First-principles-based $\pm s$-wave modelling for iron-based superconductors: Studies for specific heat and nuclear magnetic relaxation rate

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In order to consistently explain controversial experimental results on superconducting states observed by different probes in typical iron-based superconductors, we construct a realistic multi-band $\pm s$-wave pairing model by combining the quasiclassical formalism with the first-principles calculation. The model successfully resolves the controversies in contrast to the fact that simplified models such as two-band $\pm s$-wave one fail to do. A key in the model is the existence of relatively small gaps which leads to material-dependent peculiarities.

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The discovery of the iron-pnictide superconductor LaFeAs(O$_{1-x}$F$_x$)\textsuperscript{[1]} made a striking impact on materials science, because this compound includes the element of the most familiar ferromagnetic metal, Fe, as a main component. The transition temperature $T_c$ in the so-called “1111” compounds RFeAs(O$_{1-x}$F$_x$) (R=Pr, Nd, Sm) exceeds 50K, which is the highest except for high $T_c$ cuprates. In addition to the high transition temperature, the variety of related materials is quite rich. For example, “122” compounds $(A_1-x_{2}B_x)$Fe$_2$As$_2$ $(A=$Ba, Sr, Ca, $B=$K, Cs, Na) and “11” compounds Fe(Se$_x$Te$_{1-x}$) are the typical family materials, whose element substitutions are widely possible\textsuperscript{[2, 3]}. In particular, the superconductivity is surprisingly robust against substitutions of Ni and Co for Fe.

In contrast to the discovery rush of family compounds, their superconducting states still remain elusive. There is no established pairing-symmetry model explaining all experimental results consistently. In the early days, puzzling experimental data were reported. In spite of sharp resistivity drops and clear Meissner signals at the superconducting transition $T_c$, the jump of $C/T$, where $C$ is the specific heat and $T$ is the temperature, was hardly observable in 1111 compounds. The reason was initially ascribed to a large phonon contribution which masks an electronic one. Afterwards, a small jump at $T_c$ and the concave-down temperature dependence of $C/T$ below $T_c$ were confirmed in not only 1111 compounds\textsuperscript{[4, 5]} but also structurally equivalent LaFeP(O$_{1-x}$F$_x$)\textsuperscript{[6]}. This fact strongly suggests the existence of rather small superconducting gap\textsuperscript{[7]} in addition to large main gaps in the cases of $s$-wave gap. In this paper, we clarify that such a multi-gap structure consistently explains all experimental observations of 1111 compounds by means of a realistic five-band $\pm s$-wave pairing model based on a first-principles calculation. A striking result of the model is a natural reproduction of the nuclear magnetic relaxation rate $1/T_1$ below $T_c$.

On the other hand, 122 compounds experimentally exhibit large jumps and exponential behavior in $C/T$ like conventional superconductors\textsuperscript{[6, 8, 9, 10]}. Moreover, the power law in the $T$-dependence of $1/T_1$ below $T_c$ is different from that of 1111 compounds\textsuperscript{[8, 11, 12, 13]}. In fact, an angle resolved photoemission spectroscopy (ARPES) study reported that all gaps fully open and the difference between their gap amplitudes is not so significant\textsuperscript{[14]}. In this case, we reveal that the multi-gap structure according to ARPES data can consistently explain the specific heat and $1/T_1$ data without any assumptions except for $\pm s$-wave paring symmetry\textsuperscript{[13, 15]}. From the present analyses on 1111 and 122 compounds, it is found that the existence of the relatively small gap gives rise to the material variety. We believe that this fact has an key role on the quest for the superconducting mechanism.

Let us present a procedure to construct the realistic multi-band model. For the band structure around the Fermi level $E_F$, we perform a first-principles calculation\textsuperscript{[16]}, which provides multiple Fermi-surfaces and their density of states (DOS) at $E_F$ depending on the target materials. When evaluating superconducting gaps for multi-band superconductors, we examine all the experimental data and select key data. ARPES measurements are successful for 122 compounds\textsuperscript{[14]}. Therefore, we can directly fit ARPES data to determine the gap amplitudes on each band in the 122 case. On the other hand, ARPES\textsuperscript{[18]} measurements are technically difficult for 1111 compounds. Instead, we adopt data of $C/T$\textsuperscript{[6]} and the penetration depth\textsuperscript{[19, 20]} in the 1111 case. In fact, those data clearly suggest that the pairing symmetry is full-gap but a small single or small multi gaps coexist with main large gaps\textsuperscript{[19, 20, 21, 22, 23, 24]}. We describe the expression for $C/T$ here, while we refer readers to Refs.\textsuperscript{[25, 26, 27, 28, 29, 30]} for $1/T_1$. The $T$-dependence...
The intra-band interaction, and the effective coupling constant. In addition, the specific heat is evaluated by the second derivative of the free energy. The free energy can be evaluated by the quasiclassical theory of superconductivity, which is a mean field treatment convenient in evaluating superconducting properties. To calculate C/T and 1/T, we need the T-dependence of the multiple superconducting pair-potentials on each band. For this purpose, we solve the gap equations for multi-band superconductors. With Matsubara frequency \( \omega_n = (2n + 1)\pi T \), the gap equations are written as

