Effect of realistic finite-size impurities on $T_c$ in Fe-based superconductors based on the five-orbital tight-binding model

Youichi YAMAKAWA$^1$, Seiichiro ONARI$^2$, and Hiroshi KONTANI$^1$

$^1$ Department of Physics, Nagoya University, Furo-cho, Nagoya 464-8602, Japan.
$^2$ Department of Applied Physics, Nagoya University, Furo-cho, Nagoya 464-8602, Japan.

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We present a systematic study of the impurity effect on $T_c$ in Fe-based superconductors, assuming that the sign-reversal $s$-wave state due to inter-pocket repulsion ($s_{++}$-wave state) is realized. For this purpose, we introduce several realistic impurity models with non-local modifications of potentials and hopping integrals around the impurity site. When we use the impurity model parameters for 3d- and 4d-impurity atoms derived from the recent first principle study by Nakamura et al., we find that the $s_{\pm}$-wave state is very fragile against impurities: The superconductivity without impurities $T_{c0} = 30K$ is destroyed by introducing small residual resistivity $\rho_0^c = 5\zeta^{-1} \sim 10\zeta^{-1} \ [\mu \Omega cm]$ ($\zeta^{-1} = m^*/m$ being the mass-enhancement factor), consistently with the previous theoretical study for the on-site impurity model by Onari and Kontani. This result is essentially unchanged for different non-local impurity models with realistic parameters. We also discuss the effect of the impurity-induced non-local orbital order on the superconducting state.

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I. INTRODUCTION

Since the discovery of Fe-based high-$T_c$ superconductors [1], the symmetry and the gap structure of the superconducting (SC) state have been studied very intensively. It had been established experimentally that $s$-wave ($A_{1g} \text{ symmetry}$) SC state is realized in usual Fe-based superconductors. The gap structure in many optimally-doped high-$T_c$ compounds is nearly isotropic and fully-gapped [2–4], although some compounds show accidental nodal gap structure. In the phase diagram, the SC phase is realized next to the orthorhombic structure transition at $T_S$, and the magnetic order is also realized at $T_N \lesssim T_S$. Below $T_S$, the orbital polarization $n_{xz} \neq n_{yz}$ is realized [5], and sizable softening of shear modulus $C_{66}$ [6–8] indicates the development of orbital fluctuations near the orthorhombic phase. Strong spin fluctuations are also observed near the magnetic ordered phase.

These observed orbital and spin quantum criticalities have been intensively studied theoretically, since they would be closely connected to the pairing mechanism. Within the random-phase-approximation (RPA), strong spin fluctuations develop in the multiorbital Hubbard models for Fe-based superconductors. Therefore, spin-fluctuation-mediated $s$-wave state with sign reversal ($s_{\pm}$-wave state) is obtained by the RPA [9–12]. However, the RPA fails to explain the non-magnetic structure transition at $T_S$. Also, orbital-fluctuation-mediated $s$-wave state without sign reversal ($s_{++}$-wave state) is realized by introducing the quadrupole interaction $g_{\text{quad}}$ due to Fe-ion oscillations [13–15]. Even for $g_{\text{quad}} = 0$, strong orbital fluctuations are obtained by improving the RPA by including the vertex correction (VC) for the susceptibility that is dropped in the RPA [16, 17]: Since spin and orbital fluctuations mutually develop in the self-consistent VC method, both $s_{\pm}$-wave and $s_{++}$-wave states can be obtained by solving the multiorbital Hubbard model.

To distinguish between these two SC gap states, various phase-sensitive experiments had been performed [18–25]. For example, inelastic neutron scattering experiments had been performed to find the magnetic resonance scattering due to the sign reversal [19–21]. However, observed “resonance-like” hump structure can be explained even if $s_{++}$-wave state is realized [26]. Impurity effect measurement is another significant phase-sensitive experiment since $T_c$ would be strongly suppressed by inter-pocket impurity scattering of Cooper pairs if $s_{++}$-wave state is realized [22–25]. Many theoretical studies have been devoted so far [12, 27–32]. In Ref. [30], the present authors studied the impurity effect due to local nonmagnetic impurities based on the realistic multiorbital model, and showed that $T_c$ in the $s_{++}$-wave state is strongly suppressed by inter-pocket impurity scattering of Cooper pairs. However, effect of the possible non-locality of the impurity potential had not been studied.

Therefore, in this paper, we present a quantitative study of the non-local impurity effect on the $s_{++}$-wave state based on the realistic five-orbital model for Fe-based superconductors. We introduce realistic models of Fe-site substitutional impurity atoms, which contains the non-local modifications of potentials ($I, V_1, V_2$) and hopping integrals ($\Delta t$) around the impurity site, referring to a recent first principle study by Nakamura et al. [33]. In various non-local impurity models with realistic parameters, the $s_{++}$-wave state is very fragile against impurities: Original transition temperature at $T_{c0} = 30K$ is destroyed when the residual resistivity is just $\rho_0^c = 5\zeta^{-1} \sim 10\zeta^{-1} \ [\mu \Omega cm]$, where $\zeta^{-1} = m^*/m$ is the mass-enhancement factor. This result is consistent with the previous theoretical study for the on-site impurity model in Ref. [30]. Thus, experimentally observed robustness of $T_c$ against impurities in various (optimally-doped) Fe-based superconductors [22–25] would indicate the realization of the $s_{++}$-wave state.
The effect of Fe-site substitution on $T_c$ had been carefully studied in La(Fe,X)As(O,F) for X=Co,Ni [34] and in Ba(Fe,X)$_2$As$_2$ as well as Ba(Fe$_{1-x}$Co$_x$Cu$_y$)$_2$As$_2$ [35–37]. In these materials, $T_c$ is well scaled by the amount of carrier doping caused by X-atom substitutions, not by the impurity concentration irrespective of the large impurity potential [37]. This fact would mean the robustness of the SC state against strong impurity scattering in these materials as stressed in Ref. [34].

In Fe-based superconductors, impurity potential matrix $I_b(k,k')$ in the band-diagonal basis is $k$-dependent, reflecting the multi-orbital band structure [30]. However, their $k$-dependences had been frequently neglected in previous studies for simplicity. In this “constant $I_b$ model”, both the intra-band and inter-band scatterings, $I_b$ and $I'_b$, are constant parameters. In this model, the $s_\pm$-wave state can be stable against impurities when $|I'_b/I_b| \ll 1$, although it seems unrealistic since both hole-Fermi surfaces (h-FSs) and electron-Fermi surfaces (e-FSs) are composed of the common $d$-orbitals [30]. In addition, obtained results are strongly changed in the unitary and intermediate regimes once the $k$-dependence of $I_b$ is taken into account; see Sec. V C.

II. MODEL HAMILTONIAN

In this paper, we study the impurity effect based on the realistic two-dimensional five-orbital tight-binding model [9]:

$$H_0 = \sum_{k,\sigma, l,l'} \hat{h}_{k}^{ll'} c_{kl\sigma}^\dagger c_{kl'\sigma},$$  \hspace{1cm} (1)

where $\hat{h}_{k}$ is the 5 x 5 matrix given by the Fourier transformation of the hopping integral $t_{r,l,r',l'}^{0}$ introduced in Ref. [9]. Here, $l,l'$ represents the orbital indices, and $\sigma$ is the spin index. The matrix elements of $\hat{h}_{k}$ is given by the Fourier transformation of the hopping integral $t_{r,l,r',l'}^{0}$. When the electron filling per Fe-site is $n = 0.6$, there are two hole-pockets around the $\Gamma$ point, one hole-pocket around $(\pi,\pi)$ point, and two electron-pockets around $(\pi,0)$ and $(0,\pi)$ points.

In addition, we introduce the following nonmagnetic and non-local impurity potential at site $0 = (0,0):$

$$H_{\text{imp}} = \sum_{l,\sigma} c_{0l\sigma}^\dagger c_{0l\sigma} + V_1 \sum_{r} \sum_{l,\sigma} c_{rl\sigma}^\dagger c_{rl\sigma} + V_2 \sum_{r', l,\sigma} c_{r'l\sigma}^\dagger c_{r'l\sigma} + \sum_{r} \sum_{l,l',\sigma} \Delta \Sigma_{l,l'}^{(1)} (c_{0l\sigma}^\dagger c_{rl'\sigma} + \text{h.c.}) + \sum_{r'} \sum_{l,l',\sigma} \Delta \Sigma_{l,l'}^{(2)} (c_{0l\sigma}^\dagger c_{r'l\sigma} + \text{h.c.}),$$

where $I_b(k,k')$ is given by the Fourier transformation of the on-site, nearest-neighbor (NN), and next-nearest-neighbor (NNN) impurity potential, and $\Delta \Sigma_{l,l'}^{(i)}$ is the modulation of the NN or NNN hopping integrals between site 0 and site $r$. The present impurity potential model is depicted in Fig. 1.

![FIG. 1: (Color online) The present non-local impurity potential.](image)

III. GAP EQUATION, CALCULATION OF RESIDUAL RESISTIVITY

In the present model, the $T$-matrix due to infinite number of impurity scattering processes is given as

$$\tilde{T}(i\epsilon_n) = \tilde{W}(1 - \tilde{g}(i\epsilon_n) \cdot \tilde{W})^{-1},$$  \hspace{1cm} (3)

where $\tilde{g}_{r,l,r',l'}(i\epsilon_n)$ is the free Green function in real space, given by the Fourier transformation of $\tilde{G}_k(i\epsilon_n) = (i\epsilon_n + \mu - \tilde{h}_{k})^{-1}$, and $\epsilon_n = (2n + 1)\pi T$ is the fermion Matsubara frequency.

When the impurity concentration is dilute ($n_{\text{imp}} \ll 1$), the normal self-energy above $T_c$ is well approximated by the $T$-matrix approximation. It is given by

$$\delta \Sigma_k^\alpha(i\epsilon_n) = n_{\text{imp}} \tilde{T}_{k,k'}(i\epsilon_n) \big|_{k=k'},$$  \hspace{1cm} (4)

where $\tilde{T}_{k,k'}(i\epsilon_n)$ is given by the Fourier transformation of eq. (3). The retarded (advanced) self-energy is given by the analytic continuation $\delta \Sigma_k^\alpha(\epsilon) = \delta \Sigma_k^\alpha(\epsilon + i0) \cdot \text{sgn}(\epsilon)$:

$$\delta \Sigma_k^\alpha(\epsilon) = \delta \Sigma_k(\epsilon, \epsilon + (-1)i0).$$

Then, the Green function in the band-diagonal basis is $\tilde{G}_k^\alpha(\epsilon) = 1/(\epsilon + \mu - E_{\text{ak}} - i\gamma_{\text{ak}}(\epsilon))$, where $\alpha$ is the band index, $E_{\text{ak}}$ is the dispersion of the $\alpha$th band, and $\gamma_{\text{ak}}(\epsilon) = -\text{Im} \delta \Sigma_k^\alpha(\epsilon)$ is the quasiparticle damping rate due to impurities. $\gamma_{\text{ak}}(0)$ can be rewritten as

$$\gamma_{\text{ak}}(0) = -n_{\text{imp}} \sum_{k',\beta} |T_{\text{ak},\beta k'}(0)|^2 \text{Im} G_{\beta k'}(0),$$

where $T_{\text{ak},\beta k'}(0)$ is the on-site, nearest-neighbor (NN) and next-nearest-neighbor (NNN) impurity potential. $T_{\text{ak},\beta k'}(0)$ is the hopping integral between site $0$ and site $r$. The present impurity potential model is depicted in Fig. 1.

$$\gamma_{\text{ak}}(0) = \frac{n_{\text{imp}}}{4\pi} \sum_{\beta} \int_{FS,\beta} \frac{dk'}{v_{\text{F},\beta}} |T_{\text{ak},\beta k'}(0)|^2,$$  \hspace{1cm} (5)
where \( f_{FS\alpha}dk \) is the integration on the FS\( \alpha \).

When the impurity concentration is low enough, the inter-band contribution to the conductivity is negligible. If we drop the current vertex correction (CVC), the conductivity is given by

\[
\sigma_{\nu}^\text{no CVC} = \frac{e^2}{c} \sum_{k,\alpha} \int \frac{dk}{\pi} \left( -\frac{\partial f}{\partial \epsilon} \right)_{E_{\nu k}} |G^R_{\nu k}(\epsilon)|^2 v_{\alpha k,\nu}^2, \quad (6)
\]

where \( \nu = x \) or \( y \), \( f(\epsilon) = (e^{\epsilon/T} + 1)^{-1} \), \( v_{\alpha k,\nu} = dE_{\alpha k}/dk_\nu \) is the quasiparticle velocity, and \( c \) is the inter-layer distance. However, to obtain the exact conductivity for \( n_{\text{imp}} \ll 1 \), the CVC should be taken into account. The exact expression for the conductivity is given as

\[
\sigma_{\nu} = \frac{e^2}{c} \sum_{k,\alpha} \int \frac{dk}{\pi} \left( -\frac{\partial f}{\partial \epsilon} \right)_{E_{\nu k}} |G^R_{\nu k}(\epsilon)|^2 v_{\alpha k,\nu} J_{\alpha k,\nu}(\epsilon), \quad (7)
\]

Hereafter, we put \( c = 0.6nm \) that corresponds to Ba122 compounds. \( J_{\alpha k,\nu}(\epsilon) \) is the total velocity with CVC, which is given by solving the following Bethe-Salpeter equation:

\[
J_{\alpha k,\nu}(\epsilon) = v_{\alpha k,\nu} + n_{\text{imp}} \sum_{\beta',\beta} |T^R_{\alpha k,\beta',\beta}(\epsilon)|^2 |G^R_{\beta',\beta}(\epsilon)|^2 J_{\beta,\beta'}(\epsilon), \quad (8)
\]

where \( T^R_{\alpha k,\beta',\beta}(\epsilon) \) is the T-matrix in the band-diagonal basis. Here, we neglect the inter-band contribution since it is negligible when \( n_{\text{imp}} \ll 1 \).

Next, we study the impurity effect on \( T_c \). The gap equation at \( T = T_c \) in the band basis is given by

\[
Z_{\alpha k}(\epsilon_n) \Delta_{\alpha k}(\epsilon_n) = -\frac{T_c}{4\pi} \sum_{\beta,\eta} \int_{FS\beta} \frac{dk'}{v_{\beta'k'}} V_{\alpha k,\beta k'}(\epsilon_n, \epsilon_m) \times \frac{\Delta_{\beta k'}(\epsilon_m)}{|\epsilon_m|} + \delta \Sigma^a_{\alpha k}(i\epsilon_n), \quad (9)
\]

where \( \Delta_{\alpha k} \) is the SC gap function in the band-diagonal basis, and \( V \) is the pairing interaction. \( Z_{\alpha k}(\epsilon_n) = 1 + \gamma_{\alpha k}(\epsilon_n)/|\epsilon_n| \), and \( \delta \Sigma^a_{\alpha k} \) is the linearized anomalous self-energy given as

\[
\delta \Sigma^a_{\alpha k}(i\epsilon_n) = n_{\text{imp}} \sum_{\beta',\beta} |T_{\alpha k,\beta',\beta}(i\epsilon_n)|^2 |G_{\beta',\beta}(i\epsilon_n)|^2 \Delta_{\beta k'}(i\epsilon_n) = \frac{n_{\text{imp}}}{4\pi} \sum_{\beta} \int_{FS\beta} \frac{dk'}{v_{\beta'k'}} |T_{\alpha k,\beta',\beta}(i\epsilon_n)|^2 \frac{\Delta_{\beta k'}(i\epsilon_n)}{|\epsilon_n|}, \quad (10)
\]

By solving the gap equation (9) together with eqs. (4) and (10), the impurity effect on \( T_c \) for \( n_{\text{imp}} \ll 1 \) is exactly calculated within the BCS theory.

The reduction in \( T_c \) is caused by the function \( \gamma_{\alpha k} \cdot \Delta_{\alpha k}/|\epsilon_n| - \delta \Sigma^a_{\alpha k} \), which vanishes if \( \Delta_{\alpha k} \) is independent of band and momentum (=isotropic \( s_{\pm} \)-wave state) according to eqs. (5) and (10). Then, the independence of \( T_c \) against impurities is derived from this relation, known as the Anderson theorem. However, Anderson theorem is totally violated in the \( s_{\pm} \)-wave state.

In the present study, we consider the case of spin fluctuation mediated intra-orbital repulsive interaction between e-FS and h-FS. Then, the spin susceptibility is approximately diagonal with respect to the \( d \)-orbital, since it is strongly enhanced by the intra-orbital repulsion \( U \). That is, spin-spin correlation develops only in the same \( d \) orbital. By taking this fact into account, we introduce the following repulsive pairing interaction:

\[
V_{\alpha k,\beta k'}(\epsilon_n, \epsilon_n') = g \sum_l |U_{l,\alpha}(k)|^2 |U_{l,\beta}(k')|^2 R_{l,\alpha}^2 \epsilon_n \epsilon_n', \quad (11)
\]

for \( \alpha \in \alpha \)-FS and \( \beta \in \beta \)-FS and vice versa, and \( V_{\alpha k,\beta k'} = 0 \) for \( \alpha, \beta \in \alpha \)-FS or \( \alpha, \beta \in \beta \)-FS. \( U_{l,\alpha}(k) = (l, k, l, k) \) is the unitary matrix connecting between band-basis and orbital-basis, and \( D(x) = \omega_c^2/(x^2 + \omega_c^2) \), where \( \omega_c \) is the cut-off energy of the pairing interaction. In the present study, we put \( g = 3.22eV \) and \( \omega_c = 0.03eV \). In this case, a fully-gapped \( s_{\pm} \)-wave state with \( T_{\text{co}} = 30K \) is realized when \( n_{\text{imp}} = 0 \). Hereafter, we set the unit of energy is eV, and the unit of temperature is K.

IV. NUMERICAL RESULTS

A. Nakamura’s impurity model

First, we study the non-local impurity potential \( W_{\nu k}^X \) for \( X \)-atom \((X = \text{Mn, Co, Ni, Zn, Ru}) \) given by the first principle study by Nakamura et al. [33]. The derived values of the on-site impurity potential \( I \) are \( +0.28 \), \(-0.35 \), \(-0.87 \), \(-8.05 \) and \(-0.02 \) (the unit is eV) for \( \text{Mn, Co, Ni, Zn and Ru} \), respectively, as shown in Table I. Thus, \( \text{Zn atom works as the unitary impurity scattering center, whereas other 3d atoms (Mn, Co and Ni) induce intermediate impurity scattering.} \)

The off-site impurity potentials \( V_1 \) and \( V_2 \) are very small. In addition, strong modulations of NN and NNN hopping integrals \( \Delta t^{(1)} \) and \( \Delta t^{(2)} \) are induced around the impurity atom. Especially, \( \Delta t^{(1)}/t^0 \) for 4d atom Ru takes large positive value, reflecting the larger radius of \( 4d \)-orbitals. Thanks to the Nakamura’s model, we can present a quantitative analysis of the impurity effect on the \( s_{\pm} \)-wave state, by taking the non-local nature of the impurity potential appropriately.

Figure 2 show the obtained \( T_c \) as function of the (a) impurity concentration \( n_{\text{imp}} \) and (b) residual resistivity \( \rho_0 = 1/\sigma_x \) for various impurity atoms in the case of \( z^{-1} = 1 \). Although the Fe-site substitution induces the “impurity potential” and “carrier doping”, we neglect the latter effect by fixing the electron filling \( n = 6.0 \), in order to concentrate on the former effect. When the mass-enhancement factors \( z^{-1} \) is finite, the reduction of \( T_c \)
TABLE I: $I_{\text{Av}}$ is the averaged on-site impurity potential in Nakamura’s model [33]. The unit of energy is eV. $\Delta N(I_{\text{Av}})$ is the change in the local electron density at the impurity site due to $I_{\text{Av}}$ in the present model without interaction. In Nakamura’s model, the on-site potential is orbital-dependent, and $\Delta t^{(1)}$ and $\Delta t^{(2)}$ are included.

|          | Mn | Co | Ni | Zn | Ru |
|----------|----|----|----|----|----|
| $I_{\text{Av}}$ | +0.28 | −0.35 | −0.87 | −8.05 | −0.02 |
| $\Delta N(I_{\text{Av}})$ | −1.14 | +1.00 | +2.05 | +3.91 | −0.02 |

per impurity concentration, $-(T_c - T_{c0})/n_{\text{imp}}$, is renormalized by $z$, while $\rho_0/n_{\text{imp}}$ is independent of $z$ [38]. Therefore, both $n_{\text{imp}}^{\text{cr}}$ and $\rho_0^{\text{cr}} \equiv \rho_0(n_{\text{imp}}^{\text{cr}})$ are multiplied by $z^{-1}$. According to Fig. 2 (a), the critical impurity concentration for the disappearance of $T_c$, $n_{\text{imp}}^{\text{cr}}$, strongly depends on the impurity atoms: $n_{\text{imp}}^{\text{cr}} = 0.6z^{-1} \% \sim 3.5z^{-1} \%$ for 3d-impurities (Mn, Co, Ni, Zn), while $n_{\text{imp}}^{\text{cr}} = 24z^{-1} \%$ for Ru-impurities. In contrast, the values of $\rho_0^{\text{cr}}$ shown in Fig. 2 (b) are almost independent of impurities for 3d-impurity atoms ($\sim 5z^{-1}$ $[\mu\Omega\text{cm}]$), while $\rho_0^{\text{cr}} \sim 10z^{-1}$ $[\mu\Omega\text{cm}]$ for Ru-impurity.

The residual resistivity given by Nakamura parameter $W_{r_1,r_1'}^X$ is very small ($\rho_0/n_{\text{imp}} < 5 [\mu\Omega\text{cm}/\%]$) expect for $X = \text{Zn}$. One of the reasons would be that the impurity potential given in Ref. [33] may be normalized, although the bare impurity potential is required for the present study. (The normalization would caused by the modification of the wavefunction around the impurity site in solving the Kohn-Sham equation, while this process is also included in the $T$-matrix.) By taking this effect into account, we study the impurity potential $M \times W_{r_1,r_1'}^X$ with $M > 1$. To see the effect of $M$, we analyze the case of $M = 4$ in Fig. 3 for instance. We show (a) $n_{\text{imp}}$-dependence and (b) $\rho_0$-dependence of $T_c$. Note that similar results are obtained for $M \geq 4$. In this case, $T_{c0} = 30K$ is suppressed by a few percent impurity concentration. In contrast, $\rho_0^{\text{cr}}$ is approximately independent of $M$ for all impurity atoms. We stress that $\rho_0/n_{\text{imp}}$ is enlarged to $\sim 50 [\mu\Omega\text{cm}/\%]$ by taking the impurity-induced non-local orbital order into account, because of the enlarged impurity scattering cross section [39]. In this case, $s_{\pm}$-wave state is strongly suppressed, as we will show in Sec. IV C.

For the convenience of analysis, we hereafter study the ratio $R \equiv -(T_c - T_{c0})/\rho_0 = -\Delta T_c/\rho_0$ at $n_{\text{imp}} \ll n_{\text{imp}}^{\text{cr}}$: $R$ is rather independent of the impurity potential strength, and also $R$ is essentially independent of $T_{c0}$ according to the Abrikosov-Gorkov theory. In Fig. 4, we show the obtained $R$ as function of $M$ for various impurity atoms. As recognized in Ref. 2, the relation $T_{c0}/\rho_0^{\text{cr}} \sim 1.5R$ is satisfied for all atoms. By taking the mass-renormalization factor into account, we obtain that $R = 3z \sim 5z$ $[K/\mu\Omega\text{cm}]$ for all 3d-impurity atoms studied in Ref. [33], except for the Ru-impurity. (The horizontal broken line $R_{I=\infty} = 3.6 [K/\mu\Omega\text{cm}]$ is the value for the infinite on-site impurity potential ($I = \infty$) studied in Ref. [30].)

In contrast, experimentally observed $R$ in optimally doped 1111 compounds ($z^{-1} \sim 2$) and 122 compounds ($z^{-1} \sim 3$) is $R_{\text{exp}} \sim 0.1 [K/\mu\Omega\text{cm}]$ [22–25]. Therefore, the $s_{\pm}$-wave state would be too fragile against nonmagnetic impurities to explain experimental robustness of $T_c$ against impurities. Similar result was reported by Ikeda et al [40] by using the Nakamura’s impurity model.

**B. ideal non-local impurity models**

According to the first principle studies in Refs. [33, 41, 42], the impurity-induced change in the electron density is strongly localized at the impurity center. This fact indicates the smallness of the non-local impurity potentials $V_i$ in eq. (2). However, to obtain useful knowledge on the impurity effect, we introduce four ideal impurity potential models shown in Fig. 5 (a): (i) $I$-model (only on-site potential), (ii) $V_1$-model (only NN potential, without $I$),...
(iii) $V_2$-model (only NNN potential, without $I$), and (iv) $V_{As}$-model (plaquette impurity potential due to As-site substitution). Note that (ii) and (iii) are very unrealistic potentials. Here, we put $\Delta_{\text{imp}} = 0$ for simplicity.

Figure 5 (b) shows the ratio $R = -(T_c - T_{c0})/\rho_0$ at $n_{\text{imp}} = 0.1$ [%] for models (i)-(iv) as function of the impurity potential, in the case of $z^{-1} = 1$. The obtained $R$ for the $V_2$-model is as large as that for $I$-model, while those for other two models are smaller when $V_1, V_{As} < 0$. Especially, $R < 1.0$ [K/$\mu\Omega$cm] is realized for the $V_1$-model for $-1 < V_1 < 0.5$. We also show $-\Delta T_c/n_{\text{imp}}$ and $\rho_0/n_{\text{imp}}$ with CVC in Figs. 5 (c) and (d), respectively. Compared to the $I$-model, $-\Delta T_c/n_{\text{imp}}$ in the $V_1$ model is comparable, while $\rho_0$ in the $V_1$ model is much larger. For this reason, the relation $R_{I-\text{model}} \gg R_{V_1-\text{model}}$ can be achieved.

However, the above $V_1$-model without on-site potential $I$ is very unrealistic. Thus, we also introduce $I$ to the $V_1$-model: Figure 6 shows the obtained (a) $R$ and (b) $\rho_0/n_{\text{imp}}$ as function of $V_1$ with finite $I$. In the case of $|I| \geq 0.5, -\Delta T_c/\rho_0^I$ quickly approaches to the value for the $I$-model for $|V_1| \lesssim 0.2$. In real compound, the relation $|V_1| < 0.1$ is expected, as we will discuss in Sec. V A.

We also study the effect of hopping integral inhomogeneity around the impurity site. For a systematic study, we define $\Delta \tau^{(i)}$ in eq. (2) as $\Delta \tau^{(1)}_{\text{NNN}} = x_1 \cdot t_{\text{NNN}}^0$, for the NN sites ($|r| = 1$), and $\Delta \tau^{(2)}_{\text{NNN}} = x_2 \cdot t_{\text{NNN}}^0$ for the NNN sites ($|r| = \sqrt{2}$). In the case of Ru-impurity, $x_1$ and $x_2$ are positive according to Ref. [33], because of the larger radius of 4$d$-orbitals. However, we also study the case $x_i < 0$ since this situation might be realized by irradiations, by shifting the Fe-ion position outside of the FeAs plane.

In Fig. 7, we show the obtained $R$ and $\rho_0/n_{\text{imp}}$ for various on-site potential $I$ as function of $x_1$, in the case of (a)(b) $x_2 = 0$ and (c)(d) $x_2 = x_1$. In the former case, the obtained $R$ is very small for $I = 0$, while it quickly increases for finite $I$. In contrast, $R$ in the latter case is large even for $I = 0$. In both cases, the residual resistivity is very small for $x_1 > 0$, since the magnitude of the hopping integral is increased locally. Therefore, the $s_{\pm}$-wave state is strongly suppressed by the hopping integral inhomogeneity in both $x_2 = 0$ and $x_2 = x_1$ cases, except for a special case $I = x_2 = 0$.

C. impurity-induced non-local orbital order

To study the effect of a very wide-range impurity potential, we analyze the effect of the impurity-induced non-local orbital order (NL-OO) derived in Ref. [39] on the $s_{\pm}$-wave state. When this impurity-induced NL-OO is formed, the residual resistivity per 1% impurity

FIG. 3: (Color online) Obtained $T_c$ as function of (a) $n_{\text{imp}}$ and (b) $\rho_0$ using the impurity potential $4 \times W_{\text{NNN}}$.

FIG. 4: (Color online) $R = -(T_c - T_{c0})/\rho_0$ at $n_{\text{imp}} = 0.1$ [%] for the impurity potential $M \times W_X$ for various $X$ atoms. The horizontal broken line at $R_{t=\infty} = 3.6$ [K/$\mu\Omega$cm] represents the value for the infinite on-site impurity potential ($I = \infty$) studied in Ref. [30] for $z^{-1} = 1$. |$V_1| < 0.1$ is expected, as we will discuss in Sec. V A.
atoms increases to $\sim 50$ [$\mu$Ωcm], because of the enlarged impurity scattering cross section [39]. This fact would resolve the problem that the residual resistivity derived from Nakamura parameter is very small except for Zn-impurity atom.

Recent discovery of “electronic nematic transition” in the tetragonal phase, free from any lattice deformation, has been attracting great attention. For example, in “detwinned” BaFe$_2$(As,P)$_2$ [43] under very small uniaxial pressure ($\sim 5$MPa), sizable in-plane anisotropy of resistivity emerges at $T^*$, which is about 10K$\sim$100K higher than $T_S$. The nematic order is also observed in BaFe$_2$(As,P)$_2$ by the magnetic torque measurement [44]. In Ref. [39], the authors discussed the impurity-induced electronic nematic phase using the mean-field approximation in real space, by introducing the quadrupole interaction $g_{\text{quad}}$. When orbital fluctuations develop, local
impurity potential induces NL-OO with \( C_2 \) symmetry, actually reported by STM/STS autocorrelation analyses [45, 46]. The large cross section of the NL-OO gives giant residual resistivity. When \( C_2 \) nanostructures are aligned along \( a \)-axis, the in-plane anisotropy of resistivity reaches 40%, consistently with experiments [43].

![Diagram](image)

**FIG. 8:** (Color online) Obtained \( T_c \) of the \( s_\pm \)-wave state in the presence of impurity-induced NL-OO obtained for \( I = -2 \) given in Ref. [39].

In Fig. 8, we show the obtained \( T_c \) as function of \( n_{\text{imp}} \) for the (i) on-site impurity potential \( I = -2 \) and (ii) impurity-induced \( C_2 \) orbital order obtained by the mean-field approximation in real space for \( I = -2 \) and \( \beta_{\text{quad}} = 0.218 \), shown in Fig. 1 (c) of Ref. [39]. In the case (ii), the critical impurity concentration is just \( n_{\text{imp}}^{\text{cr}} = 0.3z^{-1} \) [%], which is about one-third of \( n_{\text{imp}}^{\text{cr}} \) for the case (i). The corresponding in-plane averaged resistivity is \( \rho_{\theta}^{\text{cr}} = 17.3z^{-1}[\mu\Omega\text{cm}] \), which is about four times \( \rho_{\theta}^{\text{cr}} \) for the case (i). That is, \( \rho_{\theta}^{\text{cr}} \) is enlarged while \( n_{\text{imp}}^{\text{cr}} \) is reduced when the impurity-induced NL-OO is realized. Note that the enlarged \( \rho_{\theta}^{\text{cr}} \) is still one order of magnitude smaller than experimental values (300 \( \sim \) 500 [\( \mu\Omega\text{cm} \)]).

Therefore, impurity-induced \( C_2 \) orbital order should cause strong suppression of the \( s_\pm \)-wave SC state. Similar behaviors (larger \( \rho_{\theta}^{\text{cr}} \) and smaller \( n_{\text{imp}}^{\text{cr}} \)) are also realized by impurity-induced short-range AF order in nearly AF metals, such as under-doped cuprates [47]. We consider that this impurity-induced NL-OO will also suppress the \( s_\pm \)-wave state moderately, because of the suppression in the density-of-states (pseudo-gap formation) due to the orbital (short-range) order. Under \( T_c \), the impurity-induced NL-OO will cause the “Swiss cheese hole state” in the \( s_\pm \)-wave state.

### D. derivation of \( |T_{\text{inter}}| \) and \( |T_{\text{intra}}| \)

We have introduced various non-local impurity potentials, and studied the impurity effect on the \( s_\pm \)-wave state driven by the pairing interaction in eq. (11). We find the relation \( R = 2.5z \sim 5z \) [K/[\( \mu\Omega\text{cm} \)] holds for \( 3d \) and \( 4d \)-impurity atoms, whereas \( R = 1z \sim 2z \) [K/[\( \mu\Omega\text{cm} \)] in a special model. To understand these numerical results, we analyze the average \( T \)-matrix between \( \text{FS}_\alpha \) and \( \text{FS}_\beta \):

\[
|T_{\text{inter}}|^2 = \frac{1}{6} \sum_{\alpha,\beta} \left( \int_{\text{FS}_\alpha} d\mathbf{k} \int_{\text{FS}_\beta} d\mathbf{k}' |T_{\alpha\beta,k,k'}|^2 \right) \quad (12)
\]

\[
|T_{\text{intra}}|^2 = \frac{1}{13} \left( \sum_{\alpha,\beta} \left( |e^{-\text{FS}}\mathbf{k} - \text{FS} \mathbf{k} \rangle \langle T_{\alpha\beta,k,k'} | |\mathbf{k}'\rangle \langle k' | |T_{\alpha\beta,k,k'}| \right)^2 \int_{\text{FS}_\alpha} d\mathbf{k} \int_{\text{FS}_\beta} d\mathbf{k}' \right) \quad (13)
\]

Then, the averaged ratio between inter-pocket and intra-pocket scattering amplitude would be \( i^2 \equiv |T_{\text{inter}}|^2 / |T_{\text{intra}}|^2 \).

Figure 9 (a) shows the values of \( R \) in various impurity models as function of \( x = 2\gamma^2/(1 + \gamma^2) = 2|T_{\text{inter}}|^2 / (|T_{\text{inter}}|^2 + |T_{\text{intra}}|^2) \). The CVC for the conductivity is taken into account correctly. It is found that \( R \) is approximately scaled by \( x \) for various kinds of impurities. This result is naturally understood since the \( s_\pm \)-wave state is suppressed by the inter-FS scattering, whereas both inter- and intra-FS scattering contribute to \( \rho_0 \propto \gamma \), as understood by eqs. (5) and (10). Therefore, the following relationships would be realize [12]:

\[
-\Delta T_c \propto |T_{\text{inter}}|^2, \quad (14)
\]

\[
\rho_0 \propto |T_{\text{inter}}|^2 + |T_{\text{intra}}|^2. \quad (15)
\]

We will discuss this issue in more detail in Sec. V B.

Another important finding in Fig. 9 (a) is that the value of \( t = |T_{\text{inter}}|/|T_{\text{inter}}| \) in the five-orbital model is approximately independent of the impurity potential strength (in both Born and unitary regimes), for all the impurity models studied here. This fact means that the “constant \( \tilde{t}_V \)-model can be applicable only for Born impurities, as we will discuss in Sec. V C.

In Fig. 9 (a), the values of \( R \) for \( V_1 \) and \( V_A \)-models apparently deviate from the line \( y = 3.5x \). This fact originates from the large contribution from the CVC, which becomes important when the impurity potential has finite scattering cross section, since the forward impurity scattering is correctly subtracted by taking the CVC into account. In fact, as shown in Fig. 9 (b), the relation \( R \propto x \) is apparently improved by neglecting the CVC. Therefore, we should take the CVC into account to obtain quantitatively reliable value of \( R \), especially for wide-range impurity potentials.

### V. DISCUSSIONS

In the previous section, we calculated the impurity effect on the \( s_\pm \)-wave state for various non-local impurity
models. When we use the impurity model parameters obtained by a recent first principle study by Nakamura et al., the $s_\pm$-wave state is fragile against impurities, consistently with the previous theoretical study for the on-site impurity model by Onari and Kontani [30]. This result is qualitatively unchanged for different non-local impurity models, when the parameters are realistic. Here, we present more detailed discussions.

A. Estimation of the value of $V_1$

In Fig. 5 (a), we have shown that $R = -\Delta T_{\pi}/\rho_0$ for the $V_1$-impurity model is as small as $1\times [K/\mu\Omega cm]$, which is still much larger than experimentally observed relations $R \lesssim 0.1$ [$K/\mu\Omega cm$] in single crystals [23, 24]. Moreover, as shown in Fig. 6 (a), $R$ is strongly enlarged by introducing the no-site potential $I$, which should be much larger than $V_1$ in magnitude in real impurities.

By introducing $V_1$ the electron number at the NN site of the impurity center is changed by $\Delta N_{NN} \sim -2 \times V_1$ for $|V_1| \ll 1$, according to the analysis of the present five-orbital tight-binding model. However, according to the first principle study [41], $|\Delta N_{NN}|$ would be at most $0.1 \sim 0.2$, meaning that $|V_1| < 0.1$ due to the strong screening effect in real compounds. Therefore, the effect of $V_1$ would be negligible in the study of the impurity effect in Fe-based superconductors.

B. Why $|T_{\text{inter}}| \ll |T_{\text{intra}}|$ in the $V_1$-model?

We have shown in Fig. 9 that the relation $|T_{\text{inter}}| \ll |T_{\text{intra}}|$ holds in some non-local impurity potentials. To understand the reason, we consider a orbital-less square lattice model for simplicity. In the Born approximation, the $T$-matrix for the $V_1$-model is given as

$$
T_{k,p}(\epsilon) = 4V_1^2g(0,0)(\epsilon) + 4V_1^2|g(1,1)(\epsilon)|\cos k_x \cos p_y + \cos k_y \cos p_x + 2V_1^2|g(2,0)(\epsilon)|\cos k_y - p_x + \cos(k_y - p_y)),
$$

(16)

where $g(x,y)\epsilon$ is the Green function in real space at $r = (x,y)$. The cosine terms in eq. (16) originate from the non-locality of the impurity potential. For the intra-hole-pocket scattering $(k = p = 0)$, eq. (16) gives $T_{\text{intra}} = 4V_1^2|g(0,0) + 2g(1,1) + g(2,0)|$. On the other hand, for the scattering between hole- and electron-pockets $(k = (0,0)$ and $p = (\pi,0)$), eq. (16) gives $T_{\text{inter}} = 4V_1^2g(0,0)$. Therefore, the relation $|T_{\text{inter}}| \ll |T_{\text{intra}}|$ would be possible when $g(0,0) \sim g(1,1) \sim g(2,0)$.

C. Comparison with the constant $I_b$ model

In this paper, we analyzed the impurity effect based on the realistic five-orbital model with non-local impurity potentials. On the other hand, more simple two-band model with constant $I_b$ impurity potential has been frequently used [27, 29]. Here, we discuss both the usefulness and limitations of the latter model, in which the impurity potential in the band-basis $(a, b)$ is given as

$I^b = \left( \begin{array}{c} I_b \\ I'_b \end{array} \right)$. If we assume $I_b$ and $I'_b$ are constant, then we obtain

$$
I^2_{\text{constant}} - I_b = \frac{|T_{ab}|^2}{|T_{aa}|^2} = \frac{u^2}{1 + \pi^2 N(0)|I_b|^2(1 - u^2)},
$$

(17)

where $T_{ab}$ $(T_{aa})$ is inter-band (intra-band) $T$-matrix. Here, $u \equiv I'_b/I_b$, and $N(0)$ is the density-of-states for each band. In the Born regime $\pi N(0)|I_b| \ll 1$, then $I^2_{\text{constant}} - I_b \approx u^2$ holds, and therefore the $s_\pm$-wave state is fragile against impurities except when $u \ll 1$. 

---

**FIG. 9:** (Color online) Obtained $R$’s as function of $x = 2|T_{\text{inter}}|^2/(|T_{\text{intra}}|^2 + |T_{\text{inter}}|^2)$ in the case of (a) with CVC and (b) without CVC, for 3d- and 4d-impurity atoms as well as $I$-model, $V_{As}$-model, and $V_1$-model without $I$. Note that the last potential is unrealistic. $|T_{\text{inter}}| = |T_{\text{intra}}|$ corresponds to $x = 1$. The proportional relation $R \propto x$ becomes worse by including the CVC, especially for the $V_1$-model without $I$ and $V_{As}$-model.
In the unitary regime $\pi N(0)I_b \gg 1$, the $s_\pm$-wave state is robust against impurities unless $|u| = 1$ since eq. (17) decreases in proportion to $I_b^{-2}$. However, this result is totally changed in the five-orbital model, in which $\hat{I}_b(k, k') = \hat{U}^\dagger(k) \cdot W(k, k') \cdot \hat{U}(k')$ is momentum-dependent. Once $\hat{I}_b$ is $k$-dependent, then eq. (17) does not hold as proved in Ref. [30]. Instead, the relation
\[ t_{\hat{I}_b(k, k')}^2 \sim u^2 \tag{18} \]
holds for all the impurity models studied here even in the unitary regime, as recognized by the numerical analysis in Fig. 9. Therefore, the constant $\hat{I}_b$ model is applicable to Fe-based superconductors only for Born impurities.

