Preparation of the oxypnictides and studies on their superconductivity

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LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_y$ ($x=0.11$) with various $y$ values were prepared and their electrical resistivities, superconducting diamagnetisms and Hall coefficients have been measured. $^{75}$As- and $^{135}$La-NMR studies have also been carried out. In spite of the successful Co-doping, we have not found any meaningful correlation of $T_c$ with $y$, which indicates that the $T_c$-suppression by Co-doping is considered not to be so significant as expected for superconductors with nodes. Even for superconductors without nodes, it may not be easy to expect this small effect on $T_c$ if there are two different (disconnected) Fermi surfaces whose order parameters have opposite phases.

We also show that the spin component of the Knight shift of $^{135}$La is plotted as a function of the resistivity at 30 K, where $^{135}$La-NMR measurements were successfully carried out. In the main panel of Fig. 1, $T_c$ is plotted against $\rho(30 \text{ K})$, where $100y$ values are attached to the corresponding data. Inset shows the lattice parameter $c$ against $100y$.

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was successfully carried out. In the main panel of Fig. 1, $T_c$ is plotted as a function of the resistivity at 30 K, $\rho(30 \text{ K})$. While we can find the systematic $T_c$-decrease with increasing $\rho(30 \text{ K})$, we do not find any correlation of $T_c$ with $y$, indicating that the $T_c$ value is not primarily determined by the Co concentration $y$ but by the electrical resistivity $\rho$. and therefore that $T_c$-suppression by impurity scattering is much smaller than expected for order parameters $\Delta$ with nodes on the Fermi surface. Even for superconductors without nodes, this small $T_c$-suppression

KEYWORDS: Fe pnictides, superconductivity, NMR, Knight shift, impurity effect

1. Introduction

Superconductivity in LaFeAsO$_{1-x}$F$_x$ found by Kamihara et al. 1) presented a remarkable example of $3d$ electron superconductors and a variety of superconducting compounds having FeAs layers of edge-sharing FeAs$_4$ tetrahedra with the transition temperature $T_c$ higher than 50 K have been found. 2) Because the superconductivity primarily occurs in the $3d$-electrons of the FeAs layers, 3,4) the magnetic interaction cannot be ignored in the study of the origin of the superconductivity.

We have prepared LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_y$ system ($x=0.11$) and measured their electrical resistivities $\rho$, magnetizations $M$, due to the superconducting diamagnetism $M_c$ and Hall coefficients $R_H$. We have also carried out $^{75}$As- and $^{135}$La-NMR measurements.

Here, we present results of the above measurements and argue the symmetry/orient of the superconductivity and the electronic state. 5) The $T_c$-suppression by the Co-impurities is rather weak as compared with that observed for Cu oxides. 6) We also show that the spin component of the Knight shift of $^{135}$La is almost completely suppressed by the superconductivity, confirming our previous data that the system has singlet Cooper pairs. 5)

2. Experiments

Polycrystalline samples of LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_y$ ($x=0.11; 0 \leq y \leq 0.3$) were prepared as described in ref. 5 from initial mixtures of La, La$_2$O$_3$, LaF$_3$ and FeAs with the nominal molar ratios. A SQUID magnetometer was used to measure $M_c$ and $\rho$ was measured by the four terminal method and their data are in ref. 5. From the $M_c$-$T$ curves we determined the $T_c$ values. $R_H$ was measured for samples with $y \leq 0.03$ with the magnetic field $H=7 \text{ T}$ by rotating samples. The $^{75}$As- and $^{135}$La-NMR measurements were carried out by the standard coherent pulse method, where the nuclear spin-echo intensity $I$ was recorded with the NMR frequency or applied magnetic field changed stepwise.

3. Results and Discussion

In the inset of Fig. 1, the lattice parameter $c$ of LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_y$ ($x=0.11$) is plotted against $y$. The linear relationship between $c$ and $y$ guarantees that the Co doping

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Fig. 2. (left) NMR intensities of $^{135}$La multiplied by $T$ taken at a frequency $f=44.6 \text{ MHz}$ for the sample $y=0.02$ ($T_c<5 \text{ K}$) are shown at two temperatures. (right) $T$ dependences of the NMR intensities multiplied by $T$ at $H=7.4 \text{ T}$ and the initial spin-spin relaxation rate $1/\tau_0$ ($^\circ$). Effects of magnetic ordering can be seen at ~63 K.
rate may not be easily expected, if there are two different (disconnected) Fermi surfaces whose order parameters have opposite signs. Therefore, this smallness of the $T_c$ suppression rate is important for arguments on the relative signs of $\Delta$ on two kinds of Fermi surfaces, and consistent with the superconductivity found in heavily Co-doped systems. As one of possible origins of the observed weak $T_c$-decrease with $p(30\,\text{K})$, the loss of the itinerant nature can be considered, though the intrinsic resistivity cannot be accurately estimated because of the grain-boundary effect (detailed discussion are in ref. 5). With increasing the resistivity, the behavior of the NMR spin-spin relaxation rate $1/\tau$ changes, and the initