Impurity effects on the superconducting transition temperatures of Fe pnictides and superconducting symmetry of the order parameter

M Sato,1,2,3,∗ Y Kobayashi,2,3 S. Satomi,2 T Kawamata2,3, and M Itoh2,3

1 Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan
2 Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602 Japan
3 JST TRIP Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

E-mail: m_sato@cross.or.jp

Abstract. We focus on effects of nonmagnetic impurities on the superconducting transition temperatures $T_c$ and point out, using various experimental evidences obtained for LnFe$_{1-y}$M$_y$AsO$_{0.89-x}$F$_{0.11+x}$ (Ln=La, and Nd; M=Co, Ni, Mn, Ru) systems, that the sign reversal of the order parameters $\Delta$ pointed out theoretically at the early stage of the study does not exist between disconnected Fermi surfaces around $\Gamma$ and M points. The results imply that a new pairing mechanism different from the spin-fluctuation exchange and possibly related to the orbital degrees of freedom, should be considered seriously.

1. Introduction
Although Fe pnictides have various characteristics similar to those of high $T_c$ Cu oxides, there is one remarkable difference between the two, that is, the former systems have multiband nature, while the latter systems are single band conductors. Considering this difference, we have been studying several physical quantities of the former in order not to miss a possible existence of a novel mechanism of the superconducting pairing, which may originate from the orbital degrees of freedom, for example.

In the studies, it is essential to identify the superconducting symmetry of the Fe pnictide system: While the so-called $S_\pm$ symmetry with the sign reversal of the order parameters between two disconnected Fermi surfaces around $\Gamma$ and M points in the reciprocal space, is closely connected with the spin-fluctuation-mediated pairing mechanism [1, 2], $S_{++}$ symmetry without the sign reversal may indicate a new mechanism, because the superconducting transition temperature $T_c$ as high as 55 K is difficult to be realized by the ordinary phonon mechanism. We have carried out experimental studies focusing on three physical quantities sensitive to the relative phases of the order parameters $\Delta$ around the $\Gamma$ and M points, namely doping effects of nonmagnetic impurities on $T_c$ [3, 4], magnetic excitation spectra in the superconducting state [5, 6] and characteristic of the temperature($T$) dependence of the

∗ present address: Research Center for Neutron Science and Technology, Comprehensive Research Organization for Science and Society, 162-1 Shirakata, Tokai, Ibaraki 319-1106, Japan.
# present address: Dept. of Appl. Phys., Graduate School of Engineering, Tohoku University, Sendai 980-8578, Japan.
NMR longitudinal relaxation rate \(1/T_1\) [3, 7]. In the present report, we focus on the rate of \(T_c\)-suppression by nonmagnetic impurities.

2. Effects of Fe→M (=Mn, Ru, Co and Ni) and O→F substitutions for La1111 system

2.1. Carrier number change and validity of the rigid band picture

The rate of \(T_c\)-suppression by nonmagnetic impurities is expected to be very sensitive to the relative signs of the order parameters \(\Delta_\Gamma\) and \(\Delta_M\) around \(\Gamma\) and \(M\) points. If the system has the \(S_\pm\) symmetry with opposite sign of \(\Delta_\Gamma\) and \(\Delta_M\), the scattering of the conduction electrons by doped impurities induces a significant pair breaking effect, and the superconductivity is rapidly suppressed even by the doping of nonmagnetic impurities. It is contrasted to the well-known Anderson theorem valid for ordinary \(S\)-wave superconductors with no sign reversal. We note that the \(T_c\)-suppression rate for the \(S_\pm\) symmetry is larger than that observed for high-\(T_c\) Cu oxides, because in single band systems such as Cu oxides, the scattering effect on \(T_c\) is much reduced, if the scattering potential is very large (unitary scattering)[8]. These facts present us a very effective mean to clarify whether the spin-fluctuation mechanism is relevant to the superconductivity of these Fe pnictides.

Samples of \(\text{LnFe}_{1-y}M_y\text{AsO}_{0.89}\text{F}_{0.11}\) (\(\text{Ln}=\text{La, Nd; M=Co, Ni, Ru, Mn}\)) and \(\text{LaFeAsO}_{1-x}\text{F}_x\) have been used, and first, we have studied the electrical resistivities \(\rho\), Hall coefficients \(R_H\), thermoelectric powers \(S\), and specific heats \(C\). On detailed results of these studies can be found in our previous papers referred in refs. 3 and 4, and here we just show in Fig. 1, the electronic specific heat coefficients \(\gamma\) plotted against the electron numbers \(\delta n\) introduced to the mother system \(\text{LaFeAsO}\). (In this case, the \(\delta n\) values are described as \(2y+0.11\), \(y+0.11\) and \(−y+0.11\) for \(M=\text{Ni, Co and Mn}\) on the basis of the idea that each one of Ru, Co and Ni atoms donate 0, 1 and 2 electron(s) to the conduction bands of the FeAs layers, respectively.) Comparing the data with the band calculation [9], we can find, at least in the region of \(y<1.3\), that the data can be well understood by the calculated band shape, although the peak structure of \(\gamma\) expected for \(M=\text{Ni}\) at \(2y+0.11=1.0\) is smeared out by the randomness effect. The data indicate that the rigid band picture is basically valid. In such the case, the doped atoms do not carry localized moments. (We could not distinguish whether Mn impurities carry magnetic moments [3]. The O→F substitution is also considered to donate 1 electron to the conduction bands.

Figure 2 shows the \(T\) dependences of the thermoelectric powers of \(\text{LaFe}_{1-y}\text{Ni}_y\text{AsO}_{0.89}\text{F}_{0.11}\) with those of \(\text{LaFe}_{1-y}\text{Co}_y\text{AsO}_{0.89}\text{F}_{0.11}\). We can see in the figure that the absolute value of \(S\) exhibits, roughly speaking, similar \(\delta n\) dependences for \(M=\text{Co and Ni}\), confirming again that the number of conduction electrons donated by Ni is two times larger than that by Co.

2.2. Other effects of the doping of nonmagnetic impurities

Besides the carrier number change, impurity doping induces randomness, which brings about the pair breaking due to the electron scattering by the doped impurities for systems with sign reversal of the superconducting order parameter \(\Delta\) and may also induces the electron localization. Before considering these things, we note the following. The O→F substitution introduces the change of \(\delta n\), but it does not
introduce the scattering centers to the FeAs conducting layers. It is contrasted with the fact that the isoelectronic substitution Fe→Ru introduces the scattering centers but does not introduce the change of $\delta n$. Of course, for $M=Co$ and Ni doping, both the $\delta n$ change and scattering centers of the electrons are introduced. The existence of these various different types of doping effects have presented us the opportunity to distinguish what is important in the arguments of the effect of impurity doping on $T_c$.

3. What determines the $T_c$ values?

Now, as the summary of the data we have obtained up to now, the $T_c$ values of LaFe$_{1-y}$Ni$_y$AsO$_{0.89}$F$_{0.11}$ are plotted in Fig. 3 against $\delta n$ or the electron numbers doped to the LaFeAsO [For LaFe$_{1-y}$Ru$_x$AsO$_{0.88}$F$_{0.11}$ $(x=0)$, $x+y+0.11(=y+0.11)$ is used instead of $0+0.11$ as the abscissa to describe the Ru-doping level. Therefore, it does not correspond to the electron number.] From the figure, we can extract the following. For the dopings which induce the $\delta n$ change, $T_c$ disappears at the almost common values of $\delta n$, which seem to correspond to the disappearance of the hole Fermi surfaces around the $\Gamma$ point, indicating that the rate of the $T_c$ suppression, $|dT_c/dy|$ does not depend on whether the electron scattering centers exist or not in the FeAs conducting layers, that is, the $T_c$ value is determined solely by the electron number, and therefore the pair breaking effect expected for superconducting systems with sign-reversing order parameters does not exist. If it existed, the rate $|dT_c/dy|$ were much larger than the observed values: Assuming that the $S_z$ symmetry is realized in LaFe$_{1-y}$Co$_y$AsO$_{0.89}$F$_{0.11}$, we can estimate the initial decreasing rate $|dT_c/dy|_{\mu 0}$ by applying the pair breaking equation and using the residual resistivities [3, 5]. The result is shown by the dotted line in Fig. 3. Detailed arguments can be found in our previous papers. These considerations exclude the possibility of the $S_z$ symmetry. The result is also supported by the fact that $|dT_c/dy|$ observed for the isoelectronic Ru doping is very small, showing again that the change of $\delta n$ is primarily important.