\[
\Delta_\alpha = 2\pi T \sum_{\omega_n > 0} \sum_\beta \lambda_{\alpha\beta} f_\beta(i\omega_n),
\]

\[
\Delta_\alpha^* = 2\pi T \sum_{\omega_n > 0} \sum_\beta \lambda_{\alpha\beta} f_\beta(i\omega_n),
\]

where \( \alpha \) and \( \beta \) stand for the band index, and \( \lambda_{\alpha\beta} \) is the effective coupling constant. In addition, \( \lambda_{\alpha\beta} = N_\beta \lambda_{\alpha\alpha}/N_\alpha \) with \( N_\alpha \) being DOS at \( E_F \) for \( \alpha \)-band. \( \lambda_{\alpha\alpha} \) comes from the intra-band interaction, and \( \lambda_{\alpha\beta} \), where \( \alpha \neq \beta \), gives the pair-hopping between the different bands. The effective coupling constants \( \lambda_{\alpha\beta} \)'s are employed as parameters to reproduce the experimental results for the superconducting gaps. Again, we note the selected experiment type depending on a kind of the compounds, i.e., ARPES for the 122 compounds, and the specific heat and the penetration depth for the 1111 compounds.

The quasiclassical Green’s functions \( g_\alpha(i\omega_n) \), \( f_\alpha(i\omega_n) \), and \( f_\alpha^{(1)}(i\omega_n) \) follow the Eilenberger equations as,

\[
\omega_n f_\alpha(i\omega_n) = \Delta_\alpha g_\alpha(i\omega_n),
\]

\[
\omega_n f_\alpha^{(1)}(i\omega_n) = \Delta_\alpha^* g_\alpha(i\omega_n),
\]

\[
g_\alpha^2(i\omega_n) = 1 - f_\alpha(i\omega_n)f_\alpha^{(1)}(i\omega_n),
\]

where \( \text{Re} \, g_\alpha(i\omega_n) > 0 \) for \( \omega_n > 0 \). The free energy difference between the superconducting and normal states, \( F_{\text{sn}} = F_{\text{super}} - F_{\text{normal}} \), is expressed as

\[
F_{\text{sn}} = -2\pi T \sum_\alpha \sum_{\omega_n > 0} N_\alpha \left[ 1 - g_\alpha(i\omega_n) \Delta_\alpha f_\alpha(i\omega_n) \right],
\]

which demands the solutions of Eqs. (3), (4), and (5),

\[
f_\alpha(i\omega_n) = \frac{\Delta_\alpha}{\sqrt{\omega_n^2 + |\Delta_\alpha|^2}},
\]

\[
f_\alpha^{(1)}(i\omega_n) = \frac{\Delta_\alpha^*}{\sqrt{\omega_n^2 + |\Delta_\alpha|^2}},
\]

\[
g_\alpha(i\omega_n) = -\frac{\omega_n}{\sqrt{\omega_n^2 + |\Delta_\alpha|^2}}.
\]

Note that \( f_\alpha^{(1)}(i\omega_n) \rightarrow 0 \) and \( g_\alpha(i\omega_n) \rightarrow 1 \) when \( \omega_n \gg |\Delta_\alpha| \). The cut-off frequency \( \omega_c \) is introduced as \( \sum_{\omega_n > 0} \frac{\omega_n}{\omega_n^2 + |\Delta_\alpha|^2} \). Equation (6) indicates that \( F_{\text{sn}} \) can be directly evaluated by DOS \( N_\alpha \) obtained from first-principle calculations and the gap values \( \Delta_\alpha \).
Since $C/T$ at constant volume is generally obtained by $C/T = \partial S/\partial T = -\partial^2 F/\partial T^2$, the specific heat in the superconducting state is expressed as

