-axis. The scale bar represents 50 nm. (c), (d) Scanning transmission electron microscopy energy dispersive x-ray spectroscopy mapping for Zn/Fe and Zn distributions, respectively, within the area indicated in (b), (e), (f) Schematic representation of the 2D and 3D ‘Swiss cheese’ models, respectively. The yellow oblate spheroid corresponds to the non-superconducting regions centered on Zn ions with an equatorial length $\xi_{ab}$ and a polar length $\xi_c$, from Li et al [65].

Figure 15. Magnetic susceptibility ($\chi$) versus temperature for Zn-doped parent compound LaFe$_{1-x}$ZnxAsO. The insets show the enlarged plots for samples with $x = 0$ and 0.02. The arrows indicate the anomaly in susceptibility related to structural and/or magnetic transitions, from Li et al [75].
where $\rho_0$ is the residual resistivity which will be discussed in detail in the section 4.4.2.

According to Mathiessen's rule [78], the impurity scattering rate in classical metals adds incoherently with the inelastic scattering rate in the pure material, usually owing to phonons. The normal state $\rho_{ab}(T)$ will consequently display upwards in parallel. The approximate additives of the impurity scattering was found for the $\rho_{ab}(T)$ of Zn-doped BaFe$_{1.89-2x}$Zn$_x$Co$_{0.11}$As$_2$ ($x = 0-0.08$) as shown in figure 17 [48]. However, the parallel shift phenomenon occurs at high-temperature regions. For the low-temperature regions around $T_c$, a slight upturn was observed as an increasing doping level. Such weak low-$T$ upturn behavior was also found in cuprate superconductors, which could be attributed to some factors as: (i) disorder, due to the fact that the spinless impurity may result in a scattering on magnetic perturbations induced in the planes, as discussed in section 2.2.2; (ii) charge localization, leading to a metal-insulator transition (MIT) with decreasing carrier content, which can be evidenced by the low-$T$ upturn of the Hall coefficient.

Since the impurities' suppression on $T_c$ is an additional element of characterization available, and although it is not solely linked to the properties of the normal metallic state, as discussed in section 3.2, the transport property measurement strongly depends on the crystal quality and the measurement technique. Otherwise, the impurity concentration, fractional site occupancies and actual carrier density of single crystals cannot always be accurately determined. Particle irradiation is one of the most promising methods, as one can span a series of defect concentrations using only one single crystal by increasing the irradiation dose progressively. Figure 18 shows the temperature dependence of $\rho$ for the NdFeAsO$_{0.3}$F$_{0.7}$ single crystal under the $\alpha$-particle irradiation in different steps [79]. At high-$T$ far above $T_c$, the $\rho(T)$ curves are observed as an upward parallel shift, indicating the enhancement of the hole content introduced by irradiation. On the other hand, a much more obvious upturn than that of chemical doping appeared in the low-$T$ regions, which was interpreted in terms of a MIT, the so-called Kondo-like phenomenon. Similar results were also found for the neutron irradiated polycrystalline LaFeAsO$_{0.8}$F$_{0.2}$ [80]. However, such low-$T$ upturn

![Figure 16](image1.png)

**Figure 16.** Temperature dependence of the full width at half maximum (FWHM) of $^{139}$La NMR spectra for polycrystalline LaFe$_{1-x}$Zn$_x$AsO$_{0.85}$ substituted with Zn of 0, 3% and 5%. The Zn was observed to show a weak change for FWHM. (inset) Field swept $^{139}$La NMR spectra at 50 K at 72.1 MHz. The lower panel gives temperature dependence of $^{139}$La NMR Knight shift for $H // ab$, from Kitagawa et al [76]. Reprinted with permission from [76]. Copyright 2011 by the American Physical Society.

![Figure 17](image2.png)

**Figure 17.** Temperature dependence of in-plane resistivity ($\rho_{ab}$) for the BaFe$_{1.89-2x}$Zn$_x$Co$_{0.11}$As$_2$ with a Zn content of $x = 0-0.08$, from Li et al [48].

![Figure 18](image3.png)

**Figure 18.** Temperature dependence of resistivity for the NdFeAsO$_{0.3}$F$_{0.7}$ single crystal under $\alpha$-particle irradiation in different steps, where the black curve corresponds to the pristine sample and the curves from yellow to cyan indicate the data after each step of irradiation. Inset shows magnified temperature region near $T_c$, from Tarantini et al [79]. Reprinted with permission from [79]. Copyright (2010) by the American Physical Society.
behavior was neither seen for the proton-irradiatedBa(Fe1−xCo)xAs2 single crystals [81, 82], nor electron-irradiated Ba1−xKxFe2As2 [83], BaFeAs2−xP [84] and BaFe1.76Ru0.24As2 [85]. This is probably because the defect profiles are different from those of the α-particle and proton irradiation induced samples, for which the α-particle irradiation defects were proposed as both magnetic and nonmagnetic scatterings, while the light particles of proton and electron were suggested to induce nonmagnetic ones. The scattering behavior of these experiments will be discussed in detail in section 5.

(ii) Improvement on the measurement method

The FBSs are semimetallic in the normal state, and the resistivity is generally in units of μΩ cm. Thus, it is rather challenging to measure the transport properties for a bulk crystal with a millimeter size. In the traditional four-probe measurement technique, a high current bias is often necessary to enhance the measurement resolution, especially for the Hall effect. For this reason, a high current bias is often necessary to enhance the measurement resolution, especially for the Hall effect. Therefore, we developed a micro-patterning technique to fabricate microbridges on the 122-type FBS.

Recently, we developed a micro-patterning technique to fabricate microbridges on the 122-type FBS [86, 87]. The crystal was first cleaved into pieces with 1–2 μm thickness using Scotch tape as shown from figure 10, and then glued on a Si substrate with the ab-plane parallel to the substrate surface using a thin layer of epoxy. The as-prepared crystal was then milled to a layer of 10 nm thickness by low energy argon ion beam (ion acceleration voltage of 200 V and beam current density of ~0.25 mA cm−2), and immediately covered by a 100 nm layer of Au. To improve the interface contact between gold and crystal, we annealed the sample at 300°C for 24 h under a nitrogen atmosphere, which can decrease the interface contact resistance to less than 0.1 Ω at room temperature. The crystals were fabricated as micro-devices as follows: (i) making microbridge patterns using the photolithography technique; (ii) argon ion milling the sample into a thickness of 300 nm; (iii) removing the photoresist by acetone and connecting the electrodes with silver epoxy; and (iv) etching the whole device until the crystal was completely removed except the microbridge. Note that the whole sample was etched in step (iv), except the parts under the silver paste.

Figure 19 shows a scanning electron microscopic image of a Ba0.5K0.5Fe2As2 microbridge for both in-plane resistivity measurements. We emphasize that, in the present method, a high-quality area of the crystal was carefully selected for the microbridge with a small geometry of 10 × 4 × 0.2 μm². Besides, the electrodes are SC as well, so that we can restrict the heat effects considerably. Consequently, the measurements should be more accurate than those of bulk crystals. To measure the Hall coefficient of the sample should be rotated along the axis of transverse current (Ixy) to avoid the Lorentz force along the Ixx, namely, cos(θ) Ixx = 0. The sign of the magnetic field can be changed by rotating the microbridge during the Hall coefficient measurements, where the effective magnetic field can be considered as H = H0 sin (θ) and Ixy is the transversal current, i.e. the Hall current. To avoid the magnetoresistance for the transversal electrodes, we calculated the Rxy by
Figure 21 (a) Normalized $T_c$ as a function of differential residual resistance ($\Delta \rho_0$) for single crystals BaK-Zn (Ba$_0.5$K$_0.5$Fe$_{2-x}$Zn$_x$As$_2$, $x = 0-0.15$) [48], BaK-Zn (BaFe$_{1.89}$Ru$_{0.11}$As$_2$, $x = 0-0.08$) [47], KFeS-Zn (K$_{0.9}$Fe$_{2-x}$Zn$_x$S$_2$, $x = 0$ and 0.005) [56], BaCo-irr (BaFe$_{1.85}$Co$_{0.15}$As$_2$ under different proton-particle irradiation) [81], NdF-irr (NdFeAsO$_{1-x}$F$_x$ under different $\alpha$-particle irradiation) [79], BaK-irr (Ba$_{1-x}$K$_x$Fe$_2$As$_2$ under electron irradiation) [83], BaP-irr (BaFeAs$_{1-x}$P$_x$ under different electron irradiation) [84], and BaRu-irr (BaFe$_{1.76}$Ru$_{0.24}$As$_2$ under different electron irradiation) [85]. All data are fitted linearly and marked with the same color as the data. The gray region demonstrates the located region for most points. (b) The enlarged view of the low $\Delta \rho_0$ region.

changing the sign of fields as

$$ R_{xy}(H) = \left[ R_{xy}(H^+) - R_{xy}(H^-) \right]/2. \quad (18) $$

For the present measurement setup, the resistance of the microbridge is relatively large enough, normally above 20 $\Omega$, thus we can apply such a low current as 10 $\mu$A. Figure 20 shows the temperature dependence of in-plane resistivity $\rho_{xx}$ for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ (BK), nonmagnetic impurity Zn-doped Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Zn$_{0.05}$As$_2$ (BKZn), and magnetic impurity Co-doped Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Co$_{0.05}$As$_2$ (BKCo). The values of $\rho_{xx}$ were found to be about one order of magnitude less than our previous results on bulk crystals [47], suggesting the release of scattering from impurities or other imperfections, which we can attribute to the improvement of the crystal synthesis technique and measurement setup.

(iii) Residual resistivity

Let us come back to equation (17), in which the $\rho_0$ should access zero for an ideal metal, while the appearance of nonzero $\rho_0$ is related to the scattering of carriers by the defects. However, SC of the high-$T_c$ superconductors was introduced by electron or hole doping, regardless of cuprate or FBS, for which it is hard to be free of impurity atoms and hence nonzero $\rho_0$. The behavior of the $\rho_{ab}(T)$ slope generally depends on various factors [19], including the host crystal, sample quality and doping type. In this section, we will not discuss the scattering originating from the superconductor itself, but for the external scattering from impurity, namely, the impurity-induced change of residual resistivity as $\Delta \rho_0$.

To estimate $\rho_0$ owing to the impurity scattering, one can extrapolate the $\rho_{ab}(T)$ to 0 K, or by measuring the parallel shift of the $\rho_{ab}(T)$ curves at high-$T$ as that which was done on the cuprate system [19, 88, 89]. Indeed, it is easy to evaluate from a metallic compound owing to the linear behavior of the $\rho_{ab}(T)$ slopes, while it is difficult for the nonlinear $\rho_{ab}(T)$ slopes in some materials like hole-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ and K$_{1-x}$Fe$_{2-x}$Se$_2$ [47, 78]. In figure 20 one can find that the $\rho_{ab}(T)$ slopes of Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Zn$_{0.05}$As$_2$ and Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Co$_{0.05}$As$_2$ consist of high-$T$ linear and low-$T$ nonlinear regions. The former region establishes a metallic-like resistivity dominated by phonons. The $T$-nonlinear regime can be fit using a power-law relation

$$ \rho = \rho_0 + AT^n, \quad (19) $$

where $\rho_0$ is the residual resistivity at 0 K. Surprisingly, all powers are considerably less than that of a normal Fermi liquid ($n = 2$) which is dominated by strong electron–electron interactions, probably suggesting an effect from critical antiferromagnetic fluctuations. However, it is impossible to conclude the quantum critical profile from the extrapolation of normal state $\rho(T)$ to low-$T$ since all fittings were based on the normal-state results, unless the superconductivity can be suppressed by high magnetic field. Particularly, the $\rho_0$’s of both impurity-free and impurity-doped crystals are dramatically less than previous measurements on the bulk crystals. Again, the relatively low $\rho_0$ indicates the improvement of the measurement setup.
On the other hand, the strongly low-T upturn in $\rho_{ab}(T)$ creates difficulty in the estimation of the $\Delta \rho_0$ using linear or nonlinear fitting as shown in figure 18. An alternative approach is to measure the parallel shift of the $\rho_{ab}(T)$ curves in the low-temperature region as described in [90]. In contrast, Nakajima and co-workers found no upturn in the $\rho_{ab}(T)$ curve of BaFe$_2$–$x$Co$_x$As$_2$ single crystals irradiated by protons, although the SC was depressed as well. The defects induced by the proton irradiation were suggested to be non-magnetic scattering centers, while $\alpha$-particle irradiated defects should be complex and are not only the NMI but also others that may adjust the effective carrier density.

The residual resistivity can hardly provide accurate determinations of the scattering rate directly; instead, it is a promising method for seeking information from the depression of $T_c$ induced by the scattering centers. The decrease of $T_c$ ($\Delta T_c$) can be related to $\Delta \rho_0$ as [19, 88]

$$\Delta T_c = \frac{\pi h}{4 k_B \tau}. \quad (20)$$

Here, $\tau^{-1}$ is the scattering rate, which is given by the $\rho_0$ as

$$\tau^{-1} = \frac{n e^2 \Delta \rho_0}{m^*}. \quad (21)$$

where $m^*$ is the effective mass with a value between $2m_e$ and $4m_e$, and it should be temperature-independent regardless of carriers.

Figure 21 shows the normalized $T_c$ as a function of residual differential resistance ($\Delta \rho$) for BaFe$_{1.89-2}Zn_{0.11}As_2$ ($x = 0.0-0.15$) [48], BaK-Zn-2 (Ba$_2$K$_{0.8}Fe_{2-2}Zn_{2}As_2$, $x = 0$ and 0.05) microbridges [87], BaCo-Zn (BaFe$_{1.80-2}Zn_{2}Co_{0.11}As_2$, $x = 0-0.08$) [47], KFeS-Zn (K$_{0.8}$Fe$_{2-2}$Zn$_{2}$Se$_2$, $x = 0$ and 0.005) [56], BaCo-irr (BaFe$_{1.85}Co_{0.15}As_2$ under different doses of proton-particle irradiation) [81], Nd-irr (NdFeAsO$_{0.7}$F$_{0.3}$) under different doses of $\alpha$-particle irradiation [79], BaF-irr (BaFe$_{2}$–$x$Co$_x$As$_2$ under different doses of electron irradiation) [83], BaP-irr (BaFe$_{1.75}$Ru$_{0.25}$As$_2$ under different doses of electron irradiation) [84], and BaRu-irr (BaFe$_{1.75}$Ru$_{0.25}$As$_2$ under different doses of electron irradiation) [85]. All data are fitted linearly and marked in the same color as the data. The gray region demonstrates resistance larger than the $R_g = 6.45$ kΩ.