We are aware that there are experimental reports that for Zn-doped systems, the $|dT_c/dy|$ values are rather large. However, I believe that we can explain the results by the effect of the electron localization: When the sheet resistance $R_s$ defined by using the lattice parameter $c$ as $R_s=\rho_0/c$ exceeds $h/4e^2\sim 6.45 \Omega$, $T_c$ disappears [10]. Another thing we want to stress is that if the present Fe-based superconductors with multiband natue have the $s_z$ symmetry, the absolute slope $|dT_c/dy|$ due to the electron scattering by nonmagnetic impurities is significantly larger than that expected for single band Cu oxide superconductors, even though the latter systems also have the sign-reversing $\Delta$. It is because impurities such as Zn atoms doped into the conducting planes of the single band superconductors act as the unitary scatterers, for which the $T_c$ suppression effect is much reduced [8, 11]. Therefore, for Fe pnictide systems, even if the observed $|dT_c/dy|$ is as large as that observed for Zn–doped Cu oxide superconductors, it does not indicate the existence of the pair breaking effect.

![Fig. 2 Thermoelectric powers $S$ of Ni-doped La1111 systems are shown against $T$. Inset shows the similar data for Co-doped La1111 systems for comparison.](image-url)
which of the magnetism and electron localization is exhibits the magnetic nature. We cannot distinguish the very small value of indicating that the electron localization takes place at the resistivity increases very rapidly with increasing samples is also rather large[3]. However, for the system, 4.

4. Summary
Now, our results indicate that the $S_{\alpha}$ symmetry is likely to be realized in the Fe-based superconductors. Results of the studied on the other quantities sensitive to the relative signs of the order parameters can also be explained in a consistent way by the $S_{\alpha}$ symmetry [3, 5-7]. Then, the problem is to answer the question “what is the pairing mechanism of the Fe-based superconductors?”. To investigate it, it is important to go back to the initial idea that there is a crucial difference between the Fe-based superconductors and high-$T_c$ Cu oxides, that is, in the Fe-based superconductors, there are the orbital degrees of freedom. In this sense, the role of the orbital fluctuations should be considered in a serious way [12, 13].

Acknowledgment
The authors thank Prof. H. Kontani for fruitful discussion. The work is supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and Technology and JST, TRIP.

References
[1] Mazin I I 2010 Phys. Rev. B 81 020507.
[2] Kuroki K S, Onari S, Arita R, Usui H, Tanaka Y, Kontani H, and Aoki H 2008 Phys. Rev. Lett. 101, 087004
[3] Sato M, Kobayashi Y, Lee S C, Takahashi H, Satomi E, and Miura 2010 J. Phys. Soc. Jpn. 79, 014710
[4] Kawamarta T, Satomi E, Kobayashi Y, Itoh M and Sato M 2011 J. Phys. Soc. Jpn. 80, to be published
[5] Moyoshi T, Lee S C, Tatematsu S, Yasui Y, Kobayashi Y, Sato M and K. Kakurai 2010 Physica C 470 S470-S471
[6] Tatematsu S, Yasui Y, Moyoshi T, Motoya K, Kakurai K, and Sato M 2011 J. Phys. Soc. Jpn. 80, 073703
[7] Kobayashi Y, Satomi E, Lee S C and Sato M 2010 J. Phys. Soc. Jpn. 79, 093709
[8] Onari S and Kontani H 2009 Phys. Rev. Lett. 103, 177001
[9] Singh D J and Du M-H 2008 Phys. Rev. Lett. 100, 237003
[10] Mandrus D, Forro L, Kendoziora C and Mihaly L 1991 Phys. Rev. B 44, 2418
[11] Fukuzumi Y, Mizuhashi K, Takenaka K, Uchida S 1996 Phys. Rev. Lett. 76, 684
[12] Kontani H, Saito T and Onari S 2011 arXive:1103.3360
[13] Yanagi Y, Yamakawa Yand Ono Y 2010 Phys. Rev. B 81, 054518