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To cite this article: Yunkyu Bang and G R Stewart 2017 J. Phys.: Condens. Matter 29 123003

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Topical Review

Superconducting properties of the $s^{\pm}$-wave state: Fe-based superconductors

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Received 24 October 2016, revised 27 November 2016
Accepted for publication 20 December 2016
Published 13 February 2017

Abstract

Although the pairing mechanism of Fe-based superconductors (FeSCs) has not yet been settled with consensus with regard to the pairing symmetry and the superconducting (SC) gap function, the vast majority of experiments support the existence of spin-singlet sign-changing $s$-wave SC gaps on multi-bands ($s^{\pm}$-wave state). This multi-band $s^{\pm}$-wave state is a very unique gap state per se and displays numerous unexpected novel SC properties, such as a strong reduction of the coherence peak, non-trivial impurity effects, nodal-gap-like nuclear magnetic resonance signals, various Volovik effects in the specific heat (SH) and thermal conductivity, and anomalous scaling behaviors with a SH jump and condensation energy versus $T_c$, etc. In particular, many of these non-trivial SC properties can easily be mistaken as evidence for a nodal-gap state such as a $d$-wave gap. In this review, we provide detailed explanations of the theoretical principles for the various non-trivial SC properties of the $s^{\pm}$-wave pairing state, and then critically compare the theoretical predictions with experiments on FeSCs. This will provide a pedagogical overview of to what extent we can coherently understand the wide range of different experiments on FeSCs within the $s^{\pm}$-wave gap model.

Keywords: iron-based superconductors, $s^{\pm}$-wave pairing state, superconducting properties

(Some figures may appear in colour only in the online journal)
true that these details exist in real FeSC materials and can play an important role in our complete understanding of various aspects of these materials. However, it is not our purpose to find a better fit to the experimental data. We intend to show the proof of concepts and emphasize mainly the generic features, but not the parameter-dependent tuning ability of the $s^\pm$-wave pairing state. This is due to two reasons: (1) the $s^\pm$-wave pairing state itself is an interesting new SC state, having many unexpected interesting SC properties regardless of its realization in FeSCs, hence it is worthy of study by itself; (2) the unrealistically simplified—in some sense—minimal two-band $s^\pm$-wave model, ignoring the apparent details mentioned above, is surprisingly good at explaining almost all, often either peculiar or anomalous, experimental data.

Another important purpose of this article is to provide a pedagogical, detailed exposition on how to understand the experimental data on the representative SC properties of the materials, and how to understand them theoretically, side by side. We hope this will serve as useful guidelines, in particular for young researchers in the field. Needless to say, if we omit or miss some important references for the issues dealt with in this paper, it is not intentional. We have tried our best to give fair treatment to all research papers.

1.2. A brief summary of the FeSC theories

1.2.1. Random phase approximation type theories. Immediately after the discovery of the La(O$_{1-x}$F$_x$)$_2$FeAs ($x = 0.05-0.12$) superconductor with $T_c \approx 26$ K in 2008 [11], several theorists—Mazin et al. [12] and Kuroki et al. [13] among others—carried out weak coupling BCS calculations combining the essential band structure and the antiferromagnetic (AFM) spin fluctuations arising from the local interactions between the $d$-orbital electrons of the Fe atoms. They found that the leading SC pairing solution is the sign-changing $s$-wave state: $s$-wave order parameters (OPs) formed on the hole Fermi surfaces (FSs) around the $\Gamma$ point and the electron FSs around the $M$ point in the Brillouin zone (BZ) (in this paper we use the two Fe/cell BZ if not otherwise specified). A particular (unphysical) choice from each other, therefore conveniently called as the $s^\pm$-wave state. These early theories are random phase approximation (RPA) theories, where the theory constructs the low energy effective pairing interaction by calculating a dynamic spin susceptibility $\chi_\nu(q, \omega)$ using the RPA method and solves the Eliashberg gap equation with the effective interaction. This approach is fairly standard weak coupling theory and still faces objections because the FeSC compounds are believed to be a strongly correlated electron system (SCES) like the high-$T_c$ cuprates and heavy fermion systems. Thus, there is the belief that the description of the superconductivity in the SCES should be something beyond a weak coupling BCS–Eliashberg type theory.

After these early RPA theories, more extensions and elaborations of RPA type approaches [14–17] have been applied on more realistic models of FeSC compounds for a wider parameter space of $U, U''$ (on-site Coulomb repulsions between intra- and inter-orbitals, respectively) and $J, J'$ (on-site Hund coupling and pair hopping, respectively), changing dopings and pnictogen height [15], etc. It was found that in most cases the spin susceptibility $\chi_\nu(q, \omega)$ is dominant at a large momentum $q = (\pi, 0)/(0, \pi)$. The gap solutions from the multi-band Eliashberg equations can obtain more complicated structures than the original RPA solution. It is quite natural to have strong anisotropy in the $s$-wave gap function $\Delta_{\nu}(k)$ around each FS [14, 15, 17, 18] and three-dimensional warping (along the $c$-direction). Even develop vertical line nodes can develop in the gap function with some parameters but it still remains in the $A_{\nu}$ symmetry [16]. With a particular (unphysical) choice of parameter (e.g. large values of $J$ and $J'$), the $d_{x^2-y^2}$-wave solution can also be a dominant solution [14]. Therefore, we can say that the dominant solution of the RPA approaches for FeSCs in most of the parameter space is basically the $s^\pm$-wave state.

Along this line of development, Kontani et al. [19, 20] have extended it toward a charge instability (there are many motivations for this direction, such as $C_2$ structural phase transition, stripe AFM order, many signals of nematic order/ fluctuations, etc), searching for the optimal conditions for the dominant charge/orbital fluctuations instead of the spin fluctuations as the pairing glue. These authors found two routes to enhance the charge/orbital fluctuations: (1) coupling with in-plane Fe phonons and (2) vertex correction (the usual RPA theory ignored this). Once the charge/orbital fluctuations $\chi_c$ are found to be dominant, they mediate an attractive interaction for the singlet channel (AFM spin fluctuations mediate a repulsive interaction for the singlet channel). Therefore if a dominant $\chi_c(q, \omega)$ occurs around $q = (0, 0)$, it helps any kind of SC pairing [8], and if a dominant $\chi_c(q, \omega)$ occurs at around $q = (\pi, 0)/(0, \pi)$, it will promote $s^{++}$-wave pairing and compete against $s^\pm$-wave pairing [19, 20]. Whether this scenario of pairing glue is relevant to FeSCs mainly depends on the judgment whether the choice of interaction parameters necessary for dominant charge/orbital fluctuations is physically relevant for the real compounds. Although it is still an open issue, theoretically it seems to require a rather unphysical parameter choice to obtain the dominant charge/orbital fluctuations $\chi_c$ in particular at around $q = (\pi, 0)/(0, \pi)$, and there is not such strong experimental support for the $s^{++}$-wave pairing state. For more in-depth discussion of the $s^{++}$ scenario in FeSCs see [4, 8].

A more elaborate extension of the RPA type approach is called the fluctuation-exchange (FLEX) method [21], which basically adds a self-energy correction to one-particle propagators and self-consistent vertex corrections to standard RPA type calculations, satisfying the so-called conserving approximation. This method is theoretically better justified, but empirically it has been known that the results are not necessarily better than the RPA results when the system is a strongly correlated (or strong coupling) one. Nevertheless, FLEX studies of the FeSC systems [22–24] basically produced qualitatively similar results to the RPA results.

1.2.2. Functional renormalization group technique. Another quite powerful technique is the functional renormalization group (fRG) technique. This theoretical technique is supposed to be unbiased, starting from the high energy Hamiltonians
with local interactions $U, U', J, J'$, etc. Without approximation, it simultaneously traces down, through the RG process, several instabilities of a given Hamiltonian on an equal footing—the superconductivity, spin density wave (SDW), charge density wave, etc [25–28]. Hence this technique can reveal a close competition between the superconductivity and SDW, for example, with changes of doping and other interaction parameters. For superconductivity itself, it can also trace the competition among the different Cooper channels with the SC OP decomposition using lattice harmonics: which would correspond to $s$-, $d$-, $s^\pm$-waves, etc, in the band picture. At the moment, it is fair to say that this is the most unbiased theoretical tool to study the ground state of interacting many-body systems, but its weak point is that as a numerical technique, there is a limitation the analysis of the underlying physics for a particular ground state. Nonetheless, most of the results from the fRG method [25–28] are qualitatively similar to those from the RPA type theories, and the $s^\pm$-wave state was found to be a leading SC instability in the major region of the parameters $U, U', J, J'$.

1.2.3. Local pairing approach: strong coupling theories. Then there is the local pairing approach [29–32]. This approach starts with the local magnetic Hamiltonian, $J - J'$ model, added to a itinerant part, the $'t$-$t'$-term, hence it is called the $t - J - J'$ model (the $t - J$ model is the counterpart model for the high-$T_c$ cuprates). The motivation comes from the experimental fact that the magnetism of the FeSC compounds has a strong local character as well as the itinerant magnetism. The model itself is appealing and can be theoretically justified to some extent [29, 32], however its solutions are not controlled. The simplest of all methods is to decouple the local magnetic part Hamiltonian ($J - J'$ term) by the mean field method into all possible SC pairing channels and determine the dominant pairing channel by diagonalizing the total $H$. At this level, this approach is technically nothing but BCS theory, but these authors argued that it better incorporates the physics of the high energy local interactions, such as Hund and exchange couplings, which should be important in SCESs. Interestingly, the resulting pairing solutions compare quiet well with the results of other methods such as fRG and RPA, namely the dominant pairing solution is again found to be the $s^\pm$-wave gap in the large parameter space.

With all the theories mentioned above, the so-called $s^\pm$-wave state or its continuously modified pairing state have been consistently found as the dominant pairing solution in most of the parameter space. As to the pairing mechanism, RPA and FLEX belong to the BCS mechanism. FRG and local pairing theory also belong to the BCS framework in the sense of finding Cooper pair instability, but these methods contain unknown parts for how pairing glues arise (RG) or how to solve these pairing interactions beyond a mean field method (local pairing theory). On the other hand, people with a more extreme viewpoint suspect that there should be a fundamentally different pairing mechanism beyond the BCS paradigm, within which the strong correlation effects, such as quantum criticality (QC), play an active role. In this review, we do not discuss this issue of the pairing mechanism, but will mainly focus on examining and testing the consistency of the $s^\pm$-wave pairing state in comparison with available experiments. Only in the last section 11, we will discuss "experimental hints for the pairing mechanism".

2. The $s^\pm$-wave pairing state

2.1. Phenomenological two-band model

In this paper, we use a minimal two-band model for the $s^\pm$-wave pairing state to emphasize the proof of concept and to clarify the generic properties of the $s^\pm$-wave state in order to understand the experimental data. By doing this, we can test the pairing symmetry and the structure of the gap function of the FeSC without introducing ad hoc assumptions and material-specific fine tuning. The minimal two-band model consists of one hole band and one electron band representing the generic $s^\pm$-pairing state. In real FeSC compounds, there exists more than one hole band around the $\Gamma$ point $(0, 0)$ and more than one electron band around the $M$ point $(\pi, \pi)$ in the BZ. In this paper, we use the two-dimensional BZ for two Fe/cell, as depicted in figure 1, therefore the hole (electron) band in our two-band model should represent the thermodynamic average of a group of hole (electron) bands. The model is described with the Hamiltonian consisting of two bands,

$$H = \sum_{k} e_{h}(k)h_{k,\sigma}^{\dagger}h_{k,\sigma} + \sum_{k} e_{e}(k)e_{k,\sigma}^{\dagger}e_{k,\sigma} + \sum_{kk'} V(k,k')h_{k,\sigma}^{\dagger}h_{k',\sigma}^{\dagger}h_{k',\sigma}h_{k,\sigma} + \sum_{kk'} V(k,k')e_{k,\sigma}^{\dagger}e_{k',\sigma}^{\dagger}e_{k',\sigma}e_{k,\sigma},$$

(1)

where $h_{k,\sigma}$ and $e_{k,\sigma}$ are the electron creation operators on the hole and the electron bands, respectively. $e_{h,k}(k)$ are the dispersions of the hole band and electron bands in the two-dimensional BZ, respectively. The band dispersions $e_{h,e}(k)$ need not be specified for the purpose of this paper, but the generic FS and the BZ of the model are depicted in figure 1.

The microscopic origin of the pairing interaction $V(k, k')$ could be AFM fluctuations of the magnetic moment of the Fe 3d-electrons and theoretically connected to the dynamic spin susceptibility $\chi_{s}(\omega, q)$. Many authors have calculated $\chi_{s}(\omega, q)$, mostly using generalized RPA methods [13–17, 19, 20, 22–24] starting from more microscopic Hamiltonians. When only spin degrees of freedom are considered, several theoretical results produce a common feature, i.e. $\chi_{s}(\omega, q)$ is strongly peaked at $q = (\pi, \pi)$ at low energy, indicating a nearby AFM instability, which is also qualitatively in accord with the early inelastic neutron experiments [33, 34] (see section 5 for more discussion and references). This kind of $\chi_{s}(\omega, q)$ with AFM spin fluctuations is well known to lead to repulsive interactions between electrons in the singlet Cooper channel over all momentum exchanges. However, there is also a large discrepancy between theory and experiment for the prediction of the size of magnetic moment when $\chi_{s}(\omega, q)$ is ordered. This
issue is related to the fundamental question of how localized or itinerant the $d$-electrons are inside the FeSC materials. On the other hand, a presumably more elaborate theory, which includes both orbital as well as spin degrees of freedom \cite{19, 20}, yields results for $\chi_{\text{charge}}(\omega, \mathbf{q})$ in which the orbital fluctuations are strongly peaked at $q = (0, 0)$ and lead to an attractive interaction for small momentum exchanges. There is some indirect evidence for the strong orbital/charge fluctuations, such as structural and nematic instabilities, but no clear evidence exists for strong fluctuations in the small momentum sector $\mathbf{q} \approx (0, 0)$ coming from $\chi_{\text{charge}}(\omega, \mathbf{q})$ with inelastic neutron scattering (INS).

There is much discussion about the possible origin of the pairing interactions, but in the above model, the pairing interaction $V(k, k')$ is phenomenologically defined and assumed as coming from AFM spin fluctuations. Therefore, it is all repulsive in momentum space for the singlet Cooper channel and strongly peaked around $\mathbf{q} = \mathbf{k} - \mathbf{k}' = (\pi, \pi)$ as

\[
V(k, k') = V_m \frac{\kappa^2}{|\mathbf{k} - \mathbf{k}'| - \bar{Q}^2 + \kappa^2} \tag{2}
\]

where $\mathbf{k}$ and $\mathbf{k}'$ are momenta in the two-dimensional BZ and the parameter $\kappa$ controls the magnetic correlation length as $\xi_{\text{AFM}} = \pi n a \kappa$ ($a$ is the unit-cell dimension). This interaction mediates the strongest repulsion when two momenta $\mathbf{k}$ and $\mathbf{k}'$ are spanned by the ordering wave vector $\mathbf{Q}$. This condition is better fulfilled when the two momenta $\mathbf{k}$ and $\mathbf{k}'$ each reside on the hole band and electron band, respectively, as shown in the model FS structure (see figure 1).

The SC ground state of the Hamiltonian equation (1) is solved using the BCS approximation and the two bands need two SC OPs as

\[
\Delta_h(k) = -\sum_{k'} V_h(k, k') \chi_h(k') \chi_h^\dagger(k'), \tag{3}
\]

\[
\Delta_e(k) = -\sum_{k'} V_e(k, k') \chi_e(k') \chi_e^\dagger(k'). \tag{4}
\]

After decoupling the interaction terms of equation (1) using the above OPs, the self-consistent mean field conditions lead to the following two coupled-gap equations.

\[
\Delta_h(k) = -\sum_{k'} [V_h(k, k') \chi_h(k') + V_h(k, k') \chi_h^\dagger(k')], \tag{5}
\]

\[\Delta_e(k) = -\sum_{k'} [V_e(k, k') \chi_e(k') + V_e(k, k') \chi_e^\dagger(k')]. \tag{5}
\]

where $V_h(k, k')$, $V_e(k, k')$, etc., are the interactions defined in equation (2) and the subscripts are written to clarify the meaning of $V_h(k, k') = V(k, k')$, $V_e(k, k') = V(k, k')$, etc., and $k_h$ and $k_e$ are the momentum $k$ located on the hole and electron bands, respectively. The pair susceptibilities are defined as

\[
\chi_{h,e}(k) = T \sum_{\omega_n} \frac{\Delta_{h,e}}{\omega_n^2 + \epsilon_{h,e}^2 + \Delta_{h,e}^2(k)}. \tag{6}
\]

where $\omega_n = \pi T (2n + 1)$ are Matsubara frequencies. For our purpose in this paper—which is the demonstration of principle rather than a better fitting to experimental data—one more simplification makes our discussions clearer without loss of essential features. Namely, we will assume constant isotropic s-wave gaps $\Delta_{h,e}(k) = \Delta_{h,e}$ on each band and BS averaged pairing interactions between bands (inter-band) and within each band (intra-band), such as $\langle V_h(k_h, k_h') \rangle = V_{hh}$, $\langle V_h(k_h, k_h') \rangle = V_{hh}$, and $\langle V_e(k_e, k_e') \rangle = V_{ee}$, etc. Then the coupled-gap equations (equation (5)) can be written as

\[
\Delta_h(T) = -[V_{hh} \chi_h(T) + V_{he} \chi_e(T)], \tag{7}
\]

\[\Delta_e(T) = -[V_{eh} \chi_h(T) + V_{ee} \chi_e(T)]. \tag{7}
\]

with the momentum integrated pair susceptibilities

\[
\chi_{h,e}(T) = T \sum_{\omega_n} \langle 0 \rangle_{h,e} \int_{-\omega_n}^{\omega_n} d\epsilon_{h,e} \frac{\Delta_{h,e}}{\omega_n^2 + \epsilon_{h,e}^2 + \Delta_{h,e}^2} \tag{8}
\]

\[= \langle 0 \rangle_{h,e} \int_{-\omega_n}^{\omega_n} \frac{\Delta_{h,e}(T)}{2E_{h,e}} \tanh \left(\frac{E_{h,e}}{2T} \right). \tag{9}
\]

where $E_{h,e} = \sqrt{\epsilon_{h,e}^2 + \Delta_{h,e}^2}$ and $\langle 0 \rangle_{h,e}$ are the quasiparticle excitations and the density of states (DOS) of the hole and electron bands, respectively, and $\omega_{\text{AFM}}$ is the cutoff energy of the pairing potential $V(q)$.

Assuming all repulsive pairing potentials $V_{ab} > 0$, $(a, b = h, e)$ and with a dominance of the inter-band potentials

Figure 1. (A) A typical FS of the $\epsilon_g(k)$ (red) and $\epsilon_d(k)$ (green) band of the two-band model. The AFM wave vector $\mathbf{Q}$ spans between two bands. Here we use the BZ for two Fe/unit-cell. (B) A sketch of the $s^\pm$-wave gap solution. (C) A sketch of the $s + g$-wave gap solution which can be continuously evolved from a solution of (B) without changing the gap symmetry of $\Delta_g$. 

\[\Delta_h(k) = -\sum_{k'} [V_h(k, k') \chi_h(k') + V_h(k, k') \chi_h^\dagger(k')], \tag{5}\]

\[\Delta_e(k) = -\sum_{k'} [V_e(k, k') \chi_e(k') + V_e(k, k') \chi_e^\dagger(k')]. \tag{5}\]
as $V_{hh}(=V_{eh}) > V_{he}$, $V_{ee}$, the above gap equations produce the $s^{\pm}$-wave gap solution, as proposed and reconfirmed by many authors [12–14, 30, 35–37]. A schematic picture of the $s^{\pm}$-wave state is shown in figure 1(B). Considering more realistic pairing potentials $V(k, k')$ with detailed coupling matrix element $M_{a,b}(k, k')$ including the orbital degrees of freedom ($\alpha, \beta = d_{xz}, d_{yz}$ on the bands), the isotropic $s$-wave OP on each band (figure 1(B)) can develop an anisotropy [15–18] and in its extreme case even a nodal gap is possible [16, 17] as depicted in figure 1(C). However, in this case, this nodal gap does not break any additional symmetry from the case of figure 1(B) but continuously keeps the same lattice symmetry of $A_{1g}$. As a result, the number of nodal points of figure 1(C) is eight instead of the four nodal points in a $d$-wave solution. This $A_{1g}$ nodal gap can occur either on the hole band or on the electron band depending on the details of the real FeSC compounds. There have been several theoretical predictions for a nodal gap on the electron FS around the $M$ point [14, 18, 27, 38], which recently has a supporting ARPES measurement [39]. The $A_{1g}$ nodal-gap structure with eight nodes depicted in figure 1(C) was indeed confirmed in the heavily K-doped (Ba,K)/Fe$_2$As$_2$ by ARPES experiments [40, 41] and theoretically explained [42]. There is also the possibility to have a $d$-wave nodal/nodeless gap solution [14, 30, 36, 38], with the model of equation (1) in the parameter space of interactions nearby, from the $s^{\pm}$-wave solution, because the FeSC systems are now well known to have several closely competing instabilities [16, 38].

Here we would like to emphasize that: (1) the genuine $s^{\pm}$-wave state can develop a nodal gap without changing the gap symmetry or introducing any new pairing mechanism and (2) it is certain that, depending on whether or not it has nodes, the SC gap introduces distinctively different features in the SC properties. However, the type of nodal gap in figure 1(C) does not represent anything new or novel physics, these are just accidental nodes.

2.2. Similarity to the $d$-wave solution

On the other hand, by shifting the BZ by a half unit-cell distance along either the $x$- or $y$-direction (shifting the BZ by $(\pm \pi, 0)$ or $(0, \pm \pi)$ as shown in figure 2), we can see that the genuine $s^{\pm}$-wave state appears to have the same pairing symmetry as the $d$-wave state. More precisely the $s^{\pm}$-wave state has gliding $+C_2$ symmetry and the $d$-wave state has only $C_2$ symmetry. More importantly, figure 2 also suggests a possible common pairing mechanism for both SC-gap states if both SC states are described within the weak coupling BCS theory, although many researchers believe that both high-$T_c$ cuprate and Fe-based superconductivities should be governed by theories beyond the standard BCS theory.

2.3. Some unique features of the $s^{\pm}$-wave solution

Although it is genuinely a BCS theory, the two-band $s^{\pm}$-wave superconductor described by the coupled-gap equation (equation (7)) has several novel features that are not shared with standard single-band BCS theory, and therefore are often and easily mistaken as evidence for non-BCS superconductivity. It is the main objective of this review to provide a pedagogical overview of these new SC features of the $s^{\pm}$-wave superconductor and clarify possible confusions. Those main novel features are as follows:

1. The gap sizes of $|\Delta_h|$ and $|\Delta_e|$ are not equal in general. Approximately, they are inversely related to the DOSs $N_{he}$ as $|\Delta_h| \approx \frac{N}{N_{he}}$ when $T \to 0$, and $|\Delta_h| \approx \left( \frac{N}{N_{he}} \right)^{1/2}$ when $T \to T_c$ (this second relation becomes exact when $V_{hh,eh} \gg V_{he,eh}$).

2. As a result, the gap-to-$T_c$ ratio can be much larger or smaller than the BCS prediction [43] depending on which gap size is used such as $2\Delta_h/T_c > 3.5$ and $2\Delta_e/T_c < 3.5$, where $\Delta_{h,e}$ are the gaps of the larger/smaller of $\Delta_{h,e}$. The proper ratio can be calculated with the thermodynamically averaged gap value $\Delta_{ave} = (N_{h}|\Delta_h| + N_{e}|\Delta_e|)/(N_{h} + N_{e})$, and then the ratio $2\Delta_{ave}/T_c$ can be compared to the BCS value to judge whether the given FeSC compound is in the weak coupling limit or in the strong coupling limit.

3. Because the two OPs $\Delta_{h,e}$ are coupled and induce each other, the small-gap OP only cannot be destroyed by some perturbations and the larger-gap OP still remains. This feature produces the unexpected Volovik effect in the vortex state with a magnetic field.

4. The opposite signs of the two OPs produces similar effects as in $d$-wave superconductors, such as resonant impurity scattering and suppression of the coherence peaks in nuclear magnetic resonance (NMR). On the other hand, these effects are not as perfect as for the $d$-wave because of the inequivalent size of the opposite-signed OP as $|\Delta'| \neq |\Delta|$. 

5. Finally, different combinations of the above properties produce many interesting and exotic SC properties in the $s^{\pm}$-wave state.

2.4. Experimental tests for pairing symmetries: density of states $N_{\omega}(\omega)$

Most experiments for testing the gap symmetry and gap function basically probe the shape of the DOS (see figure 3) by measuring various transport, thermodynamic, electromagnetic, and optical properties in the SC state: e.g. angle...
resolved photoemission spectroscopy (ARPES), specific heat (SH), thermal conductivity, penetration depth, NMR, optical conductivity, Raman spectroscopy, etc. Therefore, we expect that clean \( s^\pm \)-wave superconductors should display full-gap behaviors just like a standard \( s \)-wave superconductor, as shown in figure 3(C). Indeed, many FeSCs show various full-gap SC behaviors, for example, the exponentially flat temperature dependence of the penetration depth, \( \chi(T) \propto \exp \left[ -\Delta(T)/T \right] \), for SmFeAsO\(_{0.8}\)F\(_{0.2}\) [44], PrFeAsO\(_{1-y}\) [45], and (Ba,K)Fe\(_2\)As\(_2\) [46], etc.

As to the sign-changing OP nature of the \( s^\pm \)-wave state, the most direct observation would be the Josephson tunnel junction experiment, as performed with a \( d \)-wave cuprate superconductor [47]. Unfortunately, however, the \( s^\pm \)-wave state in the FeSCs does not allow any real space contacts, preferentially to each one of the two different OPs, because both OPs \( \Delta^+_1 \) and \( \Delta^+_2 \) are isotropic in the \( ab \)-plane. Thus the Josephson tunnel junction experiment is not so useful to distinguish the gap symmetry, or it has produced only limited evidence [48].

On the other hand, if only the DOS is probed, another two-gap SC state, the \( s^\pm \)-wave state (e.g. MgB\(_2\)), which has the same signs on the two s-wave OPs as \( \Delta^+_1 \) and \( \Delta^+_2 \), should have the same SC features as the \( s^\pm \)-wave superconductor. Indeed, in the clean limit SC state, many SC properties—such as the SH, thermal conductivity, penetration depth, Knight shift, etc.—of these two SC states should be identical and cannot be distinguished. However, in the last several years, it was found by many researchers that the sign-changing OP feature in the \( s^\pm \)-wave SC state can produce some unique and distinct SC properties compared to the \( s^\pm \)-wave superconductor, both in the clean limit and, in particular, in the impure case. Theoretical investigations of these new SC properties of the sign-changing \( s \)-wave superconductor have been challenging per se and their experimental comparisons with the numerous FeSCs have been very successful. As a result, the \( s^\pm \)-wave state is now mostly accepted as the standard pairing state of FeSCs, possibly with a few exceptions.

The basic principle which enables us to probe these sign-changing OPs is utilizing processes involving a large momentum exchange, \( q \sim O(\pi) \), so that it connects two OPs located on the separate Fermi pockets in the BZ. There are three possibilities:

1. **Impurity scattering.** Local impurities (both magnetic and non-magnetic impurities) scatter quasiparticles with all momentum exchanges so impurity scattering connects the OPs between the same signs as well as between the opposite signs. Therefore, the impurity scattering will change all SC properties of the \( s^\pm \)-wave state very differently from the \( s^\pm \)-wave state. This is the main process to detect the \( s^\pm \)-wave state, because impurities always exist in real materials, often unavoidably, but also controlled to some extent.

2. Some selected SC properties intrinsically contain large momentum process, so they intrinsically probe the sign-changing OP nature. Examples are the NMR relaxation rate \( 1/T_1 \), and dynamic structure function \( \chi_Q(Q,\omega) \) by INS measurement.

3. Combination of the above two processes also appears in various SC properties and results are often very interesting in unexpected ways.

### 3. Impurity effects on the \( s^\pm \)-wave state: the \( T \)-matrix theory

The study of the impurity effects on the \( s^\pm \)-wave state is an interesting and important subject. Theoretically, it is interesting because the \( s^\pm \)-wave state is a new pairing-gap state and had not studied for its impurity effects previously, and several novel impurity effects were indeed found. It also has practical importance in understanding the SC properties of FeSCs and identify the pairing symmetry.

Real materials, including SC materials, always contain impurities at some level, as well as defects where the sub-lattice site occupancy is not thermodynamically perfect. Historically, the seminal paper by Abrikosov and Gorkov [49] provided the theoretical ground to study this important effect. Using Green’s function method, these authors showed that non-magnetic impurities do not affect \( s \)-wave superconductors, confirming Anderson’s theorem [50], which was argued on the grounds of the time-reversal symmetry of the singlet \( s \)-wave superconductor. This Green’s function method for impurity scattering is very powerful to study various realistic cases, such as magnetic/non-magnetic impurities, \( s \) - and non\(-s \)-wave superconductors, etc.

The work of Abrikosov and Gorkov was a Born approximation study of the impurity scattering and this theory was soon extended to a \( T \)-matrix theory by many authors [51, 52], which includes a certain set of the multiple scattering process to infinite order at a low density limit of impurity concentration. As it is a low impurity density expansion but...
The $T$-matrix theory begins with the second order in impurity interaction. The first order diagrams are absorbed to chemical potential. The $T$-matrix was generalized to two-band matrices as $\Sigma$-matrices for the heavy fermion and high-$T_c$ cuprate superconductors by one of us [53] and we briefly explain its essence here. All impurity scattering effects in the SC state enter the pair susceptibility of the SC state as follows:

$$ T^{i}_{a}(\omega) = \frac{G^{i}_{a}(\omega_{n})}{D}, \quad (i=0,1; \ a = h,e), \quad (14) $$

$$ D = c^{2} + [G^{0}_{h} + G^{0}_{e}]^{2} + [G^{1}_{h} + G^{1}_{e}]^{2}, \quad (15) $$

$$ G^{0}_{a}(\omega_{n}) = \frac{N_{a}}{N_{tot}} \left( \frac{-\omega_{n}}{\sqrt{\omega_{n}^{2} + \Delta_{a}(k)}} \right), \quad (16) $$

$$ G^{1}_{a}(\omega_{n}) = \frac{N_{a}}{N_{tot}} \left( \frac{-\Delta_{a}}{\sqrt{\omega_{n}^{2} + \Delta_{a}(k)}} \right), \quad (17) $$

where $c = \cot \delta_{0}$ is a convenient measure of scattering strength, with $c=0$ for the unitary limit and $c > 1$ for the Born limit. $\langle \cdots \rangle$ denotes the FS average. In figure 4, we show the schematic Feynman graphs of the above formulas: figure 4(A) the renormalized pair susceptibility $\chi_{h,e}(T)$, figure 4(B) the $T$-matrix $T^{i}_{a}(\omega_{n})$, and figure 4(C) the dressed one-particle Green function $G^{i}_{a}(\omega_{n})$.

The most unique point of the impurity effects in the $s$-wave state is the term $[G^{1}_{h} + G^{1}_{e}]$ in the denominator $D$ (equation (15)). Because of the opposite signs of $\Delta_{h}$ and $\Delta_{e}$, this term becomes almost zero (it becomes exactly zero in the case of the $d$-wave state, for example). When $[G^{1}_{h} + G^{1}_{e}] \to 0$ and $c \to 0$, the $T$-matrices $T^{i}_{a}$ can develop a resonant impurity band inside the gap at $\omega = 0$, as happens in the $d$-wave state by the same mechanism. What is more interesting about

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**Figure 4.** (A) Renormalized pair susceptibility $\chi_{h,e}(T)$, including normal self-energy correction and vertex correction. (B) Definition of the $T$-matrix. Notice that our $T$-matrix begins with the second order in impurity interaction. The first order diagrams are absorbed to chemical potential. (C) A dressed one-particle Green’s function with a $T$-matrix self-energy correction. In all of the diagrams, the red cross indicates a single impurity.
the $s^\pm$-wave state is that this cancellation is not perfect, hence the term $[G^r_h + G^i_h]$ remains tiny but still finite. As a result, the impurity resonance is not located at zero energy as in the $d$-wave state, but is located at finite energies $\omega_{\text{res}} \ll \Delta_s$ symmetrically around the zero energy.

### 3.2. Impurity resonance and in-gap states

Figure 5 shows schematic diagrams of the impurity bound states with non-magnetic unitary impurities for different SC states: (A) $s$-wave, (B) $d$-wave, and (C) $s^\pm$-wave state. First, figure 5(A) shows the case of standard $s$-wave superconductors, where the non-magnetic impurities do not form an in-gap state, hence do not induce any significant changes for the SC properties. In contrast, figure 5(B) shows the case of the $d$-wave superconductor, where the non-magnetic unitary impurities induce a bound state at zero energy inside the SC gap. With a finite impurity concentration, this in-gap state forms an impurity band with a finite DOS around zero energy. This so-called in-gap state induced by impurities in $d$-wave SC states has been well studied in connection with the heavy fermion and high-$T_c$ cuprate superconductors [51, 52]. The presence of the in-gap state significantly changes all SC properties of the $d$-wave superconductor. The accurate theoretical predictions of the systematic changes of these SC properties with impurities have played a crucial role in understanding many puzzling experiments and identifying the $d$-wave gap symmetry. Finally, figure 5(C) shows the case of the $\pm s$-wave superconductor. Qualitatively and even physically we can understand it as an intermediate case between the $s$-wave and $d$-wave superconductors.

In figure 6, we illustrate how the impurity band systematically evolves inside the gap in the $s^\pm$-wave superconductor as the impurity concentration increases. The low energy DOS $N(\omega)$ is still gapped at very low impurity concentrations (figure 6(A)), then it becomes a $V$-shaped DOS (thermodynamically the same as the clean $d$-wave DOS) at the critical impurity concentration $n_{\text{imp}} = n_c$ (figure 6(B)), and finally evolves to the finite $N_{\text{imp}}(0) + V$-shaped DOS with higher impurity concentration $n_{\text{imp}} > n_c$ (figure 6(C)). This kind of systematic evolution does not occur with a $d$-wave superconductor. From the clean limit to the very low impurity concentration of $n_{\text{imp}}$, the system should show gapped $s$-wave SC behaviors. And for a finite range of concentration of $n_{\text{imp}}$ around $n_{\text{imp}}^{\text{crit}}$, the system shows $d$-wave-like SC properties unless the experimental probes go to a very low energy scale with $T$, or $\omega$, or fields $H$. For higher concentrations of $n_{\text{imp}} > n_c$, it shows dirty $d$-wave-like behaviors, yet with some differences. In this case, the low energy $N(\omega)$ becomes a $N_{\text{imp}}(0) + V$-shaped DOS, and the sharp $V$-shaped DOS continues to exist on top of a finite DOS at $N(0)$. This type of DOS (figure 6(C)) looks different to a dirty $d$-wave DOS (figure 6(B)), where the $V$-shaped DOS becomes immediately flattened with a finite DOS at $N(0)$. This difference between the dirty $s^\pm$-wave and the dirty $d$-wave superconductors can easily be discerned by measuring the SH $\chi(T)$ and Knight shift $K(T)$, for example. In the following sections, we will show in more detail how this systematic evolution of the DOS at $N(\omega) \approx 0$ in the $s^\pm$-wave superconductor can show up as various non-trivial behaviors in different SC properties, such as NMR, SH, thermal conductivity, etc.
3.3. Examples of impure SC DOS: d-wave and s±-wave states

Figures 7 and 8 show the impurity induced self-energies $\text{Im} \Sigma^{\text{imp}}(\omega)$ and the corresponding $N(\omega)$ for different impurity concentrations, $\Gamma/\Delta_0 = 0.0, 0.004, 0.015, 0.06$, respectively. For the $d$-wave state, $\Gamma/\Delta_0 = 0.0, 0.004, 0.015, 0.06$, respectively. The results are self-explanatory, as the key points were explained in the previous sections. The imaginary part of the impurity self-energy $\text{Im} \Sigma^{\text{imp}}(\omega)$ for the $d$-wave state (figure 7(A)) clearly shows the zero energy resonance peak, and it induces the zero energy in-gap states in the total DOS $N(\omega)$. In the case of the $s^\pm$-wave state, the resonance peaks shown with $\text{Im} \Sigma^{\text{imp}}(\omega)$ (figure 8(A)) are split symmetrically into four peaks $\pm \omega_1 \ll \Delta_s$ and $\pm \omega_2 \ll \Delta_L$, where $\Delta_s$ and $\Delta_L$ are the small gap and large gap, respectively. The corresponding total DOS $N(\omega)$ shown in figure 8(B) shows the systematic evolution with increasing impurity concentration. More realistic calculations with a five-orbital model also produced qualitatively similar results [54, 55].

4. Angle resolved photoemission spectroscopy

4.1. Superconducting gaps measured by ARPES

ARPES measures the quasiparticle dispersion and its spectra with energies and momenta resolved. Currently, the best energy resolution of the leading group is $\sim 1–2$ meV with synchrotron radiation light [57] and can be much better with laser lights (laser ARPES). With this level of resolution, ARPES is the most powerful and versatile experimental tool for studying the electronic properties of solids. For the correlated metals and superconductors, it can measure the spectra of the bands near the Fermi level and provide the fundamental information on the FS shapes/topology of the system. By comparison with the band calculations of density functional theory, these ARPES results can also provide information on the strength of renormalization (or effective masses $m^*$) of each band. These are the most important pieces of information to begin with for any theoretical investigation of correlated metal systems.
Using polarizations (either linear or circular) of light, it can also provide information on the orbital degrees of freedom of the bands in multi-orbital compounds such as $d$-band metals, which is another very valuable piece of information to understand these correlated metals [58–62]. Most importantly, by changing the temperature, the ARPES spectra also deliver information about how the electronic properties evolve with temperature, hence it reveals not only the SC transition but also various magnetic and orbital transitions. We refer the reader to two review papers [63, 64], among many, for these interesting issues.

In this review, since our main focus is limited to examining the consistency of the $s^\pm$-wave pairing state for FeSCs, we will only briefly touch upon a small section of the ARPES experiments on the SC gap. Concerning the SC-gap symmetry, the ARPES experiment measures the SC-gap magnitude $|\Delta(k)|$ around the FSs and its interpretation is straightforward. Ideally it measures, after the thermal factor is subtracted, the one-particle spectral density in the SC state [57, 65] defined as

$$A(k, \omega) = -\frac{1}{\pi} \text{Im} G(k, \omega) = -\frac{1}{\pi} \text{Im} \left[ \frac{\omega + \Sigma(k, \omega)}{(\omega + \Sigma(k, \omega))^2 - E^2(k)} \right]$$

with $E^2(k) = \epsilon^2(k) + \Delta^2(k)$. Therefore, tracking the FS ($\epsilon(k) = 0$), ARPES can measure the momentum-dependent SC-gap size $|\Delta(k)|$ around the FSs, but not the sign of the gap.

Typical ARPES data of $|\Delta(k)|$ for the FeSC $\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2$ [56] are shown in figure 9. Shown in the left panel are the BZ (one Fe per unit-cell) and measured FSs: the two-hole band FSs ($\alpha$ and $\beta$) around the $\Gamma$ point and the one-electron band FS ($\gamma$) around the $M$ point. In the two right-hand panels, the measured SC gaps $|\Delta_\alpha(k)|$, ($\alpha = \alpha, \beta, \gamma$), around each FS are displayed in polar coordinates. As seen, the gaps $|\Delta_\alpha(k)|$ are quite isotropic and fully opened around each FS. This was undeniable evidence for the $s$-wave superconductor.

Soon after, more systematic ARPES measurements for various FeSC compounds with different dopings were carried out. The main findings of ARPES for the FeSCs are: (1) the majority of FeSCs show almost isotropic full gaps around both the hole pockets and the electron pockets, as shown in figure 9; (2) however, many FeSCs also show varying degree of anisotropy in $|\Delta_\alpha(k)|$, as shown in figure 10 for $\text{NdO}_{0.9}\text{F}_{0.1}\text{FeAs}$ [66], and $\text{LiFeAs}$ [67]; (3) for a small number of FeSC compounds, the ARPES data of $|\Delta_\alpha(k)|$ also show strong evidence for possible nodal gaps, either in the hole pockets [40, 41] or in the electron pockets [39].

Although ARPES cannot detect the sign of the gap function $\Delta_\alpha(k)$, items (1) and (2) above are consistent with the $s^\pm$-wave pairing state.
pairing-gap scenario. Regarding item (3), possible nodal gaps, although some researchers tend to interpret the presence of a nodal gap itself as a signature for a distinct novel pairing mechanism, we think it can still be very naturally accommodated within the $s^\pm$-wave pairing scenario (see figure 1(C)). In particular, all the reported possible nodal-gap structures [39–41], either on hole pockets or on electronic pockets, did not break the $A_4$ symmetry of the compounds, therefore they all belong to the same pairing symmetry class as the standard $s^\pm$-wave gap.

For more detailed analysis, the effects and consequences of the self-energy correction $\Sigma(k,\omega)$ in equation (18) need to be included, which contains the renormalization and correlation effects from inelastic scattering as well as the impurity scattering effects. In particular, the impurity scattering induced self-energy correction plays an important role in the SC phase, as discussed in section 3. The non-magnetic impurities induce in-gap bound states (see figures 6 and 8(A)) in the $s^\pm$-wave state, which would substantially change the shape of the quasiparticle spectra $A(k,\omega)$ of equation (18) and consequently the total DOS, $N_{\text{tot}}(\omega) = \sum_k A(k,\omega)$ (figure 8(B)). In particular, with the impurity density higher than a critical amount $n_{\text{imp}}^{\text{crit}}$ the total DOS, $N_{\text{tot}}(\omega) = \sum_k A(k,\omega)$, becomes a V-shaped DOS just like a $d$-wave superconductor, as seen in figure 8(B). However, an important distinction from the $d$-wave superconductor comes from the ARPES spectra. Namely, although the total DOS looks like a $d$-wave gap, the individual quasiparticle spectrum $A(k,\omega)$ measured by ARPES experiment shows an isotropic non-zero gap $|\Delta_s(k)| \neq 0$ everywhere around the whole FS. This has been observed with numerous ARPES experiments.

4.2. Summary

The main message from the ARPES experiments regarding the SC gap in FeSCs is simple: except for a few compounds or exceptional dopings, most of the ARPES experiments with FeSCs have shown fully opened $s^\pm$-wave gaps with some degree of anisotropy around the FSs, which is consistent with the $s^\pm$-wave gap scenario. This probe itself, however, cannot tell the sign-changing nature of the $s^\pm$-gap function. On the other hand, the interesting and challenging issue is that even when the ARPES experiments measured isotropic full gaps, various other experimental probes—NMR, SH, thermal conductivity, penetration depth, etc.—have shown strong nodal-gap features (various power-law behaviors) in the SC state with basically the same (nominally) compounds for which the ARPES experiments saw full $s^\pm$-wave gaps. Resolving this contradictory dilemma is the main subject of the remaining sections.

5. Inelastic neutron scattering

5.1. Neutron resonance in the $s^\pm$-wave state

INS measures the dynamic spin susceptibility $\chi_s(q,\omega)$, and it is well known that the pairing symmetry and the gap function $\Delta_s(k)$ of equation (18). Then the denominator $\chi_s(q,\omega)$ of equation (19) is the $s$-wave superconductor, as seen in figure 8(B).

This coherence factor becomes $\sim 0$ when $\Delta_s(k) > 0$, or $\sim 1$ when $\Delta_s(k) < 0$. Therefore, depending on the SC-gap function, the INS experiments can scan over the momentum $q$ and frequency $\omega$ space to find a constructive or destructive effect from the above coherence factor.

It was noticed that this coherence factor can be utilized to identify the $d$-wave pairing state of the high-$T_c$ cuprate superconductors [68–73], because choosing $q = Q$—which connects the `+' part and the `−' part of the gap function $\Delta_d(k)$ (see figure 2)—the coherence factor is enhanced as $\sim 1$ for $\omega \sim 2\Delta_{\text{max}}$. This enhanced non-interacting spin susceptibility $\chi_s^0(q,\omega)$ can have a more dramatic effect in the interacting susceptibility than, for example, using an RPA approximation,

$$\chi_s(q,\omega) = \frac{\chi_s^0(q,\omega)}{1 - U_0 \chi_s^0(q,\omega)}$$  

where $U$ is a local interaction. As $T$ goes to zero, the real part of $\chi_s^0(q,\omega)$ has so-called logarithmic divergence at $\omega = Q$ and $\omega = 2\Delta_{\text{max}}$ [73]—this singularity will be mitigated over frequencies and momenta because of the distribution of $d$-wave gap $\Delta_d(k)$ due to the constructive coherence factor of equation (19). Then the denominator $[1 - U_0 \chi_s^0(q,\omega)]$ can approach zero near $\omega \sim 2\Delta_{\text{max}}$, for a wide range of values of $U$. As a result, the imaginary part of dynamic spin susceptibility $\text{Im} \chi_s(q,\omega)$ can form a `resonance' peak, which was detected by numerous INS experiments with cuprate as well as heavy fermion superconductors [74–77], confirming the $d$-wave pairing state in these materials. In this spin exciton (or resonance) mechanism, it is important to notice that the value of the RPA interaction $U$ does not need fine tuning due to the logarithmic divergence of $\text{Re} \chi_s^0(Q,\omega = 2\Delta_{\text{max}})$. In reality, you need a minimum strength of interaction, but there should be a wide window of strength to form a resonance, so that this spin exciton resonance mechanism should be quite universal for $d$-wave superconductors as well as $s^\pm$-wave superconductors.

The exact same mechanism for the neutron resonance can occur with the $s^\pm$-wave state because $\Delta_s(k) + \Delta_{s^\pm}(k) < 0$ if the momentum $q$ is selected to satisfy $\Delta_s(k) + \Delta_{s^\pm}(k) < 0$. Here this particular momentum $q = Q$ is the nesting vector or near to it $q = q' \approx Q$ which best connects the hole band and the electron band in FeSCs (see figure 2). This possible neutron resonance peak in the FeSCs was theoretically [78, 82, 83] suggested as a signature of the $s^\pm$-wave state, and almost simultaneously detected by an INS experiment with optimal K-doped Ba-122 [33] and La-1111 [34] in accord with the theoretical prediction. Soon numerous INS experiments with K-doped Ba-122 [84, 85], Co-doped Ba-122 [80, 86, 87], Co-doped Na-122 [81], and Fe(SeTe) [88–91] have reported the occurrence of the resonance peak below $T_c$ and the
disappearance of it above $T_c$, confirming that this resonance is related to the superconductivity and, the most natural explanation would be, with the $\pm s$-wave pairing state.

Figure 11 shows two representative theory (RPA) calculations with different choices of bands and interactions [78, 79] for the FeSCs, and share a main feature: the resonance peak appears below the SC-gap edge ($\omega < |\Delta| + |\Delta|$) at the nesting vector $q = Q$ or close, and is sharpest for the $\pm s$-wave state. These results are compare well with figure 12, which shows the representative INS experiments for various FeSCs with a resonance peak appearing below $T_c$. Therefore, the theories and experiments seem to be quite consistent with each other and support the $\pm s$-wave pairing state for the FeSCs.

5.2. Some questions on the neutron resonance in the $s^\pm$-wave state

Despite the very natural explanation for the neutron peak, some questions were raised for the $s^\pm$-wave state scenario. The main question was that the INS experiments show a much too broad resonance peak, compared to the very sharp peak from the RPA calculations (see figures 11 and 12). However, this sharpness of the resonance peak for the RPA theory calculations can be improved considering many realistic reasons, such as impurity scattering and gap anisotropy [4]. Also, the experimental data of the resonance peak shape are not always broad and can be rather sharp for some FeSC compounds (see the right-hand panel of figure 12). Nevertheless, based on this critique, Kontani and co-workers [92, 93] rejected the $\pm s$-wave scenario and proposed the $s^{++}$-wave state to explain the broad neutron peak. In this model with the $s^{++}$-wave state, the coherence factor of equation (19) is destructive, hence there is no logarithmic divergence in $\text{Re} x^0\chi$ and therefore no ‘resonance’ below $2\Delta (|\Delta| \approx |\Delta|)$ is possible. Instead, these authors claimed that the quasiparticle damping—which should be sufficiently strong because of strong correlation—should drop in the SC state but only for $\omega < 3\Delta$. Then, because of this sudden drop in quasiparticle damping, the dynamic spin susceptibility
\( \chi_s(q, \omega) \) in the SC state can have a hump-like enhancement in the region of \( 2\Delta < \omega < 3\Delta \). While the numerical calculations of \( \text{Im} \chi_s(q, \omega) \) in [93] appear consistent with the broad peak of neutron experiments, this scenario requires a fine tuning of parameters such as the damping rates in the normal state and SC state, and the RPA interaction strength to produce the sizable hump structure. Considering the almost universal observation of the neutron resonance peak in various FeSCs [33, 34, 80, 84–91], this \( s'^+ \)–wave scenario seems to be too artificial. However, this point is still under debate [94–96].

The second question is about the temperature dependence of the resonance energy \( \omega_{\text{res}}(T) \). Because the spin resonance is a particle–hole exciton in the spin channel in the SC state, the constraint of the resonance peak position should be \( \omega_{\text{res}}(T) < |\Delta_b| + |\Delta_a| \). Therefore, increasing temperature as \( T \to T_c \), it is expected that \( \omega_{\text{res}}(T) \) should decrease. Indeed, the neutron peaks of BaFe\(_{1.85}\)Co\(_{0.15}\)As\(_2\) [80] show the expected temperature variation, while the data of FeTe\(_{0.5}\)Se\(_{0.5}\) show that \( \omega_{\text{res}}(T) \) is almost temperature-independent up to very close to \( T_c \), but only the peak height decreases [97]. This needs an explanation.

5.3. Summary

The INS resonance peak in the SC state observed in numerous FeSC compounds [33, 34, 80, 84–91] is absolutely consistent with the \( s\)–wave state. The underlying mechanism of this phenomenon is the constructive coherence factor of the \( s\)–wave state, identically operating and confirmed with the \( d\)–wave cuprate superconductors. Although there are a few details—the shape of the peak spectra, the temperature dependence of the peak frequency, etc.—need improvement to fit the experimental neutron spectra, the overall consistency between theories and experiments is excellent.

6. Nuclear magnetic resonance

The NMR experiments consist of measurements of three major quantities: Knight shift \( K(T) \), \( T_1 \), and \( T_2 \) relaxation times. Among these three quantities, Knight shift \( K(T) \), and \( 1/T_1 \) directly measure the DOS of metals below and above \( T_c \), so they can provide valuable information about the SC-gap functions \( \Delta(k) \).

6.1. Knight shift

6.1.1. Clean limit. Knight shift \( K(T) \) is the relative shift of the NMR resonant frequencies between the Zeeman split energy levels of the nuclear spin of the specific ions inside the material. Zeeman energy is proportional to the total magnetic field \( H_{\text{eff}} \) at the nuclear spin, which is defined as \( H_{\text{eff}} = (1 + K(T))H_{\text{ext}} \). While there are several sources for \( K(T) \), in metallic systems, the main contribution for \( K(T) \) is the paramagnetic uniform spin susceptibility times the hyperfine coupling. Therefore, in the case of the singlet pairing superconductors, it basically measures the change of the DOS \( N(0) \) at the Fermi level of the metal as temperature varies above and below \( T_c \). For the \( s\)–wave superconductors, the theoretical formula of Knight shift is given as

\[
K(T) \sim \text{Re} \chi_s(q = 0, \omega \to 0)
\]

\[
= -\int_0^\infty d\omega \frac{\partial \chi_{\text{FD}}(\omega)}{\partial \omega} \sum_{\alpha = h, e} \left[ N_\alpha(0) \left( \frac{\text{Re} \chi_s(\omega)}{\sqrt{\omega^2 - \Delta_\alpha^2(k, T)}} \right) \right]
\]

\[
= -\int_0^\infty d\omega \frac{\partial \chi_{\text{FD}}(\omega)}{\partial \omega} \left[ N_h(\omega, T) + N_e(\omega, T) \right]
\]

where \( \chi_s(q, \omega) \) is the dynamic spin susceptibility of the conduction electrons and \( \chi_{\text{FD}}(\omega) = (1 + e^{-\omega/T})^{-1} \) is the Fermi–Dirac distribution function. \( \langle \ldots \rangle \) means an FS average and the inside expression is nothing but the normalized DOS \( N(\omega) \) in the SC state. The coherence factor for the static uniform spin susceptibility becomes \( \langle 1 \rangle \) and the uniform susceptibility limit \( q = 0 \) does not allow inter-band scattering, hence the Knight shift of the \( s\)–wave pairing state is just the summation of two \( s\)–wave Knight shifts from the hole band and the electron band, respectively.

We expect, therefore, a typical temperature dependence of an ordinary \( s\)–wave superconductor for Knight shift \( K(T) \) of FeSCs: for a singlet \( s\)–wave superconductor, a rapid drop below \( T_c \) and an exponentially flat behavior at low temperatures for \( T < T_c/3 \). However, as it is a two-band model, the gap-to-\( T_c \) ratio of the \( s\)–wave superconductor can be very different from the standard BCS value of \( 2\Delta_{\text{BCS}}/T_c \approx 3.5 \) such as \( 2\Delta_{\text{BCS}}/T_c \gg 3.5 \) and \( 2\Delta_{\text{BCS}}/T_c \ll 3.5 \), where \( \Delta_{\text{LS}} \) are the larger and smaller gaps from the hole and electron bands. Each band has its own DOS \( N(0)_{he} \) and it has been shown that in general the inverse relation \( \frac{\Delta_{\text{LS}}}{T_c} \approx \frac{N_h}{N_e} \) holds for the \( s\)–wave model when the inter-band repulsion is the dominant pairing interaction [37]. Therefore depending on the relative ratio between \( N_h \) and \( N_e \), and the choice of the gap-to-\( T_c \) ratio \( 2\Delta_{\text{LS}}/T_c \), the shape of the temperature dependence of \( K(T) \) over the wide range below \( T_c \) can be very different from the standard single-band BCS behavior. Choosing relatively larger values of \( \Delta_{\text{LS}}/T_c \), we can phenomenologically simulate the effect of the strong coupling superconductivity. For the overall temperature dependence of the gaps \( \Delta_{\text{LS}}(T) \), we use a phenomenological BCS formula, \( \Delta_{\text{LS}}(T) = \Delta_{\text{LS}}(0) \tanh(\sqrt{2\Delta_{\text{LS}}/T_c - 1}) \).

Figure 13 shows theoretical calculations of the representative cases of \( K(T) \) of the \( s\)–pairing model in the clean limit. For demonstration purposes, we chose the hole band as the main band \( (N_h = 2N_e) \) and arbitrarily chose the gap-to-\( T_c \) ratio of \( 2\Delta_{\text{LS}}/T_c \); the other parameters are then automatically determined. The case (A) with \( 2\Delta_{\text{LS}}/T_c = 3.0 \) shows typical BCS behavior: a rapid drop below \( T_c \) and exponentially flat behavior at low temperatures, indicating the presence of a full gap due to an \( s\)–wave pairing. The case (B) with \( 2\Delta_{\text{LS}}/T_c = 1.0 \) shows a much slower reduction below \( T_c \) because of the smaller gap-to-\( T_c \) ratios, but it eventually shows exponentially flat behavior at very low temperatures indicating an \( s\)–wave full gap. In both cases, (1) the clear drop of \( K(T) \) immediately below \( T_c \) indicates a ‘singlet’ pairing superconductor and (2) the exponentially flat behavior at low temperatures \( (T \ll T_c) \) indicates an \( s\)–wave (full-gap) superconductor. However, as demonstrated in (A) and (B), the convexity (down or up) of
K(T) below T_c can be anything due to the two-band (or multi-band, in general) nature of superconductivity. These genuine behaviors of the ±s-wave superconductor and its variations with different FeSCs are confirmed well by experiments, as shown in figure 14.

However, these genuine clean limit behaviors should be modified with impurity scattering. As explained in section 3, the s²-wave state easily—almost intrinsically—creates in-gap states with non-magnetic impurities, which modifies the typical full-gap (‘U’-shape) DOS into the ‘V’-shaped DOS. As a result of the Knight shift, probing the low energy DOS N(ω), the ‘s’-wave pairing evidence of the exponentially flat behavior in K(T) at low temperatures should disappear with impurities. This will be discussed in the next section.

6.1.2. With impurities. In section 3, we explained that the impurity self-energies Σ_{imp}^{0,1}(ω) can form resonance states inside the SC gap (see figure 8(A)) in the s²-wave state with non-magnetic impurities. Once Σ_{imp}^{0,1}(ω) are calculated, we include these impurity self-energy corrections into the Knight shift formula equation (23) as ω → ω = ω + Σ_{imp}^{0}(ω) + Σ_{imp}^{1}(ω) and Δ_{h,e} + Δ_{h,e} = Δ_{h,e} + Σ_{imp}^{0}(ω) + Σ_{imp}^{1}(ω) (equations (13)–(16)). The results are basically the renormalization of the DOS N_{tot}(ω) as shown in figure 8(B), and the Knight shift K(T) will probe this renormalized DOS N_{tot}(ω).

Figure 15(A) shows the calculation results of K(T) for the same model as in figure 13(A), but now including impurity scattering. In the clean case (Γ = 0.0), K(T) shows the typical s-wave Knight shift behavior, i.e. it is exponentially flat at low temperatures. But with impurity scattering rate Γ = 0.045, the low temperature part of K(T) changes to T-linear behavior, just like a clean d-wave superconductor. This is because of the ‘V’-shaped DOS at the critical impurity concentration n_{imp}^{crit} (see figures 6(B) and 8(B)). With a higher impurity concentration, Γ = 0.08Δ_c, K(T) still continues to show T-linear behavior but now on top of a constant shift K_0. These behaviors are contrasted with the Knight shift K_{d-wave}(T) in the d-wave (or any line-nodal) superconductor.
shown in figure 15(B). There, $K_{d\text{-wave}}(T)$ in the clean $d$-wave case shows the $T$-linear behavior as expected. But with impurities (non-magnetic, unitary scatterer), the $K_{d\text{-wave}}(T)$ becomes flat at low temperatures similar to the clean $s$-wave superconductor. However, the important difference is the constant part $K_0$. Therefore, the interpretation of Knight shift data $K(T)$ to identify the gap symmetry should not be judged only by the temperature dependence; the determination of the constant part $K_0 = K(T \to 0)$ at low temperatures is essential before analyzing the temperature dependence.

Figure 16 shows the $^{31}$P Knight shift of BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ [100] which shows $T$-linear behavior at low temperatures. Judging from the temperature dependence of this Knight shift data itself, whether the SC state of the BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ compound is a clean nodal-gap superconductor or a dirty $s$-wave superconductor cannot be determined for certain. We need to cross-check with other experimental probes of the SC properties to determine the most consistent pairing state. Incidentally, the authors of [100] showed that the BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ compound has a substantial amount of residual DOS $N_{res}/N_0 = 0.34$ from the measurement of the $1/T_1$ spin-lattice relaxation rate. Having this much of the residual DOS in a nodal-gap (e.g. $d$-wave) superconductor, the low temperature part of the Knight shift $K(T)$ should be flat up to at least $1/3$ of $T_c$, as demonstrated in figure 15(B). Therefore, judging from the combined data of the Knight shift and $1/T_1$ spin-lattice relaxation rate, the more consistent SC-gap state of BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ should be a dirty $s$-wave state, rather than a clean nodal-gap (or $d$-wave) state. However, in order to really pin down the correct pairing gap, it is always better to analyze more data on the SC properties from various other probes, such as penetration depth $\lambda(T)$, thermal conductivity $\kappa(T, H)$, etc. At the moment, the correct SC gap of BaFe$_2$(As$_{1-x}$P$_x$)$_2$ is still under debate.

6.1.3. Summary. Knight shift $K(T)$ measures the thermal average of the DOS $N(\omega)$ from normal to SC states, therefore its variation with temperature, in particular at low temperatures, is an excellent probe for the SC-gap structure. In the clean limit, it is straightforward to distinguish an $s$-wave full-gap (exponentially flat in $T$) and a nodal-gap (linear in $T$) superconductor. However, with a tiny amount of impurities in the cases of the $s$-wave state and $d$-wave (or any nodal-gap) state, their typical temperature dependencies of $K(T)$ are exchanged with each other: the $s$-wave gap superconductor is linear in $T$ and the nodal-gap superconductor is exponentially flat in $T$. Therefore, it is important to first determine whether the sample is in the clean limit or in dirty limit before analyzing the temperature dependence of $\delta K(T)$. Here this definition of the dirty limit is not the same as the standard definition, suchas $\lambda_{\text{imp}} \approx \xi_{\text{coh}}$ or $\Gamma_{\text{imp}} \approx (T_c, \Delta_0)$. In fact, figure 15 shows that an impurity scattering rate as tiny as $\Gamma_{\text{imp}}/\Delta_0 \approx 0.05$ is sufficient to see this dramatic change of the impurity effect on $K(T)$. Most of the Knight shift $K(T)$ experimental data on FeSCs to date appear consistent with the $s$-wave SC state.

6.2. Spin-lattice relaxation rate: $1/T_1$

6.2.1. Clean limit. The $T_1$ relaxation time is the longitudinal relaxation time of the nuclear spin returning back to the
equilibrium direction after being flipped to a 90 degree rotated direction by a pulsed field. The relaxation process needs an angular momentum and energy dissipation to the surrounding environment of the nucleus. The main source of the dissipation in metal is conduction electrons in contact with each nucleus through a hyperfine coupling, therefore it is a local probe (interaction) and can detect the change of the DOS of the conduction bands from above to below $T_c$. Theoretically it is written as

$$\frac{1}{T_1} \sim \lim_{\omega_0 \to 0} \sum_q A_{0s}^2(q) \frac{\text{Im} \chi_S(q, \omega_0)}{\omega_0}$$

where $\omega_0$ is the NMR resonance frequency and can be taken to be zero since its energy scale is much smaller than the SC-gap energy as $\hbar \omega_0 \ll \Delta_{s, c}$. In this context, it was a challenging task to explain the $s^\pm$-wave SC state. How much it is suppressed depends on the material-specific parameters of $N_{b,c}$ and $A_{0s}(q)$ is a hyperfine coupling between the nuclear moment and the surrounding conduction electrons.

A key difference from the Knight shift is that while the Knight shift measures the real part of uniform spin susceptibility $\text{Re} \chi_S(q = 0, \omega)$, the $1/T_1$ spin-lattice relaxation rate is a local probe, hence the momenta $k$ and $k'$ of each band are independently summed. This momentum integration over the whole BZ leads to several important results. First, it allows the inter-band scattering process as $...N_0(0)N_0(0)\{\Delta_{s,c}\}_k\{\Delta_{s,c}\}_{k'}$ as in the above equation (25), which leads to a destructive coherence factor for $1/T_1$ in the $s^\pm$-pairing state. In an ordinary $s$-wave superconductor, $1/T_1$ has the constructive coherence factor, $\sim(1 + \Delta_{s,c})$, which produces a coherence peak (also called Hebel–Slichter peak) in $1/T_1(T)$ just below $T_c$, because $\Delta_{s,c}^2(T)$ rapidly grows below $T_c$. But, the $1/T_1(T)$ expression in equation (25) has mixed coherence terms such as $(1 + \Delta_{s,c}(1 + \Delta_{s,c})), (1 + \Delta_{s,c}(1 + \Delta_{s,c}))$, etc, where the first term $(1 + \Delta_{s,c}(1 + \Delta_{s,c}))$ is a usual constructive (hence inducing a peak structure) coherence factor, but the second term $(1 + \Delta_{s,c}(1 + \Delta_{s,c}))$ becomes a destructive coherence factor because of the opposite signs of $\Delta_{s,c}$ and $\Delta_{s,c}$ (hence inducing a dip structure instead of a peak). As a result, we can expect that the Hebel–Slichter peak of the ordinary $s$-wave superconductors will be largely suppressed in the $s^\pm$-wave SC state. How much it is suppressed depends on the material-specific parameters of $N_{b,c}$ and $\Delta_{s,c}(T)$. Numerical calculations found that this Hebel–Slichter peak in the $s^\pm$-pairing state is almost but not completely suppressed in the clean limit; however, only a small amount of impurities is sufficient to completely erase this peak.

Figure 17 shows representative theoretical calculations of $1/T_1$ in the clean limit of the $s^\pm$-pairing state with $2\Delta_{s,c}/T_c = 3.0$. It displays the separate contributions of each term in the two-band model: two intra-band terms (the hole and electron bands), and one inter-band term. Two intra-band contributions (red squares and blue inverted triangles) to $1/T_1$ show the typical Hebel–Slichter peaks, respectively (their jump sizes are comparable to their normal state $1/T_1(T_c)$ at $T_c$). However, the inter-band contribution (green triangles) shows a dip instead of a peak. As a result, the total $1/T_1$ shows a much reduced Hebel–Slichter peak, but still with a visible magnitude. Compared to this theoretical prediction of $1/T_1$ in the clean limit of the $s^\pm$-pairing state, in the early days, several NMR $1/T_1$ experiments with FeSC compounds, in particular, the LaOFeAs (so-called 1111) compound [101–105], have reported common peculiar features: (1) no Hebel–Slichter peak and (2) $1/T_1 \sim T^2$ over all measured temperatures below $T_c$. These features were surprising and it was immediately taken as strong evidence for a nodal-gap state, such as a $d$-wave state, in FeSC materials. However, this $d$-wave or nodal-gap superconductor claim was in contradiction with other experiments (e.g. ARPES experiments [56]) which indicated an isotropic $s$-wave gap. In this context, it was a challenging task to explain the $1/T_1$ experiments with the $s^\pm$-wave model. The results of figure 17 demonstrate that the $s^\pm$-wave SC state in the clean limit is not quite consistent with these...
In particular, there is no intrinsic mechanism to explain the $T^3$ dependence with the $\pm s$-wave SC state having no nodes. In an effort to improve the reduction of the Hebel–Slichter peak as well as the power law, adding impurity damping by hand was attempted [37].

Figure 18(A) replots the same calculations for the total $1/T_1$ in figure 17, but with an artificial constant damping introduced into equation (25) by $\Gamma = \omega + i \Gamma_t$. It shows that a tiny amount of damping, $\Gamma = 0.05 \Delta_0$ (blue squares), completely erases the Hebel–Slichter peak of the clean limit result (black solid squares). In figure 18(B), the same data as in figure 18(A) are plotted in a log–log plot to examine the overall power-law behavior of $1/T_1(T)$ below $T_c$. It shows that the $s^\pm$-wave state with constant damping is only partially successful in fitting the early $1/T_1$ experiments: there is no Hebel–Slichter peak and only an approximate power law of $1/T_1 \sim T^3$. However, as shown in figure 19, almost all the early $1/T_1(T)$ data on FeSC compounds [101–105] were not just approximately but almost perfectly $T^3$ down to the lowest measured temperatures while the results in figure 18(B) for the $\pm s$-wave gap model are far from this $T^3$ behavior. To resolve this discrepancy between the experimental $1/T_1,_{\exp}(T)$ and the $s^\pm$-wave gap model, we need to study the impurity effect more closely [35, 53, 106].

### 6.2.2. With impurities.

In order to include the impurity scattering effect in the spin lattice relaxation rate $1/T_1$, we use the same formula of $1/T_1$ of equation (25) but with renormalizing $\omega$ and $\Delta_{h,c}$ by impurity self-energies as $\tilde{\omega}$ and $\tilde{\Delta}_{h,c}$, which are calculated with equations (13)–(16), respectively, using $T$-matrix theory. We considered only non-magnetic impurities. The main
effects of impurity scattering in the $s^{\pm}$-wave SC state is to create the in-gap states inside the gap energy as shown in figures 6 and 8, which directly affects $1/T_1(T)$ according to equation (25). Figure 20 shows the calculation results for $1/T_1(T)$ with unitary impurities of concentrations, $\Gamma/\Delta_c = 0.0, 0.01, 0.04, 0.08$, with $2\Delta_0/T_c = 3.0$ (with $\Delta_c/\Delta_0 = N_0/N_c = 2.5$ hence $2\Delta_c/T_c = 7.5$). Experimental data are from [103]. The curves are offset for clarity. Left: the corresponding evolution of the DOS $N(\omega)$ with the corresponding impurity concentrations. Reprinted figure with permission from [53], Copyright (2009) by the American Physical Society.

$\Delta_c = \Delta_0 \approx 0.04$ with $2\Delta_0/T_c = 3.0$ (with $\Delta_c/\Delta_0 = N_0/N_c = 2.5$ hence $2\Delta_c/T_c = 7.5$). Experimental data are from [103]. The curves are offset for clarity. Left: the corresponding evolution of the DOS $N(\omega)$ with the corresponding impurity concentrations. Reprinted figure with permission from [53], Copyright (2009) by the American Physical Society.

Figure 20. Right: theoretical calculations of $1/T_1(T)$ for the $s^{\pm}$-wave SC state, with different impurity concentrations, $\Gamma/\Delta_c = 0.0, 0.01, 0.04, 0.08$, with $2\Delta_0/T_c = 3.0$ (with $\Delta_c/\Delta_0 = N_0/N_c = 2.5$ hence $2\Delta_c/T_c = 7.5$). Experimental data are from [103]. The curves are offset for clarity. Left: the corresponding evolution of the DOS $N(\omega)$ with the corresponding impurity concentrations. Reprinted figure with permission from [53], Copyright (2009) by the American Physical Society.
proportional to \((1/\Delta_c)(c^2 + 1)\) (c = 0, for unitary impurity) [53], is less than a 10% reduction of \(T^0_c\) at most.

6.2.3. \(T^5-6\)-power in \(1/T_1(T)\). After the \(T^3\)-behavior in \(1/T_1\) was explained with the impurity states in the \(s^\pm\)-wave state, several NMR experiments reported that the power law of \(1/T_1(T)\) is not always \(\sim T^3\), but can be much steeper as \(\sim T^{5-6}\) [100, 107–110] (see figure 21), and sometimes shows a step-like structure (right-hand panel in figure 21) between \(T_c\) and \(T = 0\). Also, some authors claimed that this is evidence that the \(s^\pm\)-wave state is not the right pairing symmetry for FeSCs. However, notice that this steeper power law \(T^{5-6}\) of \(1/T_1\) observed in some of FeSC compounds (e.g. La-1111 [107, 108, 110], (BaK)Fe2As2 [109], and BaFe2(As0.67P0.33)2 [100]) always occurs near \(T_c\). As we explained above, this near-\(T_c\) property has nothing to do with a pairing-gap symmetry nor with the low energy DOS, but only reflects the gap-to-\(T_c\) ratio \(R\), which is a strong coupling effect in general. Even in a clean \(d\)-wave superconductor, the genuine \(T^3\) power law of \(1/T_1\) is obeyed only at low temperatures for \(T < T_c/3\), where the DOS \(N(\omega) \sim \omega\) governs the thermodynamic properties, and the temperature slope of \(1/T_1\) near \(T_c\) can be made arbitrarily as steep as \(\sim T^{5-6}\) by choosing a larger value of \(R = 2\Delta_0/T_c = 8\), for example see [111]. Of course, then whether the value \(R = 8\) is physically plausible or not is another question; compared to the BCS value \(R = 3.5\), the value \(R = 8\) implies that this superconductor is a strong coupling superconductor and this value is quite possible with many strongly correlated SC materials.

Similarly, the slope of \(1/T_1(T)\) near \(T_c\) of the \(s^\pm\)-wave state can be arbitrarily made steeper by choosing a larger value of \(R_{h,c} = 2\Delta_h,c(T = 0)/T_c\). For illustration, we repeated the same calculations but with a larger \(R\) value as \(2\Delta_0/T_c = 5.0\) (hence, \(2\Delta_c/T_c = 12.5\)). The results, plotted in figure 22, show the same behaviors as in figure 20 at low temperatures for \(T < T_c/3\), but steeper power laws (\(\sim T^5\)) near \(T_c\). For example, the result with the critical impurity concentration \(n_{c,imp} = (1/\Delta_c = 0.04, \text{red triangles})\) shows \(\sim T^5\) behavior near \(T_c\), but with decreasing temperature it evolves, after a short crossover, to perfect \(T^3\) behavior. With a higher impurity concentration \(\Gamma/\Delta_c = 0.08, 1/T_1\) near \(T_c\) again shows \(\sim T^3\) behavior, but it quickly goes though a smooth crossover region and eventually becomes \(T\)-linear at low temperatures because of the finite DOS \(N_0\). The most interesting behavior is for \(\Gamma/\Delta_c = 0.02\). In this case, \(1/T_1(T)\) shows \(\sim T^3\) over the entire temperature range of calculation and even shows a step-like structure at \(\sim 0.2T_c\). These features are quite similar to the data for Ba0.72K0.28Fe2As2 shown in figure 21 (right-hand panel). Perhaps, the choice of the gap-to-\(T_c\) ratio of \(2\Delta_0/T_c = 5.0(2\Delta_c/T_c = 12.5)\) used in the calculations in figure 22 might be too large for real FeSC compounds. But this was chosen to demonstrate that the slope...
near $T_c$ can be arbitrarily controlled by choosing only a different $R$ value, otherwise with the exactly same model as in figure 20. For real FeSC compounds, if we choose a different ratio $\Delta_s/\Delta_{\alpha} = N_0/N_\alpha$ (choosing a larger value, for example, $\Delta_s/\Delta_{\alpha} = 4$), the $T^{5.6}$ behavior near $T_c$ can be easily obtained with a much smaller value of $2\Delta_s/T_c \approx 6$.–8. Later, more NMR experiments were performed and some data even detected the presence of a small Hebel–Slichter peak as well as a very rapid drop in $1/T_1(T)$ [112], signatures of an $s$-wave superconductor. These behaviors are in fact quite similar to the plots of the $\Gamma \approx 0$ cases in figures 20 and 22. They also found a second bend in $1/T_1(T)$ at lower temperatures between $T_c$ and $T = 0$, indicating the presence of multiple gaps with very different sizes $|\Delta_s|$ and $|\Delta_{\alpha}|$.

### 6.3. Summary

The intrinsic behavior of $1/T_1(T)$ of the $s^\pm$-wave model should be like an $s$-wave superconductor but with a strongly suppressed Hebel–Slichter peak, because of the sign-changing OPs $\Delta_s$ and $\Delta_{\alpha}$. The frequently observed $T^5$ power-law behavior in $1/T_1(T)$ for many FeSC compounds [100–105] can be naturally understood with the $s^\pm$-wave model if the resonant impurity scattering effect is included, which renormalizes the 'U'-shaped DOS into a 'V'-shaped DOS as $N(\omega) \sim \omega$ at low frequencies. Later, researchers found steeper power $T^{5.6}$ behavior near $T_c$ in $1/T_1(T)$ for some FeSC compounds [100, 107–110]. This is not an intrinsic property related to the pairing symmetry or the gap function, but a property controlled by the gap-to-$T_c$ ratio, $R$, so this behavior can be fitted with a larger value of $R$ within the $s^\pm$-wave state model. Therefore, we can say that all experimental data for the NMR Knight shift $K(T)$ and $1/T_1(T)$ in FeSCs are consistently explained within the $s^\pm$-wave model with impurity scattering included. All early puzzles and challenges posed by NMR experiments have actually turned into strong evidence to support the correctness of the $s^\pm$-pairing state for FeSCs. It is important to notice that the unequal size of the gaps $\Delta_{s,\alpha}$—hence the unequal sizes of the DOSes $N_{s,\alpha}$—is a genuine property of the $s^\pm$-pairing state and it is a crucial factor to understand and fit the experimental data. This unequal size of gaps in the $s^\pm$-pairing state will repeatedly play a crucial role in understanding other SC properties of FeSCs.

### 7. Specific heat: temperature dependence of $C_{\text{eff}}(T)$ near $T = 0$

The SH can be arbitrarily controlled by choosing only a different $R$ value, otherwise with the exactly same model as in figure 20. For real FeSC compounds, if we choose a different ratio $\Delta_s/\Delta_{\alpha} = N_0/N_\alpha$ (choosing a larger value, for example, $\Delta_s/\Delta_{\alpha} = 4$), the $T^{5.6}$ behavior near $T_c$ can be easily obtained with a much smaller value of $2\Delta_s/T_c \approx 6$.–8. Later, more NMR experiments were performed and some data even detected the presence of a small Hebel–Slichter peak as well as a very rapid drop in $1/T_1(T)$ [112], signatures of an $s$-wave superconductor. These behaviors are in fact quite similar to the plots of the $\Gamma \approx 0$ cases in figures 20 and 22. They also found a second bend in $1/T_1(T)$ at lower temperatures between $T_c$ and $T = 0$, indicating the presence of multiple gaps with very different sizes $|\Delta_s|$ and $|\Delta_{\alpha}|$.

### 7.1. The clean limit and its evolution with impurities

The formula for the SH coefficient (also called the Sommerfeld coefficient) $C/T = \gamma(T)$ is written as follows:

$$
\frac{C(T)}{T} = \gamma(T) = -\int_0^\infty \, d\omega \frac{\partial f_{\text{FD}}(\omega)}{\partial \omega} \left( \frac{\omega}{T} \right)^2 [N_0(\omega, T) + N_\alpha(\omega, T)] \\
- \int_0^\infty \, d\omega S(\omega/T) \frac{d}{dT} [N_0(\omega, T) + N_\alpha(\omega, T)],
$$

(26)

where $S(\omega/T) = [(1 - f_{\text{FD}}(\omega)) \ln(1 - f_{\text{FD}}(\omega)) + f_{\text{FD}}(\omega) \ln f_{\text{FD}}(\omega)]$ is the Fermionic entropy of excitation energy $\omega$. We see that $\gamma(T)$ consists of two parts: (1) the first term dominates at low temperatures near $T = 0$, and (2) the second term dominates near $T_c$. In particular, the DOS $N_\alpha(\omega, \Delta_s(T))$ near $T_c$ in the second term is rapidly changing with temperature, causing the SH jump $\Delta C/T$. In order to identify the pairing-gap symmetry, the low temperature behavior of $C(T)/T$ is more useful (see the discussion below) and the SH jump $\Delta C$ is not as relevant.

As to the low temperature behavior of $C(T)$, the first term in the above formula of $\gamma(T)$ is almost identical to the formula of Knight shift $K(T)$ (equation (23)), apart from the difference of the weighting factor $\left( \frac{\omega}{T} \right)^2$. Therefore we expect $\gamma(T)$ to behave similarly to the results of $K(T)$ in, for example, figure 15. In fact, by a simple dimensional counting of the first term in equation (26), we can read $\gamma(T) \sim T^5$ if $N_\alpha(\omega) \sim \omega^5$. Hence we can read the shape of the low energy DOS $N_\alpha(\omega)$ from $\gamma(T)$. In figure 23, we show the theoretical calculations of the normalized SH coefficients $\gamma(T) = \gamma(\omega)$ of the $s^\pm$-wave and $d$-wave cases with varying impurity scattering rates for comparison. The clean limit (black squares, $\Gamma_{\text{imp}}/\Delta = 0$, shows the representative behaviors of each SC-gap structure at low temperatures: exponentially flat behavior for the $s^\pm$-wave and $T$-linear behavior for the $d$-wave case. However, with impurity scattering (we considered only non-magnetic impurities in the unitary limit), the temperature dependences of $\gamma(T)$ for both SC cases become non-trivial. For example, the $\gamma(T)$ of the $s^\pm$-pairing state for $\Gamma_{\text{imp}} > \Gamma_{\text{imp}}^* (\Gamma_{\text{imp}} \approx 0.045\Delta_c$ in this particular example case) shows $T$-linear behavior—this is a common identifier for a nodal gap. On the other hand, the $\gamma(T)$ of the $d$-wave pairing state with impurities shows a flat $T$-dependence—this is a common identifier for a $s$-wave full-gap superconductor.
These results demonstrate that the typical temperature dependencies of \( \gamma(T)/\gamma_0 \) of the two representative SC states—nodal and nodeless—can be reversed with impurity scattering: the \( \pm_s \)-wave state shows \( T \)-linear behavior and the \( d \)-wave state shows flat-in-\( T \) behavior at low temperatures. This reversing behavior with impurity happens in the exactly same manner as for the Knight shift \( K(T) \), as explained in section 5.1. Therefore, when the low temperature SH data \( \gamma(T)/\gamma_0 \) are analyzed to identify the gap symmetry, it is important first to determine whether the SC samples are in the clean limit or not, and estimate how large the \( \gamma_0 = \gamma(T = 0) \) value is, since it should be remembered that the subtracted data \( \gamma(T) - \gamma(0) \sim T^3 \) do not follow the textbook behavior of the clean \( s^\pm \)- and \( d \)-wave states. The origin of this extreme sensitivity to the impurity scattering of two SC states is the sign-changing property of the OPs in both cases.

In figure 24, the overall temperature behavior of \( \gamma(T)/\gamma_0 \) of the \( s^\pm \)-wave state are calculated. As in the Knight shift \( K(T) \) in section 5.1, the overall concavity of \( \gamma(T) \) near \( T_c \) is determined by the gap-to-\( T_c \) ratio \( R \): the larger \( R \) is, the more the shape of \( \gamma(T) \) is concave up, and the smaller \( R \) is, the more the shape of \( \gamma(T) \) is concave down. Figure 24 shows two example cases: (A) \( R = 2 \Delta_s/T_c = 3.5 \), and (B) \( R = 7.5 \). Otherwise all other parameters are the same for both cases as \( |\Delta_s|/|\Delta_d| = N_0/N_s = 2.5 \), and the same impurity scattering rate \( \Gamma_{imp}/\Delta_s = 0.1 \). It can be seen that the small-gap band (hole band (red circles) in the model calculations) is the one which is most modified by impurities leading to \( T \)-linear behavior. This is also reflected in the \( V \)-shaped DOS \( N_0(\omega) \) in the inset of figure 24(B). The large-gap band (electron band, blue triangles) appears to maintain full-gap-like behavior by showing a flat temperature dependence in the low temperature region, but this is not exactly true because it has a finite value of constant \( \gamma_0 \) at low temperatures. An interesting issue of the SH jump \( \Delta C \) versus \( T_c \) and the total condensation energy (CE), which can be extracted from the SH data as well, will be discussed in section 11.

7.2. Summary

The low temperature SH, \( C(T)/T \sim \gamma(T) \), is an excellent probe for the low energy DOS \( N(\omega) \), such that the clean \( s^\pm \)-state should display exponentially flat behavior as \( \gamma(T) \sim e^{-\Delta_s/T} \).
However, with impurities, the low energy part of the DOS $N(\omega)$ of the $s^{\pm}$-state changes drastically as shown in section 3. Increasing the concentration, the fully opened ‘$U$’-shaped DOS in the clean limit evolves to a ‘$V$’-shaped DOS as in the clean $d$-wave state, and then a ‘constant’ + ‘$V$’-shaped DOS (see figure 6). Accordingly, the measured $T$-linear $\gamma(T)$ is not necessarily evidence for a nodal gap, it could instead be a $s^{\pm}$-state with impurities. The important lesson of this section is that when the low temperature $\gamma_{\text{expl}}(T)$ is analyzed, it is primarily important to obtain a reliable estimation of the residual Sommerfeld coefficient $\gamma_0 = \gamma_{\text{expl}}(T = 0)$. Without knowing the value of $\gamma_0$ just analyzing the temperature dependence of $\gamma_{\text{expl}}(T)$ is completely misleading. Most of the SH experiments with FeSCs to date appear to be consistent with the $s^{\pm}$-state, if the $\gamma_0$ value is properly taken into account.

8. The Volovik effect: specific heat $C(H)$ and thermal conductivity $\kappa(H)$

In the previous section, we discussed that the temperature dependence of the SH $C_{\text{el}}(T)$ is a powerful probe for identifying the gap symmetry, if the non-electronic part contributions—such as from phonons, spin fluctuations, etc—are reliably subtracted. The same is true for the thermal conductivity $\kappa(T)$, which is another valuable probe for entropy change (low energy thermal excitations) of the system. Therefore, for these experimental probes, how to extract only the electronic part is always an issue. One simple way to achieve this is to go to the lowest possible temperature $T \to 0$. At very low temperatures far below $T_c$, the system is deep inside the SC phase and automatically $C(T)$ and $\kappa(T)$ contain only electronic contributions without any subtractions.

Then applying an uniform magnetic field $H$, the system enters the vortex state (also called the mixed state) with a lattice of vortices. Most unconventional superconductors are extreme type II, hence the Meissner phase exists only at a very low field limit, so we can ignore this region. Therefore, measuring $C(H, T \to 0)$ and $\kappa(H, T \to 0)$ while changing the field strength $H(< H_\text{c2})$ can tell us how the low energy DOS $N(\omega, H)$ changes in the vortex state with magnetic fields $H$. The functional dependence of $N(\omega, H)$ in a vortex state depends sensitively on the SC-gap structures, and hence reveals information about the gap symmetry. Typical structures of the DOS $N(\omega)$ are shown in figure 3 for the representative pairing states. Now, we need to study how these DOSs $N(\omega)$ change with magnetic field $H$ in the vortex state to $N(\omega, H)$, which is called the ‘Doppler effect’ or ‘Volovik effect’.

8.1. The Volovik effect in the $d$-wave state

The field-dependent DOS $N(\omega, H)$ was first studied for $d$-wave cuprate superconductors by Volovik [114] and was soon was taken up by many researchers to investigate the SH and thermal conductivity of cuprate superconductors [115, 116]. In a uniform (without fields) SC phase, Cooper pairs are formed by a pair of $(k \uparrow, -k \downarrow)$ states, and their energies in normal states are degenerate as $\epsilon(k) = \epsilon(-k)$. When the SC condensation occurs as $\Delta(k) = -\sum_{q \neq 0} V_k q^* (c_{k q}^\dagger c_{-k q})$, the quasiparticles in the SC phase are defined by the eigenenergies of the following BCS Hamiltonian matrix:

$$H(k) = \begin{pmatrix} \epsilon(k) & \Delta(k) \\ \Delta(k) & -\epsilon(-k) \end{pmatrix}$$  \hspace{1cm} (27)

whose energies are $\pm E(k) = \pm \sqrt{\epsilon^2(k) + \Delta^2(k)}$. In the vortex state with magnetic field $H$, the system is not uniform but has an array of vortices, and each vortex is carrying a circulating supercurrent $j_V(r) = \rho(\bar{\omega})$. Now imagine a Cooper pair of $(k \uparrow, -k \downarrow)$ at position ‘$r$’, the distance from the vortex core. Their normal state energies are no longer degenerate as $\epsilon(k) = \epsilon(-k)$, but are shifted in the opposite direction by riding on the supercurrent $\bar{\omega}(r)$ as $\epsilon(k) = \epsilon(-k) = \epsilon(-k) + \bar{\omega}(r) \cdot \bar{k}$. Since we are interested in the region near the Fermi level, in the limit $k_F \gg \rho(\bar{\omega})$, the normal state energies of the $(k \uparrow, -k \downarrow)$ pair become $[\epsilon(k) + \bar{\omega}(r) \cdot \bar{k}] = \epsilon(k) - \bar{\omega}(r) \cdot \bar{k}$. This is nothing but a Doppler effect and the quasiparticles in this vortex state are defined by the eigenenergies of the following modified BCS Hamiltonian matrix:

$$H_{\text{mixed}}(k, r) = \begin{pmatrix} \epsilon(k) + \bar{\omega}(r) \cdot \bar{k} & \Delta(k) \\ \Delta(k) & -\epsilon(-k) + \bar{\omega}(r) \cdot \bar{k} \end{pmatrix}$$  \hspace{1cm} (28)

The eigenenergies of $H_{\text{mixed}}(k, r)$ are $E_{\pm}(k) = -\bar{\omega}(r) \cdot \bar{k} \pm \sqrt{\epsilon^2(k) + \Delta^2(k)}$, which are not symmetric around the Fermi level but are shifted to one side. Most importantly, $E_{\pm}(k)$ are not always gapped but can hit the zero energy excitation. This is the result of pair-breaking due to the mismatch of energies, $\epsilon(k) \neq \epsilon(-k)$, of the $(k \uparrow, -k \downarrow)$ pair in the normal state. The single particle Green’s function of $H_{\text{mixed}}(k, r)$ can be written as

$$G(k, r, \omega) = \frac{[\omega + \bar{\omega}(r) \cdot \bar{k}] \tau_0 + \epsilon(k) \tau_3 + \Delta(k) \tau_1}{[\omega + \bar{\omega}(r) \cdot \bar{k}]^2 - \epsilon^2(k) - \Delta^2(k)}$$  \hspace{1cm} (29)

where $\tau_i$ are Pauli matrices. From the above Green’s function we obtain the local DOS $N(\omega, H, r) = -\frac{1}{\pi} \text{Tr} \ln \sum_{\sigma} G(k, r, \omega)$. The Doppler shifting energy is given as $\bar{\omega}(r) \cdot \bar{k} = \frac{\hbar}{m} r \cos \theta = \frac{\hbar}{2m} \cos \theta$ with normalized distance $r = \rho R$ ($\xi$ is coherence length and ‘$\theta$’ a constant of order unity). Notice that the local DOS $N(\omega, H, r)$ is a function of the distance ‘$r$’ from the vortex core as illustrated in figure 25.

The above discussion is for a single vortex. With increasing field $H$, the number of vortices is increasing as $\sim H$, or conversely the size of each vortex is decreasing as $\sim 1/H$. The typical size of the radius of a single vortex is called magnetic length $R_0 = \alpha \sqrt{\frac{\hbar}{2 \pi m}}$ (for a flux quantum, $H$ is the magnetic field, and ‘$\alpha$’ is a geometric factor of order unity) and the above Green’s function is defined only for $1 < \rho < R_0 / \xi$. When $\rho < 1$, the Doppler shifting energy $\Delta_{\text{Doppler}}$ becomes larger than the maximum gap size $\Delta_0$, therefore the SC gap should collapse for $\rho < 1$, which defines the vortex core. The thermodynamic
averaged DOS is obtained by the magnetic unit-cell averaged DOS as follows.

\[ \bar{N}(\omega, H) = \frac{\langle N(\omega, H, r) \rangle_{\text{cell}}}{\int_0^{R_H} \omega \, d^2 \vec{r} N(\omega, H, r) / \pi R_H^2}. \]  

(30)

Noticing that \( N(\omega, H, r) \sim 1/r \) from figure 25 for the \( d \)-wave superconductor, a simple dimensional counting of the above integral tells us that \( \bar{N}(\omega, H) \sim 1/R_H \sim \sqrt{H} \), which is the famous Volovik result for the \( d \)-wave superconductor [114].

All the discussions here about the Doppler shift effect in the vortex state (or Volovik effect) is a semiclassical description and a phenomenological form of the field-dependent gap size \( \Delta_0(T) = \Delta_0 \sqrt{1 - \frac{H}{H_c}} \) is used. This approximation is excellent for the weak field \( H < H_c \), but would certainly break down when \( H \rightarrow H_c \), where the quantum effect becomes more important. Nevertheless, we found empirically that this semiclassical approximation works well up to \( H \approx 0.9H_c \). For a full quantum theory—which presumably should work up to \( H_c \)—we refer the reader to [116–119].

Once \( \bar{N}(\omega, H) \) is calculated, a thermodynamic quantity such as \( C(T, H) \) can be calculated as

\[ C(T, H) = \int_0^{\infty} d\omega \left( \frac{\omega}{T} \right)^2 \bar{N}(\omega, H) \cosh^2 \left( \frac{\omega}{2T} \right). \]  

(31)

Similarly, thermal conductivity is calculated with [120]

\[ \kappa_d(T, H, r) \propto N^0 \gamma^2 \int_0^{\infty} d\omega \left( \frac{\omega}{T} \right)^2 \frac{\bar{N}(\omega, T, H, r)}{\cosh^2 \left( \frac{\omega}{2T} \right)}. \]  

(32)

\[ K_d(\omega, T, H, r) = \left\{ \frac{1}{\text{Im} \sqrt{\xi^2 - \Delta^2(k)}} \times \left[ 1 + \frac{|\xi|^2 - |\Delta(k)|^2}{|\xi|^2 - \Delta^2(k)} \right] \right\}^2. \]  

(33)

Figure 25. Illustration of the local DOS \( N(\omega, H, r) \) of the \( d \)-wave superconductor. The size of the Doppler shift energy is inversely proportional to the distance \( r \) from the core as \( \Delta \frac{\Delta_0}{\rho} \), and the DOS \( N(\omega = 0, H, r) \) at zero energy is increasing proportional to \( \Delta \). \( d \)-wave DOS \( N(\omega = 0, H, r) \) at zero energy is increasing proportional to \( \Delta \).

where \( \xi = \vec{v}(\vec{r}) \cdot \vec{k} \) and \( \langle \ldots \rangle \) means the FS average. And then longitudinal and transversal thermal conductivities are calculated as

\[ \kappa_0(T, H) = \int_{\text{cell}} \frac{d^2 r \kappa_0(\omega, T, H, r) / \pi R_H^2}{\text{cell}}. \]  

(34)

\[ \kappa_1^{-1}(T, H) = \int_{\text{cell}} \frac{d^2 r \kappa_1^{-1}(\omega, T, H, r) / \pi R_H^2}{\text{cell}}. \]  

(35)

respectively.

Figure 26 shows the numerical calculations of the transverse thermal conductivity \( \kappa_1(H) / T \) versus the normalized fields...
Hi/H_{c2} of the d-wave SC state for different impurity scattering rates $\Gamma/\Delta_0 = 0.01, 0.02, 0.05, 0.1, 0.2$, and 0.4. It indeed confirms the universal value (a constant value independent of the impurity scattering rate $\Gamma$) of $\kappa(H \to 0)/T \approx \sqrt{H}$. Figure 27 shows the results of the SH coefficient $C(H)/T = \gamma(H)$ versus $H/H_{c2}$ of the same model as in figure 26. It also shows the $\sqrt{H}$-dependence. However, the values $C(H \to 0)/T$ are not universal but increase with the scattering rate $\Gamma$ as $\gamma(H \to 0) \sim \sqrt{\Delta_0 \Gamma}$.

All these so-called Volovik effects have been well studied and confirmed with the high-$T_c$ cuprates as well as several heavy fermion superconductors [115, 116, 121]. The origin of this phenomenon is due to the thermodynamically averaged DOS $\tilde{N}(H) \sim \sqrt{H}$ in the vortex state of nodal-gap superconductors. On the other hand, simple reasoning on the Doppler effect on an $s$-wave superconductor trivially tells us that $\tilde{N}(H < H_{c2}) \approx 0$, hence measurements of $\gamma(H)$ and $\kappa(H)/T$ with $s$-wave superconductors should yield exponentially flat or activated behavior with a field as $\sim e^{-\Delta_0/H}$ at low fields. As a result, it became standard practice to take the observation of the $\sqrt{H}$-dependence in $\gamma(H)$ and $\kappa(H)/T$ as an evidence for a nodal-gap superconductor. Therefore the frequent observation of strong field dependences (in fact, approximately close to $\sim \sqrt{H}$) of $\gamma(H)$ and $\kappa(H)/T$ in many FeSCs has been taken as evidence that these FeSCs are nodal superconductors, and cast a doubt on the $\pm s$-wave pairing scenario. However, it was soon proven that a multiple band $s$-wave superconductor with different gap sizes $\Delta_1$ and $\Delta_2$ can also yield a strong field dependence on $\tilde{N}(H)$ in the vortex states as $\tilde{N}(H) \sim H$, but not as $\sim \sqrt{H}$ [122, 123].

8.2. The Volovik effect in the $s^\pm$-wave state

At the semiclassical level, which we found works well in the $d$-wave case, it is easy to understand the field dependence (Volovik effect) in the $s^\pm$-wave state. Figure 28 illustrates that Doppler shifting occurs even in a single-band $s$-wave superconductor as strongly as in a $d$-wave superconductor, but its consequences for low energy responses is null because the uniform gap $\Delta_0$ is always larger than the Doppler shifting energy $\Delta_{Doppler}$ everywhere outside the vortex core region; in other words, the region where $\Delta_{Doppler} > \Delta_0$ is by definition the vortex core where the superconductivity breaks down.

Now the question is what happens with a two-gap $s$-wave superconductor as in the $s^\pm$-wave state? If two $s$-wave OPs $\Delta_1$ and $\Delta_2$ (a larger and a smaller gap) are independent, everything is the same as for a single-band $s$-wave superconductor. But if two SC OPs are coupled by an inter-band pairing interaction $V_{inter}$, as in the $s^\pm$-wave state, there exist a finite region $(r < r^*)$, with $r^* = b\xi_{\Delta_2}/\Delta_1$, $\xi$ is coherence length, $b$ is a constant of $O(1)$ outside the vortex core, where $\Delta_{Doppler} > \Delta_2$ but $\Delta_{Doppler} < \Delta_1$, as depicted in figure 29.

In this region $(r < r^*)$, the quasiparticle excitations $N'_S(\omega, H, r)$ of the smaller-gap band allows the zero energy excitations with $\Delta_2$ to remain uncollapsed, because the SC OP $\Delta_2$ is sustained by the larger gap $\Delta_1$, through the inter-band pairing $V_{inter}$, which still survives because $\Delta_{Doppler} < \Delta_1$ in this region. The local DOS of the larger-gap band, $N_L(\omega, H, r)$, behaves the same as the single-band $s$-wave case in figure 28. With this observation, the magnetic unit-cell averaged DOS $\tilde{N}_L(\omega, H) = \langle N_s(\omega, H, r) \rangle_{cell} = \int_{\xi_{\Delta_1}}^{\xi_{\Delta_2}} d\xi N_s(\omega, H, r) / \xi_{\Delta_1}$ is readily obtained at $\omega = 0$ as follows:

$$\tilde{N}_L(\omega = 0, H) = \frac{0}{\pi R_H} = 0 \quad (36)$$

$$\tilde{N}_S(\omega = 0, H) = N_s^{\text{normal}} \frac{[(b \xi_{\Delta_2}/\Delta_1)^2 - 1] \xi_{\Delta_2}^2}{R_H} \propto H. \quad (37)$$

The above equations (34) and (35) hold as far as $\Delta_2 < \Delta_1$ and shows that the Volovik effect immediately creates a finite DOS in the isotropic $\pm s$-wave state and there is no threshold value of magnetic field $H^*$ to create the zero energy excitations. Its generic field dependence is linear in $H$ and its slope is proportional to $\sim (\Delta_2 / \Delta_1)^2$. It was found that impurity scattering will smooth this generic linear-in-$H$ field dependence and make it more sublinear and closer to $\sim \sqrt{H}$. Therefore the impurity effect is important to understand experiments.

Now having calculated the local DOS $N_s(\omega, H, r)$, $a = S, L$, it is straightforward to calculate the SH coefficient $\gamma(H) = \lim_{T \to 0} C(H, T)/T$ and the thermal conductivity $\lim_{T \to 0} \kappa(H, T)/T$ of the $\pm s$-wave state [122]. The most interesting discovery was that the slope of the field dependence, which is linear-in-$H$ in the clean limit, of $\lim_{T \to 0} \kappa(H, T)/T$ continuously increases from a very flat (when $|\Delta_2/\Delta_1| \approx 1$) to a very steep one (when $|\Delta_2/\Delta_1| \ll 1$). Therefore, the overall behavior of the $\lim_{T \to 0} \kappa(H, T)/T$ versus $H$ looks as if it evolves from a standard $s$-wave superconductor to a nodal superconductor only by changing the relative size of the two gaps $|\Delta_2|$ and $|\Delta_1|$. This behavior was exactly captured in an experiment for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with a systematic change of Co-doping ‘x’ [124] as shown in figure 30.
Figure 31(A) shows theoretical calculations of the transverse (the current in the \(ab\)-plane and \(H\) field along the \(c\)-axis) thermal conductivity \(\kappa_{HTlim}\) versus \(H\) for varying \(|\Delta\Delta| = 0.2, 0.3, 0.5, 0.7, 0.9\). The normal DOSs \(\gamma = N_{aS, L}\) for each band were assumed to be equal and the unitary impurity \((c = 0)\) with the concentration \(\Gamma/\Delta = 0.05\) was included. The overall behavior of this theoretical result is very similar to the experimental measurements of \(\kappa_{HT}/T\) for \(\text{Ba(Fe}_{1-x}\text{Co}_x\text{)As}_2\) \([124, 125]\) shown in figure 30. In particular, the systematic increase of the slope of \(\kappa_{HT}/T\) versus \(H\) with increasing Co-doping (\(x\)) and the evolution of the overall shape of the field dependence from a flat (concave up) for a smaller \(x\) to a steep (concave down, hence looking \(\sim H\)) for a larger \(x\) is exactly captured by this simple two-band \(s^\pm\)-wave pairing model.

Another important feature is that the values of \(\kappa_{HT}/\gamma H_0\) (also \(\kappa_{HT}/T\)) in the zero field limit are negligibly small for all cases, despite a substantial impurity scattering induced DOS accumulated at \(\omega = 0\), as seen in the data of \(\gamma(H = 0)\) in figure 31(B). This is even true for the \(|\Delta_0/\Delta_1| = 0.2\) case which shows the behavior \(\sim \sqrt{H}\) as in the nodal \(d\)-wave case. In fact, these extremely small values of the thermal conductivity coefficient \(\kappa_{HT}/T\) in the zero field limit were argued as evidence for an isotropic \(s\)-wave gap nature \([124, 125]\). However, it is a very puzzling feature when we note that several experiments \([126, 127]\) observed substantial values of the SH coefficients \(\gamma(H \rightarrow 0)\) with the same compounds and similar dopings.

This seemingly conflicting feature can be understood by considering the difference of the coherence factors between \(\gamma(H)\) and \(\kappa(H)/T\). Although the same DOSs \(\tilde{N}_{md, s}\) contribute to both the SH and thermal conductivity, the kernel of thermal conductivity (see equation (31)), being an energy current–energy current correlation function, contains a destructive coherence factor (the \(\sim \) sign in the numerator of the last term in equation (31)), but the SH does not have such a destructive coherence factor. Therefore we can expect a substantial
Figure 30. The electronic thermal conductivity data of Ba(Fe1−xCo,y)2As2 (filled symbols) [κ(H)/T]/[κ(H)/T] as a function of normalized magnetic field H/Hc2. Reprinted figure with permission from [124]. Copyright (2010) by the American Physical Society.

difference between γ(H) and κ(H)/T, particularly at low frequencies and low field. In the case of d-wave pairing, the same destructive coherence factor for thermal conductivity becomes very weak in the low energy limit because the nodal gap Δd(θ) linearly disappears, so that γ(H → 0) and κ(H → 0)/T behave rather similarly. The theoretical results for γ(H → 0)/γloc,N in figure 31(B) indeed show substantial values in the zero field limit γ(0,0)/γloc,N as H/Hc2 → 0, while the zero field limit of κ(H)/T in figure 31(A) is approximately zero.

The second important difference between γ(H) and κ(H)/T is that γ is the thermodynamic quantity and therefore it contains contributions both from the extended states outside vortices (which are calculated using equations (34) and (35) into equation (29)) and also from the normal states inside the vortex cores [128]. These core localized states make no contribution to the transverse thermal conductivity κ∥(H)/T due to the geometry (J ⊥ H), which is displayed in figure 31(A). In principle, theoretically, the longitudinal thermal conductivity κ∥(H)/T (J∥H) should have a similar contribution from the core states, but there is experimental difficulty and uncertainty to measure the ideal longitudinal thermal conductivity, therefore we will not consider this core correction to the longitudinal thermal conductivity κ∥(H)/T. However, the SH coefficient γ(H) always has the normal state contributions from the vortex cores and we need to correct γloc(H) as follows.

\[ γ_{\text{loc}}(H) = (1 - H/Hc2)γ_{\text{Volovik}}(H) + (H/Hc2)γ_0. \]  

(38)

In figure 32, this corrected γloc with core contribution from the result γVolovik in figure 31(B) is plotted. It shows that for relatively similar gap-size cases, such as [ΔJ/ΔK] = 0.7 and 0.9, γ(0) is very linear in H for a substantial region of fields (up to ≈Hc2/2) despite a finite γ(H → 0). Decreasing the gap-size ratio to [ΔJ/ΔK] = 0.5, 0.3, and 0.2, the field dependence of γ(H) becomes gradually more concave down. This behavior is in excellent agreement with the measurements of Ba0.6K0.4Fe2As2 [126] (≈H), (Fe0.92Co0.08)2As2 [127] (sub-linear in H), (Fe0.95Co0.045)2As2 [129] (≈H), (Fe0.85Co0.15)2As2 [129] (≈√H), and La0.6Fe1−xFexAs [130] (≈√H). Some representative experimental data for (Fe1−xCo)y)2As2 and Ba0.6K0.4Fe2As2 are shown in figures 33 and 34.

8.3. Summary

The theoretical discovery of the non-trivial Doppler effect (Volovik effect) in the s±-wave state with the magnetic field H was an unexpected surprise because the Volovik effect was considered to be a unique feature of nodal-gap superconductors, as in the d-wave SC state [114]. Therefore early experiments on a strong field dependence observed with γ(H → 0) and κ(H → 0)/T in the FeSC were interpreted as strong evidence for a nodal-gap SC state in these compounds, while other experimental probes, in particular the ARPES experiments, were clearly indicating an isotropic s-wave full-gap superconductor. However, this conflict and puzzle were nicely resolved by the Volovik effect in the ±s-wave SC state [122, 123]. In particular, the systematic evolution of the field dependence of γ(H → 0) and κ(H → 0)/T as a function of the gap-size ratio Rgap = |ΔJ/ΔK| and its excellent agreement with experiments for Ba(Fe1−xCo,y)2As2 [124, 125], not only resolve the experimental puzzle but also strengthened the validity of the ±s-wave pairing scenario for FeSCs. Of course, now it is quite certain that a few FeSC compounds indeed have nodes. However, strong field dependencies in γ(H) and κ(H)/T are not to be understood as ‘hallmark’ evidence for a nodal-gap superconductor any longer, as we have explained in this section. In particular, because the ±s-wave pairing state shows many unexpected nodal-gap-like behaviors in its SC properties, although it is nominally a full s-gap superconductor, we need more than one piece of experimental evidence—as well as cross-checking for self-consistency between different data—in order to confirm a nodal-gap superconductor. This issue will be discussed further in the next section.

9. Penetration depth

9.1. Evolution of δ(λ) of the s±-wave state with impurities

Perfect diamagnetism (the Meissner effect) is the hallmark of superconductivity, therefore the magnetic field should decay exponentially inside the superconductor. The typical decay length of the magnetic field is called the penetration depth λ and it is a function of temperature. Through the London equation, it is also related to the definition of superfluidity density ρs(T) as follows.

\[ J = J_p + J_d = -\frac{1}{4\pi\lambda^2(T)} A = -\sqrt{J_p(T)c^2/m} A \]  

(39)

\[ J = J_p + J_d = -\rho_s(T)c^2/m A. \]  

(40)
where we use the units $c = 1$ and $h = 1$. The paramagnetic current kernel $\mathbf{K}_p(T)$ is the current–current correlation function $(\langle j_a^x j_b^x \rangle)_T$ with $(a, b = x, y, z)$ at finite temperature $T$. At $T = 0$, $\lambda(T = 0)$ reaches its minimum value and the corresponding $\rho_{\text{tot}}(T = 0) = \langle j_a^x j_b^x \rangle = 0$. Therefore, we can interpret the quantity $\frac{1}{\lambda(T)}$ as a measure of the reduction of the superfluidity density by quasiparticle thermal excitation as follows:

$$\frac{1}{\lambda(T)} \sim \rho_{\text{tot}} - \rho_{\text{th}}(T).$$

And we can interpret the measurement of the penetration depth $\lambda(T)$ at low temperatures as probing the temperature dependence of the thermally excited quasiparticle density $\rho_{\text{th}}(T)$, which is governed by the shape of the DOS in the SC state $N(\omega)$ (see figure 3). As a result, we can predict that the low temperature variation of $\rho_{\text{th}}(T)$ is exponentially small for an $s$-wave superconductor, but it increases as $T$-linear with a nodal-gap superconductor. This expectation is indeed correct, therefore the gap symmetry can be identified by measuring $\lambda(T)$ at low temperatures.

$$\rho_{\text{th}}(T) \sim \lambda(T)^2,$$

with $\rho_{\text{tot}}$ being the total electron density $\rho_{\text{tot}}$ because

$$\rho_{\text{tot}}(T) = \langle j_a^x j_b^x \rangle_T = 0.$$
The final expression of equation (43) can indeed be shown as $1 - \langle N(0) \rangle_T$, namely as $\rho_{\text{tot}} - \rho_{\text{f}}(T)$. We can generalize the above formula to the $s^\pm$-wave superconductor with impurity scattering as follows:

$$K(q = 0, T) = \frac{\Delta^2}{\pi T} \sum_{\omega_n} \frac{(\omega_n + \Delta^2)^{3/2}}{\Delta^2 (\omega_n + \Delta_n^2)^{3/2}} = 2 \int_0^\infty d\omega_0 \rho_{\text{FD}}(\omega) \times \text{Re} \frac{\Delta^2}{(\omega_n + \Delta_n^2)^{3/2}}. \quad (43)$$

The final expression of equation (43) can indeed be shown as $1 - \langle N(0) \rangle_T$, namely as $\rho_{\text{tot}} - \rho_{\text{f}}(T)$. We can generalize the above formula to the $s^\pm$-wave superconductor with impurity scattering as follows:

$$K(T) = \sum_{n=\text{h,e}} N_n \pi T \sum_{\omega_n} \text{Re} \frac{\Delta_n^2}{(\omega_n + \Delta_n^2)^{3/2}}. \quad (44)$$

where $\omega_n$ and $\Delta_n$ are the quantities renormalized with the impurity self-energies $\Sigma_{\text{imp}}$ as described in section 3, and $N_n$ are the normal state DOSs of the two bands $h$ and $e$, respectively. This quantity $K(T)$ is directly proportional to the superfluid density $\rho_0(T)$ in the London limit.

Figure 34. $\Delta \gamma(H) = \left[ (C(T, H) - C(T, 0))/T \right]$ versus $H$ for $\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2$. The almost $H$-linear behavior of $\Delta \gamma(H)$ means that $\text{Ba}_0.6\text{K}_0.4\text{Fe}_2\text{As}_2$ is a full-gap superconductor with $|\Delta_\text{h}| \approx |\Delta_\text{e}|$. Reprinted figure with permission from [126]. Copyright (2009) by the American Physical Society.

Figure 35. Experimental data of the normalized superfluidity density $[\lambda(0)/\lambda(T)]$ versus $T$ of $\text{SmFeAsO}_0.8\text{F}_0.2$ (colored symbols) and theoretical fittings (colored solid lines) with the two-gap $s$-wave superconductor models, and the inset table shows the fit parameters. The black dashed line is the single-gap $s$-wave model fitting with $T_\text{c1} = 1.76$. The inset shows the low temperature data on an expanded scale, making clear the deviation of the black dashed line (single $s$-wave model) fit from the observed data. Reprinted figure with permission from [44]. Copyright (2009) by the American Physical Society.

Figure 33. $C/T$ at 2 K versus field as an indication of $\gamma$ versus $H$ for annealed single crystals of $\text{Ba}(\text{Fe}_{0.955}\text{Co}_{0.045})_2\text{As}_2$ and $\text{Ba}(\text{Fe}_{0.85}\text{Co}_{0.15})_2\text{As}_2$. Reprinted figure with permission from [129]. Copyright (2012) by the American Physical Society.
scattering rates $\Gamma/\Delta_0 = 0.0, 0.01, 0.04, 0.08$. With these impurity scattering rates, the total DOS $N(\omega)$ systematically changes from a full-gap $s$-wave type $\rightarrow$ 'V' shaped DOS $\rightarrow$ a dirty limit DOS as shown in figure 8(B). The corresponding $\rho_s(T)$ and $\lambda_L(T)$ at low temperatures continuously evolves in a sequence of the form: exponentially flat $\rightarrow \propto T^2 \rightarrow \propto T^3$ with an increase of impurity concentration. What is surprising is that the case with the critical impurity scattering rate $\Gamma_{\text{imp}}/\Delta_0 = 0.04$, which has a 'V' shaped DOS just as in a clean $d$-wave superconductor, displays $\rho_s(T), \lambda_L(T) \sim T^3$ (red circles in figure 37), instead of $\sim T$ as expected in the $d$-wave superconductor. This result tell us that although the DOS $N(\omega)$ looks the same, the dynamically shaped DOS (e.g. by self-energy correction) and kinematically shaped DOS (e.g. by the Bogoliubov quasiparticles in a $d$-wave superconductor) respond differently for the transport properties.

These results consistently explain the various temperature dependencies of the experimental data of $M$-1111 ($M = \text{Pr, Sm, Nd}$) [44, 45, 134] (flat), (Ba,K)$_2$Fe$_2$As$_2$ [46] (flat), $\text{RF}_{\text{FeAsO}}_{\text{1-y}}\text{F}_{\text{0.1}}$ ($R = \text{La, Nd}$) [135] (x $T^2$), and Ba(Fe, Co)$_2$As$_2$ [44, 45, 134] (flat).
with increasing dirtiness [138]. Vorontsov et al. [139] performed theoretical studies on the same problem, and obtained a similar result $\rho(T) \propto T^2$ for high concentrations of impurities but obtained a different result $\rho(T) \propto T^{1.6}$ for the critical impurity concentration. This difference arises from the different methods of studying the impurity scattering effects—weak coupling theory [139] and strong coupling theory [131]—when calculating the expression $K(T)$ above.

9.2. Possible nodal-gap evidence: $\delta\lambda(T) \sim T$

As discussed above, most of the FeSC compounds display a temperature dependence of penetration depth $\delta\lambda(T)$ as either exponentially flat or high power $n > 2$ in $\delta\lambda(T) \sim T^n$, consistent with the $s^\pm$-wave gap state. However, there exist a few FeSC compounds which show quasi-linear-in-$T$ behavior down to very low temperatures in $\delta\lambda(T)$, which is a type of hallmark evidence for a nodal-gap superconductor [140]. These are LaFePO [141, 142], BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ [143], and KFe$_2$As$_2$ [144].

As the data of $\delta\lambda(T)$ for LaFePO shows in figure 39, these three compounds display a temperature dependence of $\delta\lambda(T)$ quite close to linear in $T$. Although there are always some uncertainties in determining the power-law exponent due to the uncertainty of the absolute value $\lambda(T = 0)$, all three compounds produced the exponent $n \sim 1.1$–1.2. These values of the power-law exponent are not compatible with the full-gap $s^\pm$-wave pairing state unless one of the gap values $\Delta_s$ is extremely small and carrying a substantial DOS [145]. Therefore, it is reasonable to suspect that these three FeSC compounds indeed possess line nodes in their gap functions. However, even if there exist line nodes in these FeSC compounds, it can still be understood as a smooth evolution of the full-gap $s^\pm$-wave state to the $s + g$-wave gap, as depicted in figure 1(C), and does not imply a qualitatively new pairing mechanism. However, in order to confirm the existence of the line nodes, independent experimental evidence, other than the penetration depth, needs to be tested. Careful cross-checking analysis with the penetration depth $\lambda(T)$ and the thermal conductivity $\kappa(T, H)$ was carried out in [145]. The main point to check was that the $T$-linear behavior of $\lambda(T)$ down to $T/T_c < 0.05$ [141–144] implies a nodal gap but in an extremely clean limit. It is well known that a tiny amount of impurity would immediately change $\lambda(T)$ from $T$-linear to $T^2$-behavior for a nodal-gap superconductor [146]. A quantitative estimate of the impurity scattering rate $\Gamma_{\text{imp}}/\Delta_0$ compatible with the measured $\lambda(T)$—if it is assumed from a nodal gap—of these three compounds can be extracted from the data, and it was shown to be as clean as $\Gamma_{\text{imp}}/\Delta_0 < 0.02$ [145]. Then [145] cross-checked with the thermal conductivity data $\kappa(T = 0, H)$ whether these three FeSC compounds are indeed in such a clean limit.

For a nodal-gap superconductor, it was well known that $\kappa(T = 0, H \rightarrow 0)$ obtains a universal value regardless of the amount of impurity because of the cancellation between the impurity induced DOS $\rho_{\text{imp}} \sim \Gamma_{\text{imp}}$ at zero frequency and the relaxation time of the quasiparticle due to the same impurity scattering $\tau_{\text{imp}} \sim 1/\Gamma_{\text{imp}}$. Then thermal/electric conductivity obtains a universal value as $\sim \rho_{\text{imp}} \cdot \tau_{\text{imp}} \sim \text{const.}$, independent of the impurity scattering rate. Hence the values of $\kappa(T = 0, H \rightarrow 0)$ cannot tell us about the dirtiness of the superconducting samples. However, if normalized by the normal state value of $\kappa_0$, the value $\kappa_0(T = 0, H \rightarrow 0)/\kappa_0 \approx \Gamma_{\text{imp}}/\Delta_0$ becomes an excellent measure of the dirtiness of the nodal-gap SC samples [145].

Using this criterion, [145] concluded that only KFe$_2$As$_2$ is compatible with a clean nodal-gap superconductor, but the LaFePO and BaFe$_2$(As$_{0.67}$P$_{0.33}$)$_2$ compounds are in fact in an extremely dirty limit, having
from the normalized thermal conductivity data of most of the FeSC compounds. For a nodal-gap scenario to be compatible with the full-gap superconducting model, having the sign-changing OPs with these compounds cannot be understood as a nodal-gap SC state, having the sign-changing OPs with these compounds cannot be understood as a nodal-gap SC state.

This approach is (see figure 40). Indeed, thus the observed rate of the temperature dependence of \(\rho(T)\) as to the almost equal c-suppression, this model is not compatible with the above mentioned experiments show very slow decay of \(T_c\) (e.g. see figure 41), often an order of magnitude slower than the theoretical prediction with the point-like strong impurity potentials on the \(s^\pm\)-wave pairing state [53, 54].

To resolve this discrepancy, two approaches were attempted. The first one was pursued by Kontani and co-workers [19, 20], who claimed that this is the evidence that the \(s^\pm\)-wave model is not compatible with FeSCs and proposed the \(s^+\)-wave state, is a quick solution to explain the slow \(T_c\)-suppression. However this option created many more new problems which needed separate resolutions with specific mechanisms and respective fine tunings: (1) first, as to the \(T_c\)-suppression, this model is not compatible with the almost equal \(T_c\)-suppression rates with magnetic (Mn) and non-magnetic impurities [152], and (2) this model has to invent all the specific theories to explain other SC properties of FeSCs, such as NMR, penetration depth, neutron resonance, etc. which were naturally explained with the \(s^\pm\)-wave model.

In this review, we will focus on the second option, i.e. how \(T^*\)-state can be understood with the point-like strong impurity potential: (1) first, the \(T^*\)-state, is a quick solution to explain the slow \(T_c\)-suppression.

The \(s^\pm\)-wave SC state, having the sign-changing OPs \(\Delta_0\) and \(\Delta_c\), is expected to have a similar \(T_c\)-suppression rate with point-like defects as in the \(d^\pm\)-wave case [53, 54]. In the early days, this theoretical prediction of a fast \(T_c\)-suppression appeared to be inconsistent with the experimental observations [108, 152–154], where these experiments introduced various transition metal elements (Mn, Co, Ni, Cu, Zn, Ru) substituting the Fe-sites in various Fe-1111 and Fe-122 compounds. Direct doping on the Fe-sites with transition metals is expected to introduce strong random potentials onto the Fe–As plane, and is expected to suppress \(T_c\) quickly. However, the above mentioned experiments show only slow decay of \(T_c\) (e.g. see figure 41), often an order of magnitude slower than the theoretical prediction with the point-like strong impurity potentials on the \(s^\pm\)-wave pairing state [53, 54].

9.3. Summary

The \(s^\pm\)-wave pairing model is consistent with the temperature dependence of the penetration depth \(\lambda(T)\) of most of the FeSC compounds. Having sign-changing OPs, this full-gap superconductor quickly develops an in-gap state with impurities (magnetic and non-magnetic), which then causes the systematic evolution of the temperature dependence of \(\lambda(T)\) in a sequence of the form: exponentially flat \(\rightarrow\lambda(T)\rightarrow\sim T^3\rightarrow\sim T^2\) with increasing impurity concentration. This theoretical prediction is in excellent agreement with the various temperature dependencies of the experimental data of \(M\)-1111 (\(M = Pr, Nd, Sm\)) [44, 45, 135] (flat), (Ba,K)Fe\(_2\)As\(_2\) [46] (flat), and Ba(Fe,Co)\(_2\)As\(_2\) [133, 136, 137] (\(\propto T^{2.5}\)) and many others [138]. Finally, there are a few FeSC compounds showing \(T\)-linear \(\lambda(T)\), hence appearing not to be compatible with the full-gap \(s^\pm\)-wave pairing model. In particular, the nodal-gap possibility for the LaFePO and BaFe\(_2\)(As\(_{0.63}\)P\(_{0.33}\))\(_2\) compounds is strongly supported by accumulated experiments, hence this issue is not yet settled. However, even if these compounds are confirmed to be nodal-gap superconductors, it does not necessarily imply that a qualitatively different pairing mechanism other than the \(s^\pm\)-wave pairing model is realized in these compounds.

10. \(T_c\) suppression with impurities in the \(s^\pm\)-wave state

The \(s^\pm\)-wave SC state, having the sign-changing OPs \(\Delta_0\) and \(\Delta_c\), is expected to have a similar \(T_c\)-suppression rate with point-like defects as in the \(d^\pm\)-wave case [53, 54]. In the early days, this theoretical prediction of a fast \(T_c\)-suppression appeared to be inconsistent with the experimental observations [108, 152–154], where these experiments introduced various transition metal elements (Mn, Co, Ni, Cu, Zn, Ru) substituting the Fe-sites in various Fe-1111 and Fe-122 compounds. Direct doping on the Fe-sites with transition metals is expected to introduce strong random potentials onto the Fe–As plane, and is expected to suppress \(T_c\) quickly. However, the above mentioned experiments show only slow decay of \(T_c\) (e.g. see figure 41), often an order of magnitude slower than the theoretical prediction with the point-like strong impurity potentials on the \(s^\pm\)-wave pairing state [53, 54].

To resolve this discrepancy, two approaches were attempted. The first one was pursued by Kontani and co-workers [19, 20], who claimed that this is the evidence that the \(s^\pm\)-wave model is not compatible with FeSCs and proposed the \(s^+\)-wave state, is a quick solution to explain the slow \(T_c\)-suppression. However this option created many more new problems which needed separate resolutions with specific mechanisms and respective fine tunings: (1) first, as to the \(T_c\)-suppression, this model is not compatible with the almost equal \(T_c\)-suppression rates with magnetic (Mn) and non-magnetic impurities [152], and (2) this model has to invent all the specific theories to explain other SC properties of FeSCs, such as NMR, penetration depth, neutron resonance, etc. which were naturally explained with the \(s^\pm\)-wave model. In this review, we will focus on the second option, i.e. how the seemingly slow \(T_c\)-suppression observed in experiments can be understood with the \(s^\pm\)-wave model. This approach is mainly pursued by Hirschfeld and co-workers [155, 156] and we follow the main results of their recent paper [156].

### 10.1. Point-like impurities: \(U^\text{imp}_{\text{intra-band}} = U^\text{imp}_{\text{inter-band}}\)

To study the \(T_c\)-suppression by impurities in the SC state, the key concept is to distinguish two different processes: pair-breaking (\(\Gamma_{pb}\)) and pair-gluing (\(\Gamma_{pg}\)) scatterings [49]. Their leading order processes are shown in figure 42. The physical meaning of these processes is that the impurity scattering is not always acting as a pair-breaker (\(\Gamma_{pb}\)) but also acts as
a pair-gluing interaction ($\Gamma_{pg}$) depending on the gap function $\Delta(k)$. For the two-band $s^\pm$-wave state, the impurity potentials can be conveniently parameterized with two potentials, $U_{\text{intra-band}}^{\text{imp}}$ and $U_{\text{inter-band}}^{\text{imp}}$, and the two scattering rates are calculated as

$$\Gamma_{pb} = \Sigma_0^{\text{intra-band}}(\omega_n) + \Sigma_0^{\text{inter-band}}(\omega_n)$$

$$\Gamma_{pg} = \Sigma_1^{\text{intra-band}}(\omega_n) + \Sigma_1^{\text{inter-band}}(\omega_n),$$

where $\Sigma_0^{\text{intra-band}}, \Sigma_0^{\text{inter-band}}, \Sigma_1^{\text{intra-band}}, \Sigma_1^{\text{inter-band}}$ are defined in equations (13)–(16). Using the Born approximation as depicted in figure 42, a simplification occurs for the calculations of $\Sigma_0^{\text{intra-band}}$ and the two scattering rates are given, in the limit of $T \to T_c$ ($\Delta_{h,e} \to 0$), as follows:

$$\Gamma_{pb} = \Gamma_{\text{imp}} \text{sgn}(\omega_n) = \Gamma_{\text{imp}} \frac{\omega}{|\omega|},$$

$$\Gamma_{pg} = \Gamma_{\text{imp}} \left[ \tilde{N}_h(\Delta_n) + \tilde{N}_e(\Delta_n) \right] / |\omega|,$$

where $\tilde{N}_h = N_h/N_{\text{tot}}$, the normalized DOS for band $a$, and $\Gamma_{\text{imp}} = n_{\text{imp}} \pi N_{\text{tot}} U_{\text{imp}}^2$. Once $\Gamma_{pb}$ and $\Gamma_{pg}$ are calculated, the final $T_c$ suppression is written as [49]

$$\ln \frac{T_{c0}}{T_c} = \psi \left( \frac{1}{2} + \frac{\rho}{2} \right) - \psi \left( \frac{1}{2} \right),$$

where $\rho = \Gamma_{pb} / \pi T_c$ with $\Gamma_{pb} = \Gamma_{pg} - \Gamma_{pg}$ and for the small scattering limit ($\Gamma_{\text{eff}}^{\text{pg}} < T_c$), we have

$$T_c = T_{c0} - \frac{\pi}{4} \Gamma_{\text{eff}}^{\text{pg}}.$$ (49)

For an $s^\pm$-wave superconductor, $\Gamma_{\text{eff}}^{\pm} = 0$ because $\Gamma_{pb} = \Gamma_{pg}$ hence the $T_c$-suppression becomes zero, consistent with Anderson’s theorem [50]. For the $s^\pm$-wave state, because of the sign-changing OPs, the $\Gamma_{pg}$ in equation (46) becomes almost zero because $[\tilde{N}_h(\Delta_n(k))_{FS} + \tilde{N}_e(\Delta_n(k))_{FS}] \to 0$ (almost but not exactly zero) [37], hence $\Gamma_{pb} \approx \Gamma_{pg}$ and the $T_c$-suppression becomes maximum as in the $d$-wave case. The maximum $T_c$-suppression in the $d$-wave occurs due to exactly the same mechanism as $\tilde{N}_h(\Delta_{d,\text{wave}}(k))_{FS} = 0$.

Figure 43 shows the numerical results of $T_c/T_{c0}$ versus $\Gamma_{\text{imp}}/k_B T_{c0}$ of the $s^\pm$-wave model. Indeed, the $T_c$-suppression rates for the $s^\pm$- and $d$-wave states are almost equal as expected. The difference between the magnetic and non-magnetic impurities is also negligible, demonstrating the maximum pair-breaking effect of ordinary non-magnetic potential scatterers in sign-changing OP superconductors. In the right-hand panel, the same calculations were performed with an extreme DOS ratio of $N_h/N_e \approx 9$, possibly realized with heavily overdoped FeSCs, either by holes or electrons. The $T_c$-suppression rates change only by about 20%. To facilitate comparison with experimental data, the top x-axes of figure 43 are marked with the commonly used dimensionless pair-breaking parameter $g^s_p$ [156] = $\alpha$ [152] = $\Gamma_{\text{imp}}/2\pi k_B T_{c0}^2$. The critical impurity scattering rate is shown to be $g^s_p = \alpha_c \sim 1/2 \pi \approx 0.16$. Li et al [152] have calculated the five-orbital (five-band) $s^\pm$-wave model to find a value of $\alpha_c \approx 0.22$, which is a similar parameter to $g^s_p$ and is defined as $\alpha = 0.88 z \Delta \rho_0 / T_c$. As shown in figure 41, the comparison between theory and experiments shows that the $s^\pm$-wave
model with point-like impurities ($U_{\text{intra-band}} = U_{\text{inter-band}}$) definitely has a much faster $T_c$-suppression rate than the experimental data for real FeSCs. However, it should be noted that the chemical doping experiments, as in [108, 152–154], where the impurities are introduced by doping with various transition metals (Mn, Co, Ni, Cu, Zn, Ru), have many unknown parameters and effects which will affect $T_c$ by means other than the impurity potential itself, such as change of carrier density, change of pairing interactions, etc. Therefore, it is more ideal to compare the theoretical results with irradiation experiments such as proton [158, 159], $\alpha$-particle [160], and electron irradiations [156, 161].

10.2. Finite-size impurities: $U_{\text{intra-band}} > U_{\text{inter-band}}$

In order to resolve the above discrepancy between theory and experiments, Hirschfeld and co-workers [155, 156] have invoked finite-ranged impurity potentials, i.e. $U_{\text{intra-band}} > U_{\text{inter-band}}$ which is more realistic for impurities with a finite size. It is intuitively obvious that if $U_{\text{intra-band}} > U_{\text{inter-band}}$ the $T_c$-suppression of the $s^\pm$-wave model should become much slower because the pair-gluing impurity scattering rates $\Gamma_{\text{pg}}$ of equation (46) rapidly increase to finite values as

$$\Gamma_{\text{pg},h} = \frac{\Gamma_{\text{inter}}N_h(\Delta_h) + \Gamma_{\text{inter}}N_h(\Delta_h)}{|\omega|},$$

$$\Gamma_{\text{pg},e} = \frac{\Gamma_{\text{inter}}N_e(\Delta_e) + \Gamma_{\text{inter}}N_e(\Delta_e)}{|\omega|},$$

(51)

where $\Gamma_{\text{inter}} = (U_{\text{inter}}^\text{imp})^2 \pi N_0 \rho_{\text{imp}}$ are the inter- and intra-band impurity scattering rates in the Born approximation. Then the effective pair-breaking rate $\Gamma_{\text{eff}} = \Gamma_{\text{pg}} - \Gamma_{\text{pg}}$ also rapidly decreases, hence the $T_c$-reduction is also reduced according to equation (47) or equation (48).

Prozorov et al [156] performed the systematic calculations of $T_c$ of the two-band $s^\pm$-wave model with $U_{\text{intra-band}} > U_{\text{inter-band}}$ and at the same time, they calculated the theoretical residual resistivity $\rho_0$ using the same parameters. Thus they produced the consistent theoretical data for $T_c/\Delta$ versus $\rho_0$ to be directly compared to experimental data. Figure 44 shows these results. The results show that the $s^\pm$-wave model with finite-ranged impurity potentials ($U_{\text{intra-band}} > U_{\text{inter-band}}$) can perfectly fit the experimental data from Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ with electron irradiation, with a moderate ratio of $\alpha = U_{\text{inter}}^\text{imp}/U_{\text{intra}}^\text{imp} = 1.0, 0.65$, and 0.5. Reproduced from [156]. 

Figure 44. Data for $\Delta T_c/\Delta \rho_0$ versus $\Delta \rho_0$. The symbols show experimental data from Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$ ($x = 0.24$) with electron irradiation. The solid curves are theoretical results with different $\alpha = U_{\text{inter}}^\text{imp}/U_{\text{intra}}^\text{imp} = 1.0, 0.65$, and 0.5. Reproduced from [156].
\( T_c \)-suppression with electron irradiation have ruled out the possibility of the \( s^\pm \)-wave state in Ba(Fe\(_{1-x}\)Ru\(_x\))\(_2\)As\(_2\) and support the \( s^\pm \)-wave state. In figure 44, we see that there is still a large discrepancy between the transition metal doping experiments of Li et al [152] (which show the average \( T_c \)-suppression rate \( \approx 50 \text{mK} \mu \Omega \text{cm}^{-1} \)), which is seven times faster than the electron irradiation data of figure 44) and the theory. However, as we have mentioned, transition metal doping experiments contain unknown factors/effects other than pure impurity scattering.

10.3. Summary

The message of this section is simple. The \( s^\pm \)-wave pairing model is intrinsically sensitive to impurity scattering (both magnetic and non-magnetic) because of the sign-changing OPs as in the \( d \)-wave pairing state. On the other hand, it is also true that most experiments on \( T_c \)-suppression with transition metal dopings and irradiations show a much slower rate of \( T_c \)-suppression compared to the theoretical prediction for \( T_c \)-suppression in the \( s^\pm \)-wave state with point-like impurities.

Initially, this discrepancy between theory and experiments was taken as evidence for the inadequacy of the \( s^\pm \)-wave pairing model for FeSCs. However, more realistic consideration of the impurity potentials—which should have a finite size (not point-like)—leads to a finite-ranged impurity potential \( U^{\text{imp}}(q) \) in momentum space. It implies \( U^{\text{imp}}_{\text{inter-band}} > U^{\text{imp}}_{\text{intra-band}} \) in the two-band \( s^\pm \)-wave model, and the systematic theoretical calculations of \( T_c \) with \( U^{\text{imp}}_{\text{inter-band}}/U^{\text{imp}}_{\text{intra-band}} = \alpha (\ll 1) \) can produce an arbitrarily slow \( T_c \)-suppression rate with the \( s^\pm \)-wave state by choosing a smaller \( \alpha \) value [155, 156]. Although this problem of the \( T_c \)-suppression in FeSCs is still under debate among researchers, we can say that the \( s^\pm \)-wave pairing model can be compatible with experiments if the introduced impurities in real materials are not point-like but finite-sized defects.

11. Experimental hints for the pairing mechanism

Up to this section, we have investigated the various SC properties of the \( s^\pm \)-wave SC state and their compatibility with experimental data, and we did not examine much the possible pairing mechanism of the \( s^\pm \)-wave SC state. In section 2, we have only briefly described a minimal two-band BCS model, so as to visualize the succinct features of the \( s^\pm \)-wave pairing state, but did not imply that this is the ultimate pairing mechanism of the FeSCs. Even as a BCS theory, this two-band model, being a minimal phenomenological model, ignored all the details of bands (five or ten bands, depending on the choice of the unit-cell) and orbital degrees of freedom as well as the details of the pairing interactions \( V(k, k') \) and their coupling matrix elements \( M^{ab}_{\alpha\beta}(k, k') (\alpha, \beta = \text{orbital indices}; a, b = \text{band indices}) \), etc. Furthermore this minimal BCS model has completely ignored any correlation effects, which should be reasonably strong in the FeSC materials. Therefore, up to this section, although we have demonstrated the compatibility of the \( s^\pm \)-wave pairing state with the SC properties of almost all available experiments on FeSCs, it does not provide much suggestion as to the nature of the pairing mechanism.

On the other hand, many researchers believe that the FeSC materials are intermediate to strongly correlated systems. Roughly speaking, its correlation is weaker than that of the cuprate superconductors because the parent undoped compounds of FeSCs are still in the metallic SDW state. The cuprate parent compounds are Mott AFM insulators, and also weaker than the heavy fermion SC systems because the renormalization factor of the quasiparticle masses of the FeSCs—in particular, of Fe-pnictides [165]—are a factor of 2–5 at most [166–169], while the typical renormalization factor of the heavy fermions is from several tens to several hundreds. Nevertheless, these three classes of unconventional SC compounds can display quite similar phase diagrams: namely, the common AFM correlation—seen in all the cuprates, most FeSCs, and some the heavy fermions—is weakened by tuning the system parameters such as doping, fields, pressure, etc., and at the point of \( T_N \rightarrow 0 \) or at some distance from it, the quasiparticles are maximally renormalized (or completely broken down) defining the ‘quantum critical point’ (QCP). As shown in figure 45, all these three classes of SC materials have the maximum \( T_c \) around the hypothetical QCP (although where the pseudogap temperature \( T^* \rightarrow 0 \) in the phase diagram is still under discussion) and display a dome shape of the SC phase in the \( T_c \) versus tuning parameter phase diagram.

Hence many researchers suspected that the superconductivity in FeSCs—regardless of the SC-gap symmetry—should be organized by some novel and unconventional pairing mechanism, or at least a non-BCS type pairing mechanism. And indeed there exist strong experimental indications supporting this idea, which are the anomalous scaling relations of (1) the SH jump \( \Delta E \) versus \( T_c \) and (2) CE \( \Delta E \) versus \( T_c \). Pioneered by Canfield and co-workers [170], and supported by the same and other researchers [113, 129, 171–178], is the anomalous scaling law of \( \Delta C \sim T_c^3 \), obeyed by over 50 FeSC samples, while the standard BCS theory predicts \( \Delta C \sim T_c \). This observation is indeed quite non-BCS-like and appears to be in accordance with the idea of QC fluctuation [179] driven superconductivity. And, more recently, Xing et al [180] and Kim et al [181] have advanced this observation further to collect data for CE (\( \Delta E \)) versus \( T_c \), and have also found a scaling relation of \( \Delta E \sim T_c^{3.5} \) for about 30 FeSC samples, again strongly deviating from the BCS prediction \( \Delta E \sim T_c^2 \). These seemingly very non-BCS-like scaling relations together indicate that the pairing mechanism of the FeSCs should be, at least, of non-BCS type, and most probably should be intimately connected to the QC fluctuations.

However, in this section, we will discuss how these two seemingly non-BCS-like scaling relations can be consistently explained with the minimal two-band BCS model of the \( s^\pm \)-wave state described in section 2 [182, 183]. This is a surprising result, but on the other hand it just demonstrates the fact that a multi-band BCS superconductor can have many novel and qualitatively new SC properties, which are not to be expected in a single-band BCS superconductor. As to the pairing mechanism, the simultaneous explanation of two anomalous scaling relations with the BCS two-band model of the \( s^\pm \)-wave state strengthened the speculation that the fundamental pairing mechanism of FeSCs is basically a...
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BCS theory, in a very general sense, i.e. the itinerant fermionic carriers (quasiparticles) are glued into Cooper pairs by an exchange of non-phononic boson fluctuations and this process is described by a general BCS–Eliashberg formalism.

11.1. BNC scaling of specific heat jump $\Delta C$ versus $T_c$

The strong power-law behavior of the SH jump $\Delta C$ versus $T_c$ ($\Delta C \sim T_c^\alpha$, $\alpha \approx 3$), first observed by Bud’ko, Ni and Canfield (BNC) [170], has been confirmed with several families of FeSC compounds with various dopings by several research groups [113, 129, 171–178].

It is well known that the BCS theory [43] of superconductivity predicts the universal ratio $\Delta C/T_c = 1.43\gamma$ ($\gamma = \frac{2e^2}{3}N(0)$ is the Sommerfeld coefficient of the normal state), hence the BCS scaling law should be $\Delta C \sim T_c$—from a naïve point of view assuming that $\gamma$ and $T_c$ are not related [181]. Therefore, the experimental observation by BNC [170], $\Delta C \sim T_c^3$ for a family of doped Ba(Fe$_{1-x}$TM$_x$)$_2$As$_2$ compounds with $TM = Co$, Ni, is a very intriguing behavior and has stimulated active investigations both experimentally and theoretically. After this original work [170], this so-called BNC scaling relation was expanded with an increasing list of iron pnictide and iron chalcogenide SC compounds [129, 172–177, 180, 188, 189], hence strengthening the speculation that some generic mechanism must exist behind this unusual scaling behavior.

However, more recent works showed that this BNC scaling is not a perfect relation and there exist a few compounds showing varying degrees of deviations. For example, the observation of a strong deviation from the BNC scaling in K-doped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ for $0.7 < x < 1$ [171] is contrasted to Na-doped Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ (0.1 $\leq$ $x$ $\leq$ 0.9) [172], which displays an excellent BNC scaling. The authors of recent studies [178] with Na-doped K$_{1-x}$Na$_x$Fe$_2$As$_2$ claimed that $\Delta C \sim T_c^2$ fits the data better, instead of $\sim T_c^3$, although the data for this compound are limited to a very narrow range of $T_c$ variation.

3 The FeSe/STiO$_3$ monolayer system [206–208] might be an exception, in which, in addition to a non-phononic pairing boson, it appears that a phonon participates as a secondary boson to boost the SC pairing.