(iv) Residual resistance per plane

The residual resistance may vary from crystals, and some intrinsic defects such as grain boundary or magnetic domain may contribute additional scattering as well, thus one can hardly obtain accurate determinations of scattering rate directly from the resistivity results. Instead, further seeking the residual resistance per plane ($\Delta \rho_{G}$) is a promising approach. In a 2D system, the $\Delta \rho_{G}$ can provide crucial information for the scattering rate of conduction electrons by the impurity potential. $\Delta \rho_{G}$ can be described as $\Delta \rho_{G} = \Delta \rho_{F}/t$, where $t$ corresponds to the distance between the nearest neighboring SC layers. Once $\Delta \rho_{G}$ reaches the limit of

![Figure 22. Normalized $T_c$ as a function of residual differential resistance per plane ($\Delta \rho$) single crystals BaK-Zn (Ba$_2$K$_{0.8}$Fe$_{2-2}Zn$_{2}$As$_2$, $x = 0-0.15$) [48], BaK-Zn-2 (Ba$_2$K$_{0.8}$Fe$_{2-2}Zn$_{2}$As$_2$, $x = 0$ and 0.05) microbridges [87], BaCo-Zn (BaFe$_{1.80-2}Zn$_{2}Co$_{0.11}$As$_2$, $x = 0-0.08$) [47], KFeS-Zn (K$_{0.8}$Fe$_{2-2}$Zn$_{2}$Se$_2$, $x = 0$ and 0.005) [56], BaCo-irr (BaFe$_{1.85}$Co$_{0.15}$As$_2$ under different doses of proton-particle irradiation) [81], Nd-irr (NdFeAsO$_{0.7}$F$_{0.3}$) under different doses of $\alpha$-particle irradiation [79], BaF-irr (BaFe$_{2}$–$x$Co$_x$As$_2$ under different doses of electron irradiation) [83], BaP-irr (BaFe$_{1.75}$Ru$_{0.25}$As$_2$ under different doses of electron irradiation) [84], and BaRu-irr (BaFe$_{1.75}$Ru$_{0.25}$As$_2$ under different doses of electron irradiation) [85]. All data are fitted linearly and marked in the same color as the data. The gray region demonstrates resistance larger than the $R_g = 6.45$ kΩ.](image-url)
metallic conductivity $R_\rho = h/4e^2 = 6.45 \text{ k}\Omega$, the metallic nature of the material will be depressed, as a result of the electron localization. Such a method was successfully applied to analyze the cuprate system, for instance, YBa$_2$Cu$_6$O$_{7-\delta}$ 

Figure 23. Temperature dependence of the in-plane Hall coefficient ($R_H$) for single-crystalline (a) BaFe$_{2-x-y}$Zn$_x$Co$_y$As$_2$ and (b) Ba$_{0.5}$K$_{0.5}$Fe$_{2-x}$As$_2$ ($M = \text{Mn, Ru, Co, Ni, Cu and Zn, nominal } x = 0.05$), from Li et al [47].

Figure 24. Contours of $R_H$ for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ (BK), Ba$_{0.5}$K$_{0.5}$Fe$_{2-x}$Zn$_x$Co$_y$As$_2$ (BKZn) and Ba$_{0.5}$K$_{0.5}$Fe$_{1.95}$Co$_{0.05}$As$_2$ (BKC0) with respect to magnetic fields and temperatures. The white dotted line separates two temperature regions demonstrating linear (left side) and nonlinear (right side) field dependent regions for $R_\rho(H)$, where we define the crossover temperature as $T_c \sim 250 \text{ K}$ for BK and $\sim 240 \text{ K}$ for BKC0, which separates the two temperature regions as $H$-dependent and $H$-independent $R_\rho(H)$, from Li et al [87].

For the 122-system, regardless of $p$-type or $n$-type, substitution of Zn enhances the $\Delta_{\rho\rho}$ remarkably and depresses the superconductivity at 6 k\Omega. The $\alpha$-particle irradiated NdFeAsO$_{0.7}$F$_{0.3}$ single crystal demonstrates a slightly larger critical point of $\Delta_{\rho\rho}$ ($\sim 7.5 \text{ k}\Omega$). In addition, the $K_{0.8}$Fe$_{2-y}$Zn$_y$Se$_2$ exhibits an intense increase of $\Delta_{\rho\rho}$ ($\sim 8.7 \text{ k}\Omega$) with only 0.25 at.\% of Zn doping, where the superconductivity was completely depressed. Indeed, the critical point of $\Delta_{\rho\rho}$ may be less than the present values, due to the lack of intermediate doping levels. The superconductivity of $\alpha$-particle irradiated NdFeAsO$_{0.7}$F$_{0.3}$ and $K_{0.8}$Fe$_{2-y}$Zn$_y$Se$_2$ is suppressed at the metallic limit point 6.45 k\Omega, suggesting a possible effect from electron localization. In contrast, the proton-irradiated BaFe$_{1.85}$Co$_{0.15}$As$_2$ single crystal, electron-irradiated Ba$_{1.76}$Ru$_{0.24}$As$_2$ and Ba$_{0.5}$K$_{0.5}$Fe$_{2-x}$Co$_x$As$_2$ microbridges exhibit considerably smaller critical points below 1.5 k\Omega, being far away from 6.45 k\Omega. However, another important parameter should be taken into account, i.e. the carrier density ($n$). For instance, in the electron-type superconductors, the electron-provider, e.g. Co, contributes to the scattering as well. Therefore, the scattering factor can be revised as $\Delta_{\rho\rho}$, for which the Hall coefficient measurements are essential.

(v) Carrier density

Different from the normal metal, the Hall coefficient of a FBS displays temperature-dependent behavior, which is one
of the important signatures of the normal state as those of the cuprate systems. In the cuprate superconductors, Anderson [91–93] proposed an unconventional approach to deal with the anomalous Hall effect, namely, the NMI doping effect on the carrier density and Hall angle. As substitution for Fe atoms in the Fe2X2 plane, the Zn impurity provides a large negative scattering potential (around −8 eV [10]). However, the Zn substitution negligibly changes the electronic structure, which was supported by the 75As NMR and NQR measurements on La(Fe1−xZnx)AsO0.85 polycrystal [76]. In addition, the 139La NMR spectra indicated that the substituted Zn could not cause any static moments around the impurity [76], different from that of cuprate systems in which both local spin susceptibility and staggered susceptibility are prominently enhanced around the Zn site, within a radius of the antiferromagnetic correlation length ξAF.

Up to now, apart from a few reports on Hall effect measurements on the Zn-doped polycrystals, there have only been studies on the in-plane Hall effect on 122-type single crystals, namely, the n-type BaFe2−2xZnxCo2xAs2 and p-type Ba0.5K0.5Fe2−2xM2xAs2 (M = Fe, Mn, Ru, Co, Ni, Cu and Zn) as shown in figure 23 [47]. The data of the impurity-free crystals are compatible with the earlier data. Regarding the normal state, no significant change of Hall coefficient is induced by the Zn substitution in the under-, optimal- and over-doped regimes of Co in the n-type BaFe2−2xZnxCo2xAs2, indicating that the substitution is truly isovalent which negligibly changes the carrier density. The weak carrier density change in the p-type Ba0.5K0.5Fe2−2xZnxCo2xAs2 was likely caused by transfer of carrier type from hole to electron since it is anomalous that the Zn impurities resulted in a negative RH. Here, it should be noted that the present system has a multiband nature with both electron and hole carriers. The results for the Zn-doped samples may suggest that the electron carrier becomes dominant with the existence of the substitution. However, such Hall experiments were implemented on a bulk crystal, while the Hall resistance was generally rather small owing to the bulk size and in-plane metallic behavior, thus we can hardly understand the nature of Zn impurities’ effect on the in-plane scattering.

To enhance the Hall signal we recently developed a method to measure the transport properties on single-crystalline microbridges as shown in figure 19. Since the thickness of the microbridge can be down to 91 nm or less, the in-plane resistance and Hall resistance (under magnetic field of 5 T) at room temperature were up to 20Ω and 0.5Ω, respectively, which provides an impressive way to study the accurate transport properties of the metallic Fe-based superconductors. Figure 24 shows contours of RH for Ba0.5K0.5Fe2As2 (BK), Ba0.5K0.5Fe1.95Zn0.05As2 (BKZn) and Ba0.5K0.5Fe1.95Co0.05As2 (BKCo) measured in various magnetic fields and temperature regions. For the BK, RH shows two pronounced H-dependence regions, which are an H-dependent region above 250 K and an H-independent below ~250 K as described above. In the H-independent region, the RH behaves positively indicating hole-type carriers, while a negative RH(H) phenomenon is observed at relatively low

![Figure 25](image_url). The Hall angle cot θH = ρxx/ρxy for a systematic set of BK, BKZn and BKCo. The high-temperature data can be easily fitted by a square law cot θH = αT2 + C, from Li et al [87].
field condition in the \( H \)-dependent region, suggesting a Hall sign reversal occurs which indicates that the electrons dominate the carriers. However, further increasing of field turns the sign back to positive. Meanwhile, the negative \( R_{\parallel H} \) appears in a narrow temperature region between 290 and 330 K.