![FIG. 10: (Color online) Obtained $-\Delta T_c/\gamma$ of the $s_\pm$-wave state in the two-band constant $\hat{I}_b$ model studied in Ref. [27]. The horizontal axis is $x \equiv 2u^2/(1 + u^2) = 2I_b^2/(I_b^2 + I_b^0)$. $I_b' = I_b$ corresponds to $x = 1$.](image)

Figure 10 shows the $-\Delta T_c/\gamma$ in the two-band constant $\hat{I}_b$ model as function of $x \equiv 2u^2/(1 + u^2) = 2I_b^2/(I_b^2 + I_b^0)$, in case that the $s_\pm$-wave state due to inter-band repulsion is realized. In this model, $-\Delta T_c/\gamma$ is given by eq. (12) of Ref. [27]. Note that $\rho_0 \propto \gamma$. We see that the relationship $-\Delta T_c/\gamma \propto x$ holds only in the Born regime $\pi N(0)I_b \ll 1$. However, the relation $-\Delta T_c/\gamma \ll x$ is realized in the unitary and intermediate regimes except for $|u| \sim 1$.

Based on the constant $\hat{I}_b$-model, Ref. [32] mentioned that the $s_\pm$-wave state with $T_{c0} = 30K$ disappears for $\rho_0^\sigma \approx 100 \,(1000) \,[\mu \Omega \cdot cm]$ at $u = 0.5 \,(0.2)$ in the intermediate regime $\pi N(0)I_b \sim 2.5$, and tried to explain the experimental small impurity effect on $T_c$ based on the $s_\pm$-wave scenario assuming that $u \ll 0.5$. However, we obtain $t = u \sim 1$ for the realistic impurity models of $3d$-impurity atoms as shown in Fig. 9. In addition, $\rho_0^\sigma$ given in Ref. [32] is very overestimated for $u \ll 0.5$, since they apply the constant $\hat{I}_b$-model to the intermediate regime and the CVC for the resistivity is dropped. In fact, we obtain $\rho_0^\sigma = 17.3z^{-1} \sim 50 \,[\mu \Omega \cdot cm]$ for the impurity-induced NL-OO in Fig. 8; $t = u \sim 0.4$ in this case would be the lower limit for realistic impurity models for Fe-based superconductors.

In this paper, we studied the effect of in-plane impurities. In the case of “out-of-plane” impurities, the radius of the impurity potential $\rho$ could be much longer than the lattice spacing $a_{Fe-Fe}$ [48]. In this case, the relation $u = |I_b'/I_b| \ll 1$ might be realized because of the suppression of large angle scattering, and then the $s_\pm$-wave state would be robust against impurities. Therefore, study of the out-of-plane impurities would not be useful to distinguish between $s_{+-}$ and $s_\pm$-wave states.

VI. SUMMARY

Based on the realistic five-orbital model for Fe-based superconductors, we have presented a systematic study of the impurity effect on the $s_\pm$-wave SC state. We studied impurity model parameters for $3d$- and $4d$-impurity atoms obtained by a recent first principle study [33], in addition to various non-local impurity models. The obtained values of $R = -\Delta T_c/\rho_0$ for $n_{imp} \ll 1$ as function of $x = 2[T_{int}^2]/(T_{int}^2 + T_{intra}^2)$ are summarized in Fig. 9. According to the Abrikosov-Gorkov theory, $R$ is essentially independent of $T_{c0}$.

The main results are shortly summarized as follows:

(i) For $3d$-impurity atoms, $|T_{int}/|T_{intra}| \gtrsim 0.9$ is realized, and we obtain $R = 3z \sim 5z \,[K/\mu \Omega \cdot cm]$, which is comparable to $R_{I=0} = 3.6z \,[K/\mu \Omega \cdot cm]$ for the on-site model with $I = \infty$. Also, $\rho_0^\sigma \sim 5z^{-1} \,[\mu \Omega \cdot cm]$ for $T_{c0} = 30K$.

(ii) For Ru-impurity atoms, $|T_{int}/|T_{intra}| = 0.6 \sim 0.7$ is realized, and both $R$ and $1/\rho_0^\sigma$ are about half of those for $3d$-impurity atoms.

(iii) For impurity-induced NL-OO model, which gives a very wide-range impurity potential, we obtain $|T_{int}/|T_{intra}| \sim 0.4$ and $R \sim 1.5z \,[K/\mu \Omega \cdot cm]$. Similar result is obtained for the $V_{As}$-model and $V_1$-model with finite $I$.

(iv) The CVC is important to obtain reliable $R$ and $\rho_0^\sigma$: $R$ is approximately doubled by CVC for $V_1$- and $V_{As}$-impurity models, for example.

(v) In case we use the “constant $\hat{I}_b$ impurity model” by putting $|I_b'/I_b| = |T_{int}/|T_{intra}|$, we have to keep in the Born regime $\pi N(0)I_b \ll 1$, especially when $|I_b'/I_b| \ll 1$.

The abovementioned results are essentially consistent with the previous theoretical study for the on-site impurity model by Onari and Kontani [30]. Experimentally, the critical value of $\rho_0$ for the disappearance of $T_{c0} \approx 30K$ is $300 \sim 500 \,[\mu \Omega \cdot cm]$, which means that the averaged mean-free-path is comparable to the lattice spacing ($\sim 0.3nm$) as discussed in Ref. [30]. Therefore, exper-
In this paper, we have introduced only the repulsive pairing interaction due to spin fluctuations. When both spin and orbital fluctuations strongly develop, inter-orbital attractive interaction and intra-orbital repulsive interaction coexist. This situation is naturally expected near the orthorhombic phase, and is actually reproduced by the SC-VC theory based on the Hubbard model [16]. Then, the present study indicates that impurity-induced crossover form $s_{\pm}$-wave to $s_{++}$-wave states would be realized in some Fe-based superconductors [13, 49].

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