Figure 45. The phase diagrams of the three most studied classes of unconventional superconductors. (A) Cuprate superconductor (YBCO). Reprinted by permission from Macmillan Publishers Ltd: Nature [162], copyright (2007). (B) Heavy fermion superconductor (CeRhIn$_5$). Reprinted by permission from Macmillan Publishers Ltd: Nature [163], copyright (2008). (C) FeSC (Ba-122). Reprinted from [164]. Copyright (2010), with permission from Elsevier.

The commonality is obviously that the $T_c$ versus tuning parameter (dopings and pressure) relation defines a dome-shape phase having a maximum $T_{c\text{max}}$ around a hypothetical QCP at which the correlation effect is strongest.
attributed the origin of $\Delta C \propto T_c^3$ to the anomalous temperature dependence of the normal state electronic SH with the scaling form $C_{\text{elec}}^n \propto T^3$ due to the critical fluctuations near the QCP. A problem of this theory is that (1) this hyper-scaling argument applies to the bosonic critical fluctuations and bosonic SH, hence the fermionic SH jump $\Delta C_{\text{elec}}$ is irrelevant to the QC fluctuations. Furthermore, there is no experimental evidence of $C_{\text{elec}} \propto T^3$ (apart from phonon SH $C_{\text{ph}} \propto T^3$) for a wide doping range of the FePn/Ch superconductors. All three theories mentioned above are single-band theories and do not particularly utilize the unique properties of the FePn/Ch superconductors.

11.1.2. The theory of the two-band $s^\pm$-wave model. The key idea of this theory is that multi-band systems should have a contribution of $\Delta C_i$ from each band ‘i’ as

$$\Delta C = \sum_{i=e,h} N_i(0) \left( -\frac{d\Delta_i^2}{dT} \right) |T_i|.$$ (52)

The two-band $s^\pm$-wave model described in section 2 has an interesting inverse relation between the DOS $N_i$ and the SC gap $\Delta_i$, such as $N_e \propto \Delta_e$ as $T \to T_c$ and $N_h \propto \frac{1}{\Delta_h}$ as $T \to 0$ [37]. Therefore the total SH jump can possibly have a temperature relation very different from a single-band BCS prediction $\Delta_C^{\text{BCS}} \propto T_c$.

Another ingredient of the model is ‘doping’ to simulate the series of experimental data, for example, of figure 46. The data of the Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ series in figure 46 is a collection of data from samples with different doping ‘x’ of the Na element, which introduces more ‘hole’ carriers into the compound. In the case of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ series, the doping ‘x’ introduces more ‘electron’ carriers to the compound. To simulate this series of doping in the two-band model, we first note that the undoped parent compound BaFe$_2$As$_2$ is a compensated metal, hence has the same number of electrons and holes, i.e. $n_h = n_e$. Therefore it is a reasonable approximation to assume $N_e \approx N_h$ at no doping, and then the doping of holes (K, Na, etc.) or electrons (Co, Ni, etc.) is simulated by varying $N_h$ and $N_e$ while keeping $N_e + N_h = N_{\text{tot}} = \text{const}$. Admittedly this modeling of doping is much too simple, but the assumption $N_{\text{tot}} = \text{const}$ is only for convenience and can be relaxed. The real important parameter of this model is the relative sizes between $N_e$ and $N_h$, but not the total DOS $N_{\text{tot}}$; these specific pieces of information are all absorbed in the plot of $\Delta C/(N_{\text{tot}})$ versus $T_c/(N_{\text{tot}})$ as implicit parameters. Therefore, it is not even necessary to know the exact relation between the actual doping concentration ‘x’ of real compounds and the values of $N_{\text{tot}}$ in our two-band model. For more details, the readers can see [182, 183].

Figure 47 shows the results of numerical calculations of $\Delta C(N_{\text{tot}})$ versus $T_c/(N_{\text{tot}})$, which are calculated with the coupled-gap equation (5) at $T \to T_c$ and the above equation (52). The results faithfully reproduce the anomalous BNC scaling as well as some deviations shown in the experimental data of figure 46. First, the results with a wide range of the non-pair-breaking impurity scattering rate $\Gamma = 0.05 \sim 0.15$ show the BNC scaling $\Delta C \propto T_c^3$. With decreasing the scattering

![Figure 46. $\Delta C_p$ at the SC transition versus $T_c$ for the Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ series, plotted together with literature data for various FeAs-based SC materials. The plot from [171] was updated to include published data for K$_{1-x}$Na$_x$Fe$_2$As$_2$ ($0 \leq x \leq 0.31$), Ca$_{1-x}$Na$_x$Fe$_2$As$_2$, Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ ($x = 0.35, 0.4$), and LaFeAsO$_{0.1}$F$_{0.1}$ [178, 184–187]. The line corresponds to $\Delta C \sim T_c^3$. Numbers near the symbols are Na concentrations $x$. Reprinted figures with permission from [171, 172]. Copyright (2014) by the American Physical Society.](image-url)
rate $\Gamma_0/\Lambda_{hi} = 0.02$, and 0.0, the scaling relation continuously becomes weaker up to $\Delta C \sim T_c^{1.4}$ at $\Gamma_0/\Lambda_{hi} = 0.0$ in figure 47. Therefore, the gentler scaling power $\Delta C \sim T_c^{\gamma}$, observed in the series of $K_1-xNa_2Fe_2As_2$ [178], can be understood. In the extreme clean limit with $\Gamma_{hi}/\Lambda_{hi} = 0.0$, the scaling relation approaches $\Delta C \sim T_c^{1.4}$, which is still steeper than the observed relation $\Delta C \sim T_c^{\gamma}$ of $Ba_{1-x}K_xFe_2As_2$ for $x > 0.7$ [171]. Therefore, the data for the $Ba_{1-x}K_xFe_2As_2$ series for $x > 0.7$ appears out of the scope of the minimal two-band $s^\pm$-wave model. However, it should be noticed that the $Ba_{1-x}K_xFe_2As_2$ compound has the Lifshitz transition for $x > 0.7$, where the electron band around the $M$ point sinks below the FS [192], hence the simple two-band model does not apply any more in this region of K-doping. Finally, the numerical resultsshowing the super strong scaling power $\Delta C \sim T_c^{\gamma}$ are only for the demonstration of an unrealistic amount of impurity scattering rate $\Gamma_0/\Lambda_{hi} = 0.5$.

In summary, figure 47 shows that the BNC scaling is a generic property of the two-band BCS model with a dominant inter-band pairing interaction as $V_{inter} > V_{intra}$, unless an extreme choice of model parameters is made. Calculations for this two-band model suggest that the origin of the anomalous BNC scaling behavior is nothing else but the kinematic relation of the two-band $s^\pm$-wave model, i.e. $\frac{\Delta N_s}{\Delta N_w} \sim \frac{\Delta N_s}{\Delta N_w}$ as $T \to T_c$. This robustness of the BNC scaling relation of FeSCs continues even in the coexistence region of AFM and superconductivity [129], as shown in the left-hand panel of figure 48. The numerical results in the right-hand panel of figure 48 show that the two-band $s^\pm$-wave model can faithfully generate the robust BNC scaling relation with and without AFM order ($M_{AFM}$).

Figure 47. Numerical calculations of $\Delta C/T_c$ versus $T_c$ with dimensionless coupling constants $V_{int} = 2.0$ and $V_{ intra} = 0.5$, for different impurity scattering strengths of $\Gamma_0$ and $\Gamma_e$ (in units of $\Lambda_{hi}$). The horizontal dashed line is the BCS limit of 0.936$N_0$ and the dotted lines of $\sim T_c^0$ (BNC scaling) and $\sim T_c^3$ (super-strong scaling) are guides for the eyes. Reproduced from [182]. © IOP Publishing Ltd. All rights reserved.

11.2. Condensation energy $\Delta E$ versus $T_c$

The CE $\Delta E$ of a superconductor is defined as the energy difference between the normal state and the SC state of the same system. In general, the size of the CE of any phase transition is a measure of how much more stable the ordered state is compared to the normal state, hence the CE is naturally related to the ordering (pairing) energetics and transition temperature $T_c$. For example, the magnetic transition with local moments, such as a classic limit of the Heisenberg model and Ising model, has the relation $\Delta E_{mag} \propto T_c$, while the BCS theory of the one-band superconductor predicts $\Delta E_{BCS} \propto T_c^2$ [43]. In view of this, as show in figure 49, the observation by Xing et al. [180] and Kim et al. [181] of $\Delta E \propto T_c^\gamma$ ($\gamma \approx 3.5$) for various FeSCs is very intriguing and should contain the crucial information about the SC pairing mechanism of the FeSCs.

11.2.1. Other theories.

As described in the introduction of this section, many researchers tend to connect some novel features of FeSCs to the QCP or the strong correlation effect. According to Zaanen’s hyperscaling argument [179], the SH at the normal state follows the scaling relation as $C \sim T^3$. However, it was already pointed out that these critical fluctuations, which would cause $C \sim T^3$, are not fermionic fluctuations, hence have no direct connection to the SH jump and the CE of the SC transition that is the fermionic reconstruction of the system. Nevertheless, the authors of [180] extrapolated the QCP relation $C \sim T^3$ to the electronic SH as $C \sim N_0T \sim T^3$, to obtain $N_0 \sim T^2$. Combining this result with the single-band BCS CE, $\Delta E = \frac{1}{2}N_0\Delta_0^2$ (where again the BCS relation $\Delta_0 \sim T_c$), it leads to $\Delta E \sim T_c^3$, close to the experimental observation $\Delta E \sim T_c^{3.5}$. As a ballpark estimation, this result appears to be not bad, but as we mentioned above we believe that this QCP scenario contains several inconsistent logical loopholes.

Another suggestion about the CE scaling was given by one of us [181], and it was shown with an extensive amount of collected data that this seemingly non-BCS scaling relation of CE, $\Delta E \sim T_c^{3.4-3.5}$ (in simple BCS theory, $\Delta E_{BCS} \sim T_c^2$) is actually obeyed not only by FeSCs but also by medium- ($\lambda = 0.46$) to strong-coupled phonon-mediated BCS superconductors (with $T_c > 1.4$ K), as shown in the left-hand panel of figure 50. However, it was also shown that many other superconductors, such as the phonon-mediated BCS superconductor MgB$_2$, heavy fermion and cuprate superconductors, etc, fail to follow anywhere close to this scaling. Nonetheless, in [181] it was found that all these superconductors—both those which do and those which do not follow the CE $\sim T_c^{3.5}$ scaling relation—obeys the universal scaling relation $\Delta E/\gamma \sim T_c^{2}$, as shown in the right-hand panel of figure 50. This surprisingly universal scaling relation $\Delta E/\gamma \sim T_c^2$ does not yet have a theoretical explanation, but it is suggestive of a renormalized BCS relation, namely the BCS prediction $\Delta E = \frac{1}{2}N_0\Delta_0^2$ with $\Delta_0^2 \sim T_c^2$, but replacing the DOS $N_0$ by a renormalized Sommerfeld constant $\gamma \sim N_0/(1 + \lambda)$, ($\lambda$ = dimensionless coupling constant).
Although it needs more a specific theory, this interpretation as a renormalized BCS relation suggests that the correlation or interaction effect could be an underlying origin of this anomalous scaling relation of the CE for the two-band \( \Delta \) model. Therefore the successful reproduction and explanation of these two seemingly non-BCS scaling relations do not primarily depend on the fine structure or ad hoc assumptions, and it is the exactly same model which already successfully explained the BNC scaling \( \Delta C \sim T_C^3 \). Here again the underlying mechanism for this success, which generates such a fast variation of the CE versus \( T_C \)—one order of magnitude faster than the single-band BCS theory—is the kinematic constraint \( \frac{\Delta C}{\Delta n} \sim \Delta P \) as \( T \to 0 \) of the two-band BCS model with a dominant inter-band pairing interaction.

Adding a repulsive intra-band interaction \( V_{\text{intra}} > 0 \) in the model increases the scaling power, but only slightly. However, adding an attractive intra-band interaction \( V_{\text{intra}} < 0 \) reduces the scaling power \( \beta \) quickly to the BCS value \( \beta_{\text{BCS}} \approx 2 \). All these interesting variations of the CE scaling behavior in multi-band superconductors can be understood from the fact that the CE gain \( \Delta E < 0 \) in the SC transition from the metallic state is a subtle balance/competition between the kinetic energy loss \( \Delta \Delta E > 0 \) and the potential energy gain \( \Delta \Delta P < 0 \). For more detailed discussions, we refer to [183]. In the right-hand panel of figure 51, the calculation results of CE \( \Delta E \) versus \( T_C \) including impurity scattering are shown. It shows that only a tiny amount of impurity scattering \( (V_{\text{imp}}/\Delta n \approx 0.02-0.03) \) is sufficient to increase the scaling power to an experimental value as \( \beta \to \beta_{\exp} \approx 3.5 \).
behaviors with the minimal two-band $s^\pm$-wave pairing model is an unexpected and surprising result. Together with the previous sections, which showed the extremely good compatibility of the $s^\pm$-wave gap with virtually all available experiments, the successful explanation of two anomalous scaling relations in this section strengthens the validity and consistency of the $s^\pm$-wave model as a correct theory for FeSCs. This leads us to speculate that the fundamental pairing mechanism of FeSCs is basically a BCS theory. Namely, strong correlation effects, abundantly observed in the normal state of the FeSCs, exist and renormalize the effective mass $m^*_{qp}$ of quasiparticles, the DOS $N_{b,c}$, the pairing interactions $V_{\text{inter, intra}}(q)$, etc. However, when the system enters the SC transition, the pairing mechanism and pairing energetics seem to be governed by the BCS pairing mechanism but with a non-phononic bosonic glue.

12. Conclusions

In this paper, we have reviewed the generic SC properties of the $s^\pm$-wave pairing state and critically examined them in comparison with the available experiments on FeSC compounds. The generic SC properties of the $s^\pm$-wave pairing state are as follows. (1) It is a $s$-wave full-gap superconductor with varying degrees of gap anisotropy; the gap function $\Delta(k)$ has no nodes. (2) However, the sign-changing OPs substantially modify the usual $s$-wave coherence factor of the large momentum exchanging processes such as, INS neutron scattering, the NMR $1/T_1$ spin-lattice relaxation rate, and various impurity scattering effects. (3) Combinations of (1) and (2) generate various nodal-gap-like SC features in different experimental probes. These nodal-gap-like features often cannot be distinguished from a real (kinematic) nodal gap, such as the $d$-wave SC-gap state, with a single type of experimental probe. Therefore, cross-checking with different probes is important to confirm the presence or absence of gap-nodes in the gap function $\Delta(k)$. The origin of the nodal-gap-like behaviors in the $s^\pm$-wave pairing state can be various. They can be due to the ’$V$’-shaped DOS dynamically induced by impurity scattering, not from the kinematic constraint of the nodal gap function $\Delta(k)$ itself. They can also be due to the size difference between multiple gaps, for example, $|\Delta_b| > |\Delta_c|$ or vice versa or the inverse relation(s) $\frac{N^b_{\text{ext}}}{\Gamma} \approx \frac{|\Delta_b|}{|\Delta_c|}$. Finally it can be due to combinations of some of these. In this review, we have explained how these various mechanisms can generate nodal-gap-like behaviors in the $s^\pm$-wave pairing state and made comparisons with the relevant experiments, side by side. As
a result, we have shown that almost all nodal-gap evidence—as initially conceived—in FeSCs turned out to be supporting evidence for the $s^\pm$-wave pairing state.

Through the cross-checking between theory and experiment, a few FeSC compounds were indeed found to have a nodal gap, for example, K-overdoped (Ba,K)Fe$_2$As$_2$ by ARPES [39–41], and FeSe by scanning tunneling microscopy measurements [193]. However, these nodal gaps still obey $A_{1g}$ crystal symmetry, which can be continuously evolved from the $s^\pm$-wave pairing state. Therefore the origin of the nodal gap in these compounds is not like that for a $d$-wave nodal gap, and these nodes are accidental nodes. There exist other strong candidates for a nodal gap from the penetration depth and thermal conductivity measurements, such as BaFe$_2$(As,P)$_2$ [143, 144, 150] and LaFePO [141, 142], which need to be confirmed with different probes. We summarize the situation as follows. The absolute majority of the FeSCs have multiple $s$-wave full gaps, but often display nodal-gap-like behaviors in various SC properties, which is consistent with the generic $s^\pm$-wave pairing state. A few FeSC compounds were confirmed or have a strong possibility to have nodal gaps. The confirmed nodal-gap structure preserves the same $A_{1g}$ symmetry as the $s^\pm$-wave pairing state, hence they are accidental nodes. We expect that the not-yet-confirmed ones also belong to the same category, even if these compounds indeed possess a nodal gap. Therefore, as to the pairing symmetry and pairing mechanism, finding a nodal gap or not in the FeSCs is not an essential issue. The $s^\pm$-wave pairing state remains valid as the standard paradigm of the FeSCs.

As mentioned in the introduction, identifying the gap symmetry and gap function does not mean identifying the pairing mechanism, but only providing some constraints for the correct theory. There is seldom a direct experimental probe for the pairing mechanism, because the mechanism is usually an idea and concept which cannot be seen. It can be at best agreed on only through circumstantial evidence with the extensive consistency checks with experiments. In section 11, we discussed a possible explanation of the anomalous scaling behaviors, observed in the SH jump versus $T_c$ and the CE versus $T_c$ for about 40–50 FeSC samples, with a generalized BCS theory. This issue is not yet closed, and other theoretical explanations based on the strong correlation might be possible. At the moment, the BCS pairing mechanism—with a non-phononic pairing boson—for the FeSCs is not a very exciting idea, but at least it is very much consistent with the $s^\pm$-wave pairing model in understanding these anomalous scaling behaviors.

There are several important experimental probes not covered in this review, for example, infrared spectroscopy and tunneling spectroscopy, simply because we do not have sufficient expertise and time to cover these specialized subjects which have a vast amount of research papers. Nevertheless, we can say that these powerful spectroscopic tools also support the $s^\pm$-wave pairing state with almost all FeSC compounds [194–196], except a few, for example, FeSe [193]. We refer to the already existing excellent review articles [197–200] and references therein for further discussions of these specific experimental probes. We also did not discuss electronic Raman spectroscopy. Although this experimental tool has played a very active role in investigating the $d$-wave superconductivity in the high-$T_c$ cuprate superconductors [201], it has not been as actively used with FeSCs. One reason is that the FeSC compounds are multi-band systems with many complicated FSs, while the cuprates have a single large FS. As a result, the symmetry analysis of Raman spectra becomes more complicated and has more uncertainty [202, 203]. Nevertheless, some interesting physics has been uncovered uniquely with Raman spectroscopy, such as new collective modes [204], anomalous phonon frequency shifts [205], etc, in the SC phase. Again, to date Raman spectroscopy experiments are mostly consistent with the $s^\pm$-wave pairing state.

Finally, the so-called heavily electron-doped iron selenide (HEDIS) systems, such as the FeSe/SrTiO$_3$ monolayer system ($T_c \approx 60–100$ K) [206–208], A$_x$Fe$_y$Se$_z$ (A = K, Rh, Cs, TI, etc) ($T_c \approx 30–40$ K) [209–211], (Li$_{1-x}$Fe$_x$OH)FeSe ($T_c \approx 40$ K) [212], and pressurized bulk FeSe ($T_c \approx 37$ K) [213], are posing a serious challenge to the standard paradigm of the $s^\pm$-wave pairing state for FeSC compounds, which was the only pairing state covered in this review. These HEDIS systems share one distinct common factor, which is completely different from the other standard FeSC systems, namely, they do not have hole pockets around the $\Gamma$ point in the BZ and have only electron pockets at the $M$ points. Without hole pockets, it is immediately clear that the standard picture of the $s^\pm$-wave pairing state cannot be formed (see figure 1). Understanding the superconductivity in HEDIS systems is currently the hottest subject in FeSC research, with the pressing fundamental questions: (1) Why and how is $T_c$ so high, up 100 K? (2) What are the pairing mechanism and pairing state with only electron pockets at the $M$ point? (3) Does the standard paradigm of the $s^\pm$-wave pairing state continue to work or not? We do not discuss this extremely important subject in this review, but it is a rapidly developing subject and there already exists a growing volume of research papers, we refer the reader to [9, 214–217] and references therein.

Acknowledgments

YKB acknowledges NRF Grant 2016-R1A2B4-008758 funded by the National Research Foundation of Korea, and GS acknowledges a DOE grant, Office of Basic Energy Sciences, DE-FG02-86ER45268.

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