$$C_s - C_n = -\frac{\partial^2 F_{sn}}{\partial T^2}, \quad (10)$$

where $C_{s(n)}$ is the specific heat of the superconducting state (normal state). We can rewrite $C_n/T$ as $\gamma_n$, which is the Sommerfeld coefficient. Thus, we numerically calculate $\partial^2 F_{sn}/\partial T^2$ to obtain $C_s/T$. As for $1/T_1$, we use the measured structural data \[2\]. The obtained Fermi surfaces are displayed in Fig. 1(b). The calculation gives DOS’s at $E_F$, which are input parameters in the gap equations (1) and (2) and the free energy (6). Each DOS at $E_F$ is written as $N_\alpha$, where $\alpha$ is numbered as $\alpha = 1, 2, 3, 4, 5$ from $\Gamma$ point (zone center) to X as shown in Fig. 1(b), and $\alpha = 1$ to 3 (4 to 5) correspond to hole (electron) bands. Throughout this paper, we adopt $\pm$s-wave pairing model since other choices fail to reproduce the experimental data consistently. The positive (negative) sign is assigned to $\Delta_\alpha$ of hole (electron) bands ($\Delta_\alpha$ are assumed to be real). The $T$-dependence of $\Delta_\alpha$ is calculated so as to follow the ARPES result \[14\] (Case B1) as shown in Fig. 1(c). On the other hand, in Fig. 1(d) we show, for comparison, the result (Case B2) with the minimum $|\Delta_3|$ being slightly bigger than the ARPES result. Figure 1(e) shows the $T$-dependences of $C_s/C_n$. Both Cases B1 and B2 show no significant difference from the weak coupling single-band Bardeen-Cooper-Schrieffer (BCS) result. One of the reasons is that the weighting of the small-gap band is small compared to total one, i.e., the ratio $N_3/N_1$ is 0.2, where $N_1$ is the total DOS ($N_t = \sum \alpha N_\alpha$). Moreover, the gap-amplitude difference between the minimum $|\Delta_3|$ and the maximum $|\Delta_2|$ is not so large, where $|\Delta_3|/|\Delta_2| \sim 0.5$ ($\sim 0.7$) for Case B1 (B2). On the other hand, the influence of $|\Delta_3|/T_c \sim 2$, which is bigger than the single-band’s value 1.76, slightly enhances $C_s/T$ at $T_c$. As a result, the difference in $C/T$ becomes small among Case B1, B2 and single-band case. The $T$-dependences of $C/T$ in Cases B1 and B2 are consistent with the experimental observations \[5\].

On $T$-dependence of $1/T_1$, both the cases show significant differences from the single-band BCS case as shown in Fig. 1(f). The coherence peak just below $T_c$ is absent in both Cases B1 and B2, because the cancellation between “+” and “−” signs of $\Delta_\alpha$ is effective. In contrast, in the single-band BCS case, even if the damping rate of the quasiparticle is taken large as $\eta = 0.1 T_c$, the peak is clearly identified as seen in Fig. 1(f). Moreover, the low-lying excitation arising from the small gap $|\Delta_3|$ alters $T$-dependence of $1/T_1$ compared to the single-band s-wave case. We point out that the five-band model Case B1...
played in Fig. 2(b), where $\Gamma$ (zone center) to M. The five Fermi surfaces are displayed in Fig. 2(h), where $N_1$, $N_2$, $N_3$ ($N_4$, $N_5$) are the DOS at $E_F$ of hole (electron) bands. We prepare two types of multi-gap structures, Cases L1 and L2, whose $T$-dependences of $\Delta_\alpha$ are plotted in Figs. 2(c) and 2(d), respectively. These are estimated by experimental data of $C/T$ and the penetration depth, because direct experimental ARPES data of the gaps are not presently available in 1111 compounds. Case L1 gives the jump of $C/T$ at $T_c$ decreases. For comparison, we note that the small gap in the 122 compounds as shown in Fig. 1(e) is not enough to reduce the jump of $C/T$ like the present 1111 compound case. In addition, Case L2 reproduces the concave-down behavior as observed in LaFeAsO as shown in Fig. 2(a). GGA with measured structural parameters [34], we obtain the band structure of LaFeAsO successfully reproduces the experimental results of $C/T$ and $1/T_1$[4,13].

We next turn to 1111 compounds. At first, based on GGA with measured structural parameters [34], we obtain the band structure of LaFeAsO as shown in Fig. 2(a). The band index is also numbered as $\alpha = 1, 2, 3, 4, 5$ from $\Gamma$ (zone center) to M. The five Fermi surfaces are displayed in Fig. 2(h), where $N_1$, $N_2$, $N_3$ ($N_4$, $N_5$) are the DOS at $E_F$ of hole (electron) bands. We prepare two types of multi-gap structures, Cases L1 and L2, whose $T$-dependences of $\Delta_\alpha$ are plotted in Figs. 2(c) and 2(d), respectively. These are estimated by experimental data of $C/T$ and the penetration depth, because direct experimental ARPES data of the gaps are not presently available in 1111 compounds. Case L1 gives the jump of $C/T$ at $T_c$ decreases. For comparison, we note that the small gap in the 122 compounds as shown in Fig. 1(e) is not enough to reduce the jump of $C/T$ like the present 1111 compound case. In addition, Case L2 reproduces the concave-down behavior as observed in LaFeAsO as shown in Fig. 2(a). GGA with measured structural parameters [34], we obtain the band structure of LaFeAsO successfully reproduces the experimental results of $C/T$ and $1/T_1$[4,13].

Finally, we add a note that the momentum dependence of the gap amplitudes is reported by some recent experiments [35,36,37] of the related compound. Such an anisotropy can be easily implemented in the present framework.

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