Effect of transition-metal substitution in iron-based superconductors

S L Liu\textsuperscript{1} and Tao Zhou\textsuperscript{2}

\textsuperscript{1} College of Science, Nanjing University of Posts and Telecommunications, Nanjing 210003, People’s Republic of China
\textsuperscript{2} College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People’s Republic of China

E-mail: shengli_liu@hotmail.com

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Abstract
We study theoretically the effect of transition-metal (TM) substitution in iron-based superconductors through treating all of the TM ions as randomly distributed impurities. The extra electrons from TM elements are localized at the impurity sites. In the meantime the chemical potential shifts upon substitution. The phase diagram is mapped out and it seems that the TM elements can act as effective dopants. The local density of states (LDOS) is calculated and the bottom becomes V-shaped as the impurity concentration increases. The LDOS at the Fermi energy $\rho(\omega = 0)$ is finite and reaches the minimum at the optimal doping level. Our results are in good agreement with scanning tunneling microscopy experiments.

1. Introduction
The iron-based superconductors have been studied intensively since their discovery [1]. It is widely believed that the main physics in this family is within the iron–arsenic planes. Superconductivity can be realized by doping either holes or electrons into the system.

The transition-metal (TM) elements (such as Co or Ni) are widely used to achieve superconductivity by substituting the iron ions [2–4]. However, this substitution is significantly different from that of other doped materials, because the TM ions enter the conducting planes and may also act as the impurities. The competition of the doping effect and the impurity effect in TM-doped materials is of great interest. The scattering effect induced by the impurity has been studied intensively and it has been proposed to account for many unusual physical properties [5–14]. Very recently, the effect of Co substitution in the Na(Fe$_{0.95}$Co$_{0.05}$)As compound has been studied experimentally, where the number of defects is very close to the ratio of the chemical composition of Co/(Fe+Co) in the sample [15]. Since all of the TM ions enter the conducting planes, the impurity concentration is expected to equal the doping density. However, so far little attention has been paid to this issue when studying the impurity effect, which may explain some unusual experimental observations for the TM-doped compound.

The TM substitution effect has attracted broad interest [16–21]. For Co(Ni) substitutes, it is reported that the extra electrons are concentrated at the Co or Ni sites according to the first principle density functional method [16–19]. Very recently, based on an x-ray absorption experiment it was also indicated that the electronic occupations of the iron sites stay constant as the cobalt density changes in the BaFe$_{2−2x}$Co$_{2x}$As$_2$ compound [20], which is similar to the findings in a Ca(Fe$_{0.944}$Co$_{0.056}$)$_2$As$_2$ sample by the measurement of resonant photoemission spectroscopy [21]. These results lead to a fundamental question, that is, whether the TM substitutes provide doping carriers to the system. On the other hand, numerical calculation based on first principles reveals that the Fermi energy shifts upon TM substitution although the extra electrons are localized around the impurity site [17–19]. Angle-resolved photoemission spectroscopy (ARPES) experiments on BaFe$_{2−2x}$Co$_{2x}$As$_2$ [22, 23] have shown the evolution of the Fermi surface with Co substitution, which also suggests that the cobalt atoms should be treated as dopants. Thus at this stage the TM substitution effect is non-trivial and rich in physics. Studying this issue...
theoretically may provide insightful hints to clarify the mechanism of superconductivity.

In this paper, we study cobalt doped material and treat all of the cobalt ions as the randomly distributed impurities. The order parameters and the Fermi energy are obtained self-consistently with the two-orbital model and the Bogoliubov–de-Gennes (BdG) equations. The extra electrons are totally located at the impurity sites and the electron filling on the Fe site stays the same upon substitution. In the parent compound, the spin-density-wave (SDW) order is revealed due to the Fermi surface nesting. A rigid shift of the Fermi energy occurs upon substitution, which would break the Fermi surface nesting and suppress the SDW order. As a result, the superconducting (SC) order shows up. These results are qualitatively the same as the ones previously reported in the clean system [24]. Thus we suggest that the cobalt substitutes should be treated as the effective dopants although the extra electrons are localized. The local density of states (LDOS) is also studied and we propose that it is necessary to take the disordered impurities into consideration when elucidating some striking features revealed by scanning tunneling microscopy (STM) experiments.

2. Model and Formulation

We start from a two-orbital model including the hopping elements, pairing term, on-site interactions and impurity part [5, 11, 24], expressed by

\[ H = H_{\text{t}} + H_{\Delta} + H_{\text{int}} + H_{\text{imp}}. \]  

The hopping term \( H_{\text{t}} \) can be expressed by

\[ H_{\text{t}} = \sum_{i\mu\nu\sigma} (t_{i\mu\nu} c_{i\mu\sigma}^\dagger c_{i\nu\sigma} + \text{H.c.} - t_0 \sum_{i\mu\sigma} c_{i\mu\sigma}^\dagger c_{i\mu\sigma}, \]  

(2)

where \( i, j \) are the site indices and \( \mu, \nu = 1, 2 \) are the orbital indices, and \( t_0 \) is the chemical potential. The second term is the on-site interaction term \( H_{\text{int}} \) can be written as [11, 12, 24, 25]

\[ H_{\text{int}} = U \sum_{i\mu\sigma} \langle n_{i\mu\sigma} \rangle n_{i\mu\sigma} + U' \sum_{i\nu\sigma, \sigma' \neq \sigma} \langle n_{i\mu\sigma} \rangle n_{i\sigma\sigma'} + \langle U' - J_H \rangle \sum_{i,\mu \neq \nu, \sigma} \langle n_{i\mu\sigma} \rangle n_{i\nu\sigma}, \]  

(4)

where \( n_{i\mu\sigma} \) is the density operator at the site \( i \) and orbital \( \mu \). The inter-orbital on-site interaction \( U' \) is taken to be \( U = 2J_H \).

\( H_{\text{imp}} \) is the impurity part of the Hamiltonian. It should include the potential scattering and the magnetic part for cobalt substitutes. Here we consider the potential scattering at the cobalt substitutes, which should play the dominant role according to first principles calculations [14, 16–20] and the recent experiment [15]. Then this term is written as

\[ H_{\text{imp}} = \sum_{i\mu\sigma} V_{i\mu\sigma} c_{i\mu\sigma}^\dagger c_{i\mu\sigma}. \]  

(5)

The Hamiltonian can be diagonalized by solving the BdG equations self-consistently,

\[ \sum_j \sum_{\nu} \left( \begin{array}{cc} H_{i\mu\nu} & \Delta_{i\mu\nu}^+ \\ \Delta_{i\mu\nu}^- & -H_{j\nu\sigma} \end{array} \right) \left( \begin{array}{c} u_{i\mu\sigma}^- \\ v_{j\nu\sigma}^- \end{array} \right) = E_n \left( \begin{array}{c} u_{i\mu\sigma}^+ \\ v_{j\nu\sigma}^+ \end{array} \right), \]  

(6)

where the Hamiltonian \( H_{i\mu\nu} \) is expressed by

\[ H_{i\mu\nu} = -t_{i\mu\nu} + \left[ U' \langle n_{i\mu\sigma} \rangle + (U - 2J_H) \langle n_{i\mu\sigma} \rangle \right] + (U - 3J_H) \langle n_{i\mu\sigma} \rangle + \sum_m V_{i\delta_i m} - t_0 \right] \delta_{\mu\nu} \delta_{\sigma\nu}. \]  

(7)

The SC order parameter \( \Delta_{i\mu\nu} \) and the local electron density \( \langle n_{i\mu\sigma} \rangle \) are obtained self-consistently,

\[ \Delta_{i\mu\nu} = \frac{V_{i\mu\nu}}{4} \sum_n (u_{i\mu\sigma}^+ v_{j\nu\sigma}^n + u_{j\nu\sigma}^+ v_{i\mu\sigma}^n) \tanh \left( \frac{E_n}{2k_B T} \right), \]  

(8)

\[ \langle n_{i\mu\sigma} \rangle = \sum_n |u_{i\mu\sigma}^+|^2 f(E_n) + \sum_n |v_{i\mu\sigma}^n|^2 [1 - f(E_n)]. \]  

(9)

Here \( f(x) \) is the Fermi distribution function and \( V_{i\mu\nu} \) is the pairing strength.

The LDOS is expressed by

\[ \rho_{\mu}(\omega) = \sum_{i\mu\sigma} \delta(\omega - E_n) + |v_{i\mu\sigma}^n|^2 \delta(E_n + \omega), \]  

(10)

where the delta function \( \delta(x) \) has been approximated by \( \Gamma/\pi(x^2 + \Gamma^2) \) with the quasiparticle damping \( \Gamma = 0.01 \).

The hopping constants used in this two-orbital model are expressed as [5]

\[ t_{i\mu, j\mu} = t_1, \quad \tilde{t} = \tilde{x}, \tilde{y}, \]  

(11)

\[ t_{i\mu, j\nu} = \frac{1 + (-1)^i t_2}{2} + \frac{1 - (-1)^i t_2}{2}, \]  

(12)

\[ t_{i\mu, j\nu} = \frac{1 + (-1)^i t_3}{2} + \frac{1 - (-1)^i t_3}{2}, \]  

(13)

\[ t_{i\mu, j\nu} = \mu \neq \nu. \]  

(14)

In the following presented results, the hopping constants are chosen to be \( t_1 = 1.0, 0.5, -1.8, 0.03 \). The chemical potential \( t_0 \) is determined by the average electron filling per site \( \langle n \rangle = 2 + x \), where \( x \) is the impurity concentration. The on-site Coulombic interaction is taken as \( U = 3.26 \) and the Hund coupling \( J_H = 1.4 \). The pairing is chosen as next-nearest-neighbor (NNN) intraorbital pairing with the pairing strength \( V = 1.0 \), which will reproduce the \( s_\pm \) pairing symmetry [26–29]. The numerical calculation is performed on a 24 \( \times \) 24 lattice with periodic boundary conditions. To calculate the LDOS, a 40 \( \times \) 40 supercell technique is used.

3. Results and Discussion

We plot the spatial distribution of the SC order parameter \( \Delta_i = \frac{1}{4} \sum_{\alpha \neq \mu} \Delta_{i\alpha, i\mu + \alpha \mu} \), the magnetic order \( M_i = \frac{1}{4} \sum_{\alpha \neq \mu} (n_{i\mu + \alpha \mu} - n_{i\mu - \alpha \mu}) \), and the particle number \( n_i = \sum_{\mu} n_{i\mu\sigma} \)
Figure 1. (a)–(c) Intensity plots of the SC order parameter, magnetic order and particle number with the impurity concentration $x = 0.03$, respectively. (d) The two-dimensional cut of the above parameters along $y = 18$.

in figures 1(a)–(c), respectively. Throughout the paper, the scattering potential is kept as $V_s = -3.5$. Figure 1(d) displays the two-dimensional cut of all of the parameters. As seen, in the presence of impurities, the amplitude of the SC order parameter is not uniform. It is reduced at and around the impurity sites. The magnetic spin order is antiferromagnetic along the $y$ direction and ferromagnetic along the $x$ direction, which is consistent with the $(\pi, 0)/(\pi, \pi)$ SDW in the extended/reduced Brillouin zone. This is qualitatively the same as the previous theoretical calculation [24, 25]. At and around the impurity sites, the magnetic order $M_i$ is suppressed. The particle number is about 3.0 at the impurity sites and recovers to 2.0 when away from the impurity sites. This result indicates that the electron filling on Fe sites does not change upon cobalt substitution. This is in accord with the numerical results of the first principles calculation [16–19] and recent experiments [20, 21].

The average electron density per Fe site $n_{Fe}$ and the chemical potential $\mu_0$ as a function of the impurity concentration $x$ are plotted in figure 2(a). As shown, the electron density is almost unchanged ($\approx 2.0$) for all of the impurity concentrations we consider, indicating that the extra electrons of impurity atoms are indeed localized around the impurity sites. This is consistent with the first principles calculation [16–19]. In the meantime, the chemical potential increases monotonically with increasing substitution level $x$. This result confirms the numerical results of the first principles calculation [17–19] and is consistent with the ARPES experiments [22, 23].

The average amplitudes of the SC order and magnetic order as a function of the temperature and impurity concentration $x$ are shown in figures 2(b) and (c) respectively. For the fixed impurity concentration $x = 0.03$, as seen in figure 2(b), both the magnetic order and the SC order decrease as the temperature increases and two transition temperatures are revealed. At zero temperature, as seen in figure 2(c), the magnetic order decreases monotonically with increasing $x$ and vanishes around $x \approx 0.06$. The SC order increases as $x$ increases in the low substitution region and reaches its maximum at $x = 0.06$. Then it decreases with further increase of $x$. The calculated phase diagram is plotted in figure 2(d). It can be seen that the magnetic order and SC order coexist in the low impurity concentration region. The magnetic order decreases abruptly at $x = 0.06$, corresponding to the quantum critical point at this concentration. This is in good agreement with the experimental results on BaFe$_{2-x}$Co$_x$As$_2$ [30, 31].

The SC order appears as the magnetic order is suppressed and it reaches its maximum as the magnetic order disappears. All of the obtained results are qualitatively consistent with the previous calculation by merely taking into account the doping effect [24].

We have demonstrated that the Fermi energy increases as the impurity concentration $x$ increases. The phase diagram and the order parameters as a function of $x$ also indicate that the impurities indeed act as the effective ‘dopant’,
although the electron densities on Fe sites do not change. However, the fundamental question still remains about how the TM substitution controls the phase diagram. Actually, for TM-doped materials, the competition of the SDW and SC orders should play the essential role. There are two origins accounting for the SDW instability. One is the Fermi surface nesting [32] and the other is the exchange interactions between local moments [33]. Here, we focus on the Fermi surface nesting. The SDW order reaches the maximum value for the parent compound due to the perfect nesting at zero doping. The SC order is induced by the spin fluctuation [27, 28] and is also related to the Fermi surface nesting. Nevertheless, for the parent compound the SC order could not survive due to the suppression effect by the SDW order. The suppression of the SDW order by the Fermi level shift is widely accepted and should occur in nearly all high-$T_c$ SC materials. Recently the suppression by the impurity effect has attracted broad interest. In the Ba(Fe$_{1-x}$Ru$_x$)$_2$As sample, the Fermi level does not change with Ru substitution, while the phase diagram is similar to those of other 122-compounds [34]. This result suggests that the impurity (disorder) may also suppress the SDW state [35]. Both the impurity effect and the shifts of the Fermi energy would suppress the SDW order and then the SC order shows up upon substitution. Actually, here the disorder and the impurities play the important role in this system and to
The energy dependent LDOS of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconductor in the low substitution region. Inset: the energy dependent LDOS with doping $x = 0.07$ without impurity. (a) Similar to (a) but in the high substitution region. Inset: the energy dependent LDOS with doping $x = 0.06$. Then it increases with further increase of $x$. As seen in the inset of figure 4(b), $\rho(\omega = 0)$ scales with $|x - x_m|$. This is a striking feature and is in good agreement with the STM experiment [38]. For a comparison we also plot $\rho(\omega = 0)$ as a function of doping density without considering the impurity scattering. As seen, $\rho(\omega = 0)$ is very low and almost doping independent. Physically, the number of quasiparticles decreases as $T_c$ increases and reaches its minimum at the maximal $T_c$. Hence, the LDOS at the Fermi level reaches its minimum near the optimal doping level. Our results show that the impurity effect is essential when explaining some striking features of the STM experiments.

In summary, the TM substitution effect in iron-based superconductors was studied by solving the BdG equations self-consistently. We investigated the cobalt substitution effect and the cobalt atoms were considered as randomly distributed impurities with negative scattering potential. It was shown that the extra electrons are localized around the impurity sites, while the chemical potential increases with increasing impurity concentration. These results are in accord with recent first principles calculation and ARPES experiments. The obtained phase diagram was qualitatively consistent with previous reports for the BaFe$_{2-x}$Co$_x$As$_2$ superconductors. It was found that the energy dependent LDOS spectrum is V-shaped, and the LDOS at the Fermi energy $\rho(\omega = 0)$ is finite and depends on the impurity concentration. These features are in agreement with STM experiments on BaFe$_{2-x}$Co$_x$As$_2$ material.

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