On substitution of nonmagnetic Zn ions into the BK, the \( R_{\parallel H} \) is increased to about twice the original magnitude, and the field dependent behavior is modified as well, i.e. the \( R_{\parallel H} \) is independent of field in the whole temperature region and the negative \( R_{\parallel H} \) disappears, indicating \( H \)-independent carriers at all temperatures. For the magnetic impurity Co substituted BK, the \( R_{\parallel H} \) becomes more complicated: (i) the \( R_{\parallel H} \) demonstrates a pronounced increase; (ii) \( R_{\parallel H} \) reveals intense \( H \)-dependent behavior at high temperature, and the \( T_{\parallel H} \) (\( \sim 240 \) K) is slightly smaller than that of BK; and (iii) the negative \( R_{\parallel H} \) regime exists at almost the whole \( H \)-dependent region, and the saturated high field is essential to suppress the negative \( R_{\parallel H} \). These data suggest that the carriers are electron-type at almost all fields above the \( T_{\parallel H} \) (240 K). However, the carriers of both BKZn and BKCo are similar to those of BK below the \( T_{\parallel H} \), which seems like that the impurities induce modification only on the electron pocket but not on the hole pocket. To confirm the possible effect of \( \text{Co}^{2+} \) and \( \text{Zn}^{2+} \) on the electronic state, it is necessary to study the Hall angle for both impurity-free and impurity-doped samples.

(vi) Hall angle

To explore the impurity effects on the electronic state, Anderson proposed a picture for describing the Hall angle (\( \cot \theta_H \)) within the framework of the Luttinger-liquid theory which can be expressed as \([91–93]\)

\[
\cot \theta_H = \frac{\rho_{xx}}{\rho_{xy}} = \alpha T^2 + C,
\]

where \( \rho_{xx} \) and \( \rho_{xy} \) are the longitudinal and transversal resistivity, respectively, and \( \alpha \) is a parameter depending on the energy-scale of the spinon–spinon scattering

\[
\alpha = \frac{m_s}{eH \tau_M},
\]

where \( m_s \) and \( W_s \) are the effective mass and the bandwidth of spin excitations, respectively, and \( C \) is the in-plane impurity contributed scattering rate

\[
C = \frac{m_s}{eH \tau_M}
\]

in which \( \tau_M \) is the impurity contribution. Therefore, the \( \cot \theta_H \) depends only on the transverse scattering lifetime (\( \tau_M \)), which is determined mainly by spinon–spinon interactions and characterized by a \( T^2 \) dependence. Among the appealing features of the theory few parameters are required to describe the normal-state transport, and the understanding of the general features of the normal-state properties does not involve details of the electronic structure. In the cuprate superconductors, for instance YBCO, the quantity \( C \) behaves as a linear function of Zn-doping level (\( \alpha \)) while \( \alpha \) is a constant \([94, 95]\), the slopes of various crystals are consequently a constant regardless of the Zn-doping levels.

Figure 25(a) shows the \( T^2 \) dependence of \( \cot \theta_H \) for \( \text{Ba}_0.5\text{K}_0.5\text{Fe}_{1.95}\text{Zn}_{0.05}\text{As}_2 \) (BKZn) and \( \text{Ba}_0.5\text{K}_0.5\text{Fe}_{1.95}\text{Co}_{0.05}\text{As}_2 \) (BKCo) superconductors, which are abbreviated as BK, BKZn and BKCo, respectively. All crystals exhibit a nonlinear change with \( T^2 \) in the high-\( T \) region. For instance, for BK the nonlinear \( T^2 \) dependence appears above 250 K, suggesting a larger power of \( T^n \) with \( n > 2 \). The crossover temperature, however, is in accordance with both \( T^2 \) and \( T_H \) as discussed above. As nonmagnetic Zn substitution, the \( \cot \theta_H \) shows weak nonlinear change at high-\( T \). For the magnetic Co impurity the \( \cot \theta_H(T^2) \), however, indicates a dramatic modification from that of BK at high-\( T \). Since the Hall signals are rather small at this temperature region, where sign reversal takes place as discussed above, we can barely acquire reliable information from these results. We then focus on the low-\( T \) regions where the \( \cot \theta_H \) demonstrates a linear change with \( T^2 \). Figure 25(b) gives the linear fitting of \( T^2 \) for \( \cot \theta_H \) of BK, BKZn and BKCo at \( T < 140 \) K. The \( \alpha \) (\( C \)) is observed as \( 2.69 \times 10^{-3} \) (3.96), \( 2.43 \times 10^{-3} \) (15.38) and \( 3.48 \times 10^{-3} \) (12.84) for BK, BKZn and BKCo, respectively. The Zn seems unlikely to change the slope of \( \cot \theta_H \) from that of BK, which could be understood in terms of equation (22). The behavior of \( \cot \theta_H \) is consistent with the

![Figure 26. The C/T versus T^2 plots for (a) Co_{1+y}Te_{0.6}Se_{0.4} and (b) Cu_{1+y}Te_{0.6}Se_{0.4}, from Zhang et al [99].](image-url)
intrinsic relaxation rate of the elementary excitations (spinons) in the normal state, but not a ‘transverse’ relaxation rate. Indeed, the weak modification of Zn of the spin state was confirmed by the $^{75}$As NMR and NQR measurements on La (Fe$_{1-x}$Zn$_x$)AsO$_{0.85}$ polycrystal [2]. The $^{139}$La NMR spectra also indicated that the substituted Zn could hardly induce static moments around the impurity [2]. On the other hand, the Zn substitution increases the in-plane impurity scattering rate dominated $C$ (15.38) of BK (3.96). It is reasonably well understood because the Zn provides a large negative scattering potential (around $-8$ eV [1]) within the Fe$_2$As$_2$ plane. The Zn increases the residual resistivity in linearity and consequently suppresses the superconductivity as described in figures 21 and 22. Substitution of Zn on YBCO demonstrated a similar parallel shift of the cot $\theta$ versus $T^2$ curves with different doping levels [94, 95].

4.5. Heat capacity

It is essential to understand whether a NMI can induce a local moment on its vicinity, especially in the low enough temperature regions. Transport property measurements can hardly be carried out below $T_c$, unless one uses extremely high fields, large current density or heavy level impurity doping. Technically, the upper critical fields $H_{c2}$ for FBSs are quite high, for instance, the $H_{c2}$ for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ was found to be around 55 T [96]. In other cases, the heavy level impurity-doped crystals are often confronted with disorder and inhomogeneous distribution problems. STM measurement is the best method to explore the low-$T$ local moment of Zn as discussed in detail in section 3. Alternatively, low-$T$ heat capacity measurement is a simple approach owing to the bulk properties. From low-$T$ heat capacity measurements, applying a magnetic field will split the free Zn-induced moments into a two-level system and a Schottky anomaly should appear [97, 98].

A recent study on optimal Fe$_{1+y}$Te$_{1-x}$Se$_x$ ($x \approx 0.4$) showed that the Co or Cu substitution for Fe mainly serves as scatters rather than charge carrier doping [99]. In comparison with Cu doping, the Co substitution shows a less evident suppression effect on superconductivity while it exhibits a stronger influence on magnetism. Upon substitution of Co for
where \( A \) is a constant parameter depending on the compound.

Figure 27 shows fitting results for the \( \Delta \lambda(T) \) of the \( e \)-irradiated \( \text{Ba}_{1-x} \text{K}_{x} \text{Fe}_{2} \text{As}_{2} \) single crystals. To eliminate the uncertainty related to the upper fitting limit, several fittings were applied with a variable high-temperature end of the fitting range, namely, \( T_{up}/T_{c} \approx 0.1 \) to 0.3, while keeping the lower limit at the base temperature. The heavily doped samples exhibit strong saturation behavior with large exponent values, \( n > 3 \). For the samples close to the optimal doping, namely, \( x = 0.24 \) and 0.32, the exponent \( n \) remained high \((n = 3)\) and increases with decreasing \( T_{up}/T_{c} \). This implies that the temperature dependent \( \lambda(T) \) remains exponential at low temperatures with the addition of nonmagnetic scattering, and consequently supports the isotropic gap-like single-band \( s \)-wave or multiband \( s_{\pm} \) wave. For the most under-doped state with \( x = 0.19 \), there is a clear evolution toward the \( T^{2} \) relation, which reveals the changes from exponential in the clean limit to \(~T^{2}\) in the dirty limit, and supporting the nodeless \( s_{\pm} \) pairing.

4.7. Electronic thermoelectric power

The transport properties, for instance the Hall effect, are measured for the whole compound, but some compounds, like \( \text{BaFe}_{2-2x} \text{Zn}_{2} \text{Co}_{2} \text{As}_{2} \), have already doped with other elements that will strongly influence the Hall effect. Therefore, two scattering rates occur unless it is an ‘ideal’ pure single crystal. However, it is even harder to perform quantitative comparisons between samples than for the residual resistivity. Thus, the data can hardly provide the determination of the physical origin for the actual difference between the two scattering rates alone, for which some additional experiments such as electronic thermoelectric power on the Zn-substituted single crystals will be very helpful. In this case we can systematically study the electronic thermoelectric power in the SC states of various Zn-doped compounds, and explore if Zn has contributed to the normal-state electronic or SC states, as has been comprehensively studied in cuprates [100].

5. Impurities in the superconducting state

5.1. \( 11 \)-system

The \( 11 \)-system is featured without the separating blocking layer among the FBS family. The substitution of impurity is indeed onto the Fe-site rather than other sites within the blocking layer as that occurs in other systems. Zhang and co-workers showed that among the \( 3d \) transition metals from Cr to Zn, only the Co, Ni and Cu with smaller ionic radii for valence state \(^{2+}\) can substitute effectively for Fe in \( \text{Fe}_{1-x} \text{Te}_{1-y} \text{Se}_{x} \). The substitutions of any \( 3d \) metals with the concentration of \( \sim 5\% \) can lead to the formation of a spin-glass state and the suppression of superconductivity. As shown in figure 28, in contrast to the Co substitution which slightly suppresses the superconductivity, the Cu and Ni substitutions with the same concentration completely destroy the superconductivity.

5.2. \( 1111 \)-system

As briefly introduced in section 1, the Fe-based \( 1111 \)- and \( 122 \)-system are the two preferred systems for studying NMI substitution effects. The Zn-doping study was first carried out on the \( 1111 \)-system which possesses the highest \( T_{c} \) among the FBSs. The first observation of \( T_{c} \) suppression was reported by Guo et al in polycrystalline Zn-doped \( \text{LaFeAsO}_{0.85} \) [46]. Figure 29 presents the magnetic susceptibilities of the \( \text{LaFe}_{1-x} \text{Zn}_{x} \text{AsO}_{0.85} \), which manifest a large \( T_{c} \) decrease from 26 K to zero only by a minimal amount of Zn (\(<3\% \) substitution. The results indicate that the conventional \( s \)-wave model is highly unlikely for \( \text{LaFeAsO}_{0.85} \), but the \( s_{\pm} \) wave model and the nodal \( d \)-wave model both remain possible. Li and co-
workers [101, 102] also studied the Zn-substitution effects on SC of the polycrystalline LaFe$_{1-y}$Zn$_y$AsO$_{1-x}$F$_x$. As shown in figure 30, the $T_c$ suppression by Zn was only observed in the fluorine over-doped regime, whereas in the fluorine under- and optimal-doped regimes, the $T_c$ was even slightly enhanced which was unusual and had never been found in any other superconductors. Seen from the temperature dependent resistivity of the fluorine under-doped samples, the low-$T$ upturn was gradually suppressed by Zn impurities and the carrier density was also enhanced, indicated by the Hall measurements. Apart from the influence of the polycrystalline nature of the samples, one can hardly explain the Zn effects according to the discussion in section 4.4. It appears that the Zn substitution might improve the disorder or other intrinsic reasons. Later theoretical study from their colleagues suggested that the presence of a Zn impurity could induce an electron transferring from As to Fe atoms in both the fluorine...
could be helpful to elucidate this phenomenon. Further experiments on the single crystals under-doped and over-doped regions and modify the local lattice structure. Figure 32 gives the $T_c$ as a function of impurity content for the $RFe_1-xM_xAsO_{0.89}F_{0.11}$ polycrystal, where the $R =$ La and Nd, and $M = \text{Mn and Co}$, from Sato et al [13]. Reprinted with permission from The Physical Society of Japan.

under-doped and over-doped regions and modify the local lattice structure. Further experiments on the single crystals could be helpful to elucidate this phenomenon.

Li and co-workers also studied the Zn-substitution effect on the n-type 1111-system [103]. Figure 31 shows the Zn content dependent $T_c$ of polycrystalline $LaFe_{1-x}zCo_yZn_xAsO$ in the cobalt under-, optimal- and over-doped regimes. Different from their previous results on the $p$-type $LaFe_1-yZn_xAsO_{1-x}F_x$, SC in these samples was suppressed by Zn doping in all cobalt-doped regimes. The SC disappears at a Zn content of about 12 at.%, 4 at.% and 3 at.% for the cobalt under-, optimal- and over-doped regimes, respectively. The slopes of $T_c(x)$ are similar for the optimal- and over-doped regimes and both of them are more sharp than that of under-doped case.

In addition, Sato and co-workers suggested that the Co impurity should act as a NMI compared with the host atom Fe. They studied the substitution effects of Mn and Co on $RFe_2AsO_{0.89}F_{0.11}$ ($R =$ La and Nd) polycrystalline samples [13]. Figure 32 gives $T_c$ as a function of the impurity content for $RFe_1-xM_xAsO_{0.89}F_{0.11}$ ($R =$ La and Nd; $M = \text{Co and Mn}$). In these cases, the Co ion was believed to provide two electrons to the host conduction bands and was characterized as a NMI. Ni [104] and Ru [105] were considered as non-magnetic as well. The SC was completely suppressed with Co impurity content of 7.5 at.%, suggesting that the $T_c$ suppression rate is in accordance with the $LaFe_1-xCo_yZn_xAsO$ case as discussed above. It is worth noting that magnetic impurity of Mn introduced more dramatic $T_c$ suppression than any other impurities.

5.3. n-type 122-system

Up to now, most of the NMI study on FBS was reported on polycrystals as introduced above. Nevertheless, a single crystal has sizable and atomically ordered surfaces, which is crucial for surface sensitive measurements and scattering behavior within the SC plane, as discussed in sections 4.1 to 4.3. Consequently, the growth of Zn-doped single crystals is of great importance for studying the intrinsic Zn impurity effects. Since it is rather difficult in the growth of single crystals for the 1111-system, the well-studied 122-system is a promising candidate for the study.

Utilizing the high-pressure technique, Zn impurities were successfully doped into the single crystal in the 122-system, as discussed in section 4.1. Figure 33 summarizes for the results of $T_c$ suppression as a function of the impurity concentration for $BaFe_{2-x}Zn_xCo_{2-x}As_2$ ($M =$ Zn, Mn) [44]. Here, the $T_c$ is derived from the resistivity. SC is fully suppressed by Zn at the common doping level of ~8 at.%, regardless of the under- ($y = 0.045$), optimal- ($y = 0.055$) and over-doped ($y = 0.11$) regimes. The suppression rate for the Zn doping was roughly estimated by applying a linear function fit to the data, giving 2.31, 3.63 and 2.45 K at 1.0% for the under-, optimal- and over-doped states, respectively. The $T_c$ decreasing rates by Zn change little from the under- to over-doped SC states, being a remarkable feature discovered in this study. Clearly, the rates are much smaller than that expected for the $s_{+\pm}$ wave model (25 K at 1.0%, see below), indicating that the observed SC is very robust against the

**Figure 32.** The $T_c$ as a function of impurity content for the $RFe_1-xM_xAsO_{0.89}F_{0.11}$ polycrystal, where the $R =$ La and Nd, and $M = \text{Mn and Co}$, from Sato et al [13]. Reprinted with permission from The Physical Society of Japan.

**Figure 33.** Impurity concentration $x$ dependence of $T_c$ for $BaFe_{2-x}Zn_xCo_{2-x}As_2$ single crystals, where the impurities $M =$ Mn and Zn, and the $T_c$ were derived from resistivity. The data shown by the broken line are from the samples prepared under ambient pressure, from Li et al [44].
NMI than the expectation for the $s_\pm$ wave SC state. Similar results were also found in the Zn-doped BaFe$_{1.92-x}$Zn$_x$P$_{0.08}$As$_2$ single crystals [106]. For a comparison, the data for polycrystalline BaFe$_{1.87-x}$Zn$_x$Co$_{0.13}$As$_2$ prepared under ambient pressure are co-plotted by a dotted line in figure 32. The discrepancy between the present and the earlier data is probably due to overestimation of the Zn content in the ambient-pressure sample. Since the Zn substitution is not easily caused by the low melting point and high volatility of Zn-containing compounds, it is uncertain whether Zn can be substituted into the Fe-site by the normal ambient-pressure synthesis. The suppression rate for the magnetic Mn doped sample was estimated to be 6.32 K at $1\%$, which is still quite a lot smaller than the theoretical value for the $s_\pm$ wave model [10, 11]. Figure 34 shows the SC phase diagram of BaFe$_{2-x}$Zn$_x$Co$_2$As$_2$, where $T_c$ is determined by the resistivity measurements. As previously mentioned, SC is suppressed by the common doping level of Zn, $\sim 8\%$.

Similar $T_c$-suppression behavior was reported by Nakajima et al [81], which was caused by the application of 3 MeV proton irradiation on BaFe$_{2-x}$Co$_x$As$_2$ single crystals at under-, optimal- and over-doping levels. Figure 35 shows the normalized $T_c$ for crystals under different irradiation doses, where $T_{c0}$ is the $T_c$ irradiation-free sample. In all the doping regimes, $T_c/T_{c0}$ decreases linearly with increasing dose, whereas the slopes are different with respect to the doping regimes, from which the over-doped case was estimated as the most drastic SC suppression effect. In contrast, the $T_c$ in the optimal-doping regime was relatively robust against irradiated defects than other regimes. Such sample-dependent $T_c$ suppression behavior seems inconsistent with that of the chemical-doping results discussed above. Detailed analysis of the $\rho$ and pair-breaking will be discussed in section 5.

### 5.4. p-type 122-system

Cheng et al studied the Zn and Mn substitution effects on SC of the p-type polycrystalline Ba$_{0.43}$K$_{0.57}$Fe$_{2}$As$_2$ synthesized under ambient pressure (see figure 36) [49]. They found that the Mn doping depressed the SC transition temperature drastically with a rate of $\Delta T_c/Mn = -4.2$ K at $1\%$. Transport property measurement revealed that the Mn doping enhanced the $\rho_0$ significantly, and induced strong local magnetic moments ($\sim 2.58 \mu_B$) for distinct pair-breaking. Such results were consistent with those of Mn doping in other systems [44]. In contrast, the $T_c$ and $\rho_0$ were observed as almost independent of Zn doping. The weak Zn-substitution effect is only similar to that of the Zn under- and optimal-doped LaFeAsO$_{1-\delta}$F$_\delta$ system [101].

To elucidate the real effect of Zn, the Zn-doped p-type Ba$_{0.43}$K$_{0.57}$Fe$_{2-x}$M$_x$As$_2$ single crystals were synthesized by the high-pressure technique introduced in section 4.1. The magnetic and nonmagnetic elements around Fe in the element periodic table were selected as the dopants, including 3$d$ metals of Mn, Co, Ni, Cu and Zn, and 4$d$ metal of Ru [47]. The decreases of $T_c$ determined by $\rho$ and $\chi$ data ($T_{c\rho}$ and $T_{c\chi}$)
with the dopant concentration \( x \) are given in figure 37. The suppression rate by Zn was estimated at 2.22 K/\% by applying a linear function fit to \( T_c \) versus \( x \), which is in accordance with the results for the BaFe\(_{1.89-2x}\)Zn\(_2\)Co\(_{0.1}\)As\(_2\) superconductors. Applying a linear function fit to \( T_c \) versus \( x \), the suppression rates for Mn, Ru, Co, Ni and Cu are 6.98, 0.27, 1.73, 2.21 and 2.68 K/\%, respectively. Based on the density functional calculations, it was found that the impurity atoms in iron-based superconductors could be classified into three groups according to the scattering potential: (i) Mn (0.3 eV), Co (−0.3 eV) and Ni (−0.8 eV), (ii) Ru (0.1 eV) and (iii) Zn (−8 eV) [107]. Among these impurities, the nonmagnetic Zn works as a unitary scattering center due to the quite strong potential compared to the bandwidth. Consequently, it is expected to have strong pair-breaking effect on the SC with the anisotropic SC gap. The observed robustness of SC against Zn seems to contradict the \( s_{\pm} \) wave model. As discussed in section 2.2.2, the reduction in \( T_c \) due to the impurity is 25 K at 1.7\%. It has also been mentioned that \( T_c \) will be weakly suppressed by the impurities in the \( s_{\pm} \) wave state in contrast to \( s_{\pm} \) wave state. Among these impurities, Mn has the strongest suppression effect, even though it is much weaker than that expected for the \( s_{\pm} \) wave model (25 K at 1.7\%). The negligible suppression effect by Ru is consistent with the results for the 1111-system [13], for which we will not discuss this isovalue-doping effect in this review.

In addition, Tan and co-workers [56] grew Cr, Mn, Co and Zn-substituted K\(_{0.8}\)Fe\(_{1.73}\)Zn\(_2\) single crystals as can be seen in figure 38. The \( T_c \) was drastically depressed by substitution of Cr, Co and Zn for Fe, regardless of magnetic or nonmagnetic impurities. It is interesting that all impurities showed a similar suppression rate of about 30 K/\% approaching the value expected for the \( s_{\pm} \) wave model (25 K at 1.7\%), and only about 1 at.\% of dopant could kill the SC completely. On the other hand, these impurities induced drastic enhancement of residual resistivity, especially for nonmagnetic Zn, which resulted in a change of \( \rho_0 \) of about 0.25 at.\%. The dramatically large change of \( \rho_0 \) may indicate the occurrence of serious disorder [19, 41, 88] as analyzed in section 4.4. It is rather surprising that the SC of K\(_{0.8}\)Fe\(_{2-\gamma}\)Se\(_2\) behaves as exceptionally robust against the Mn substitution which even induced a slight increase in \( T_c \). The result seems likely in contrast with the Anderson theory introduced in section 2.2. The manganese atoms generally work as a strongly magnetic scattering center in superconductors regardless of any order parameters, namely, it should suppress the \( T_c \) for both isotropic and anisotropic pair symmetry. In addition, substitution of Mn introduces drastic charge localization and hence results in MIT in the low-\( T \) region of \( p-T \) curves, which was actually absent in this experiment. The authors attributed this anomalous phenomenon to the decrease of SC volume fraction owing to the non-SF islands around the Mn dopants. If so, the crystal may consist of two phases including a SC K\(_{0.8}\)Fe\(_{2-\gamma}\)Se\(_2\) and a non-SF Mn-rich phase, hence, the present results may not be considered to be an intrinsic substitution effect.

### 6. Pair-breaking

As discussed in section 2.2, we are far from understanding the nature of NMI scattering based on an individual analysis of doping level dependent \( T_c \). Instead, one should study various properties, among which the pair-breaking rate is the most important issue. The pair-breaking rate from NMI can be calculated as [11]

\[
\alpha = \frac{zh\gamma}{2\pi k_B T_c},
\]

where \( \gamma \) is the electron scattering rate; \( T_c \) is the \( T_c \) of the Zn-free compound. Based on the five-orbital model for the 122-system, theoretical study proposed a relation between \( \gamma \) and \( \Delta \rho_0 \) as [11]

\[
\Delta \rho_0 (\mu \Omega \text{cm}) = 0.18 \gamma \text{ (K)}.
\]

Here \( \Delta \rho_0 \) is the difference of the residual resistivity between the Zn-doped and Zn-free crystals. For the \( s_{\pm} \) wave state, SC should vanish in the range of \( \alpha > \alpha^c = 0.22 \) [11]. Thus, taking the results of Zn-doped BaFe\(_{1.89-2x}\)Zn\(_2\)Co\(_{0.1}\)As\(_2\) single crystals as an example, we can estimate the \( \alpha \) (figure 39) through

\[
\alpha_1 = 0.88 \frac{\Delta \rho_0}{T_c} \tag{28}
\]

and using \( z = 0.33 \) or 0.50, where the effective mass for the calculation of \( z \) is from the ARPES experiments [52]. To obtain the elastic scattering rate, we also calculated the pair-breaking parameter using equation (17) as

\[
\alpha_2 = \frac{zh\gamma}{2\pi k_B T_c} \tag{29}
\]

by deriving \( \gamma \) using the relation [11]

\[
\gamma = \frac{ne^2 \Delta \rho_0}{2m} \tag{30}
\]
where \( n \) is the carrier number estimated from the Hall data. Both the \( \alpha_1 \) and \( \alpha_2 \) data change roughly linearly; thereby we applied a linear function fit to the data and estimated the critical pair-breaking parameters as 7.64, 11.49 and 6.76 for \( \alpha_1 \) \((z = 0.33)\), \( \alpha_1 \) \((z = 0.05)\) and \( \alpha_2 \), respectively. In addition, using the relation

\[
\alpha_c = \frac{\hbar^2 \rho_0}{4\pi T_c 0 \mu_0 \lambda_0^2},
\]

we obtained \( \alpha_3 \approx 2.58 \) for \( \lambda = 195 \text{ nm} \) \([83]\). Obviously, the pair-breaking parameters experimentally estimated for the present system are far above the limit \( \alpha_c = 0.22 \) for the \( s_\pm \) wave model, suggesting that the \( s_\pm \) wave model may not be a candidate for the 122-type superconductor.

Figure 38. (a) The plot of the \( T_c \) value versus \( x \) for the K\(_{0.8}\)Fe\(_{2-y}\)M\(_y\)Se\(_2\) \((M = \text{Cr, Mn, Co and Zn})\) samples. (b) The plot of the residual resistivity versus \( x \), from Tan et al \([56]\).

Figure 39. \( T_c / T_c^0 \) versus \( \alpha \) with various calculations for BaFe\(_{1.89}\)Zn\(_2\),Co\(_{0.11}\)As\(_2\) \((x = 0.08)\) using equations \((28), (29)\) and \((31)\), from Li et al \([48]\).

Figure 40. Normalized critical temperature \( T_c / T_c^0 \) as a function of normalized scattering rate. The Ba(Fe,Co)\(_2\)As\(_2\) single crystals were irradiated by proton irradiation. Dashed lines are linear extrapolations. \( \alpha_c^\parallel \) is the critical scattering rate expected in the \( s_\pm \) wave model, from Nakajima et al \([81]\).
It is possible that the $\alpha_1$, $\alpha_2$ and $\alpha_3$ are slightly overestimated if $\Delta \rho_{\text{imp}}$ is overestimated due to the grain boundary or undetected electrically resistive factors. For further clarification, we made another estimation regarding the critical impurity concentration for the $s_\pm$ wave state ($n_{\text{imp}}^\pm$). Since Zn ($I > 1$ eV) corresponds to $n_{\text{imp}}^\pm \sim 0.5\zeta/T_c$ (K), we predicted $n_{\text{imp}}^\pm$ to be 0.01 (0.015) for $z = 0.5$ (0.33); obviously, the experimentally determined $n_{\text{imp}}$ of 0.08 for $T_c = 0$ is much higher than the theoretical values. Thus, the quantitative discussion regarding the $n_{\text{imp}}$ does not accept the $s_\pm$ wave model for the BaFe$_{1.89}$Co$_{0.11}$As$_2$ superconductor as well.

Nakajima and co-workers [81] also calculated the pair-breaking rate on their proton-irradiated Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ single crystals, as can be seen from figure 34. Using equation (26) they found that the critical scattering rates were 6.1, 3.5 and 2.4 for the under-, optimal- and over-doped regimes, respectively. The results are very much in accordance with the chemical doping data as shown in figure 40. Note that the critical pair-breaking rates of all samples are much higher than that expected for the $s_\pm$ pairing scenario ($\approx 0.22$).

On the basis of previous pair-breaking analysis for the $n$-type BaFe$_{1.89}$−2Zn$_2$Co$_{0.11}$As$_2$ superconductors, Li et al also calculated the pair-breaking rate for the $p$-type Ba$_{0.5}K_{0.5}$Fe$_2$−2Zn$_2$As$_2$ ($M = \text{Mn, Ru, Co, Ni, Cu and Zn}$) single crystals [47]. Here $\alpha$ can be estimated from equation (26) using $z = 0.50$ as shown in figure 41. The $T_c/T_{c0}$ changes against $\alpha$ in a roughly linear way; thereby we applied a linear function fit to the data and estimated the critical pair-breaking parameters as 6.52, 5.23, 4.24, 5.41 and 6.05 for impurities of Mn, Co, Ni, Cu and Zn, respectively. The comparable result was obtained for the pair-breaking effect of Zn in the BaFe$_{1.89}$−2Zn$_2$Co$_{0.11}$As$_2$ system as $\alpha = 11.49$ with $z = 0.5$. The results are consistent with the proton-irradiated Ba(Fe, Co)$_2$As$_2$ experiments [81]. Obviously, the pair-breaking parameters experimentally estimated for the present system are far above the limit of $\alpha_\pm = 0.22$ expected from the $s_\pm$ wave model, suggesting that the $s_\pm$ wave model may be unlikely in the 122-type FBS.

To understand the relatively low pair-breaking rate of Zn on the 122-type iron pnictides, Chen and co-workers [58] calculated the disorder effects of Zn impurities in the strong (unitary) scattering limit on various properties of the system in the case of $s_\pm$ wave pairing symmetry, by solving the lattice Bogoliubov–de Gennes equation (BdG) self-consistently. Figure 42 shows the suppression effect of Zn on the superfluid density in BaFe$_{2−x}$Zn$_x$Co$_2$As$_2$. The local superfluid density was found to decay significantly with an impurity content of 3.83% at zero temperature as visualized in figure 42(a). As a result, the zero temperature bulk superfluid density $\bar{\rho}_s$ and $T_c$ are completely destroyed by $\sim 8\%$ of Zn impurities, implying the importance of spatial disorder-induced fluctuations. However, the decrease rate of $\bar{\rho}_s$ is larger than that of $T_c$, which was attributed to the ‘Swiss cheese’ scenario for a short-coherence superconductor. Further corroborating with Umura plot provides further proof for the
different rates of suppression as shown in figure 42(c). The Uemura plot indicates the breakdown of the Abrikosov–Gor’kov theory for impurity-averaged Green’s functions. The numerical results are in agreement with the experiments, namely, SC phase is fully suppressed close to the critical impurity concentration of roughly $n_{\text{imp}} \approx 8\%$.

For the Zn-substitution results of the 1111-system from Li et al [103], recent simulation studies also showed the scattering rate. Figure 43 gives the calculation of $T_c$ for Zn scattering rates and the experimental results for impurity content dependent $T_c$. They suggested that FBS might be characterized by the strength of the effective on-site pairing potential $g_0$, and proposed three types of cases for the disorder effect: (i) large $g_0$ (figure 43(a)), where the on-site pairing dominates, and $T_c$ is independent of Zn doping. The experimental results of under- and optimal-doped LaFe$_{1-x}$Zn$_x$AsO$_{1-y}$F$_y$ were believed to be consistent with this case (figure 43(b)). (ii) Weak $g_0$, SC is destroyed by the impurity. The authors considered the results for overdoped LaFe$_{1-x}$Zn$_x$AsO$_{1-y}$F$_y$, LaFe$_{1-x}$Zn$_x$AsO$_{1-y}$ and BaFe$_{2−x}$Zn$_x$Co$_2$As$_2$ satisfied in this model. (iii) $g_0 \approx g_2$, $T_c$ is initially suppressed rapidly with Zn doping, and then saturates with a certain doping level. The data from polycrystalline SrFe$_{1.8−x}$Zn$_x$Co$_2$As$_2$ were classified to this case.

For a comparison, we summarized the above data of the NMI study on single crystals in figure 44. The $T_c/T_{\text{c,0}}$ curves locate at three different regions marked as I, II and III in figure 44(b).

Region I: for the K$_{0.8}$Fe$_{2−y}$Zn$_y$Se$_2$ data, although the SC was depressed with substituting only 0.25 at.% of Fe-sites by Zn, the change of residual resistivity $\Delta\rho_0$ was quite high at about 1320 $\mu\Omega$ cm, as a result the critical pair-breaking rate is still large at around 19.94. Nevertheless, we cannot define 19.94 as the real critical pair-breaking rate of K$_{0.8}$Fe$_{2−y}$Zn$_y$Se$_2$, unless one can grow more crystals with SC partially suppressed by Zn to fit the linear function of $T_c/T_{\text{c,0}}$ versus $\alpha$, namely, the critical $\alpha$ may be more or less than 19.94. One may be confronted with a technical difficulty during the crystal growth due to the extremely low doping level as <0.25 at.%. Larger pair-breaking rates are also observed in the Zn-substituted 122-type crystals, regardless of $p$-type Bi$_{0.4}$K$_{0.6}$Fe$_2Zn$_2$As$_2$ or $n$-type BaFe$_{1.89−x}$Zn$_x$Co$_{0.11}$As$_2$, whose critical $\alpha$ are mostly as 11. Nevertheless, the evaluation of well-characterized microbridges exhibits a considerably smaller critical pair-breaking rate of 1.32, which should be close to the nature of the pair-breaking rate. With respect to the calculation from Efremov et al [14], the critical pair-breaking rate for the $s_\pm$ wave model was estimated as $\alpha_s^\text{crit}(T_{\text{c,0}} = 25 K) = 28$ with inter- to intra-band scattering ratio $\alpha_+ \equiv u/v = 1$ from equation (15), much larger than that expected from Onari’s model ($\alpha_s^\text{crit} = 0.22$) [11]. In the case of Onari’s model, the authors considered a ‘natural’ formulation for impurity potential, i.e. diagonal on the basis of the five Fe $d$-orbitals, automatically leading to significant inter-band scattering if one transforms back to the band basis. From Efremov’s estimation [14], however, the
Figure 44. (a) $T_c/T_{c0}$ versus $\alpha$ for various single crystals, here all samples are under the optimal-doped regimes. (b) Enlarged view of the low pair-breaking region. The pair-breaking rate $\alpha$ was estimated as equation (28) for single crystals BaK-Zn (Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, $x = 0$–0.15) [48], BaK-Zn-2 (Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, $x = 0.05$–0.08) [47], KFe$_2$-Zn (K$_{0.8}$Fe$_2$As$_2$, $x = 0$ and 0.005) [56], BaCo-irr (BaFe$_{1.89}$Co$_{0.11}$As$_2$, $x = 0.05$–0.08), BaRu-irr (BaFe$_{1.76}$Ru$_{0.24}$As$_2$, $x = 0.05$–0.08), KFeS-Zn (K$_{0.8}$Fe$_2$As$_2$, $x = 0$ and 0.005) [56], BaCo-irr (BaFe$_{1.85}$Co$_{0.15}$As$_2$, under different proton-particle irradiation) [81], Ndf-irr (NdFeAsO$_{0.7}$F$_{0.3}$ under different $\alpha$-particle irradiation) [79], BaK-irr (Ba$_{1-x}$K$_x$Fe$_2$As$_2$ under electron irradiation) [83], BaP-irr (BaFe$_{1.85}$Co$_{0.15}$As$_2$, under different electron irradiation) [84], and BaCo-Zn (BaFe$_{1.85}$Co$_{0.15}$As$_2$, under different electron irradiation) [85]. $\alpha_{c}^\pm$ is the pair-breaking parameter expected for the $s_\pm$ wave model, and it was calculated to be around 0.22. All data are fitted linearly and marked in the same color as the data.

7. Summary

In this review, we gave an overview of the theoretical and experimental progress in nonmagnetic impurity substitution studies on Fe-based superconductors. A number of scientists have proposed two highly promising order parameter symmetries, i.e. the multi-gap $s_{\pm}$ and $s_{\pm}$ wave. Because of the complex gap structure and exceptional magnetic and metallic behaviors of Fe-based superconductors, the influences of the nonmagnetic defects may vary in chemical potential, impurity disorder, inter- and intra-band scattering features and electron localization. This creates difficulties in obtaining important information for the understanding of the symmetry of the superconducting order parameter. Experimentally, the first concern regarding the defects is naturally focused on sample quality. Zn impurities have been successfully substituted into the single-crystalline 122-type superconductors, providing significant results by various measurements. Considering the effects of Zn impurities, the largest is found in its immediate neighborhood within a ball region, which has not yet been investigated using local probes such as NMR, NQR, $\mu$SR or STM, but proved by superconducting order-parameter phase-slip phenomena in the Zn-doped nanowires, in which the radius of the correlation length of order around the non-superconducting regions around Zn was observed as a few lattice spacings. A single impurity also influences the electronic state and local moment, the magnetic response of the Fe$_2$X$_2$ planes both on the macroscopic scale as the antiferromagnetic state and local scale of moment.
Most of the experiments on the effects of nonmagnetic impurities are from the transport properties. The Zn ions provided direct modifications of the superconductivity, including the suppression of critical temperature and the enhancement of residual resistivity. In particular, the superconductivity disappears when the residual resistance per plane accesses the quantum resistance limit (6.45 kΩ). The Hall measurements demonstrated that Zn impurities contributed weak modification of the carrier densities. However, the Zn seems unlikely to change the slope of the $T^2$ dependent Hall angle, suggesting the inducing in-plane impurity scattering rate with substitution of Zn. On the other hand, Zn ions can also influence the heat capacity, the London penetration depth, the electronic thermoelectric power and so on.

On the basis of these experiments we emphasize the qualitative feature of impurities’ effects on the superconducting state for many FBS systems. Considering an overall good agreement between many different experiments on different materials systems, we can safely conclude that the nonmagnetic impurity can suppress the superconductivity without major concerns about sample quality variations. In summary, the pair-breaking rates of nonmagnetic defects on various superconductors are collected to compare with various theoretically approaches. The pair-breaking rates of the electron-irradiated 122-type crystals and the Zn-doped microbridges are consistent with the theoretically calculated wave function for the $s_d$ wave ($\alpha_d^2 = 0.22$), which provide strong evidence for the $s_d$ wave as the nature of pairing symmetry in Fe-based superconductors, but not an isotropic gap symmetry. However, we can hardly exclude a much more complex symmetry, the $s+if$ wave, which also behaves with strong anisotropic gap symmetry. Further experimental and theoretical investigations are still required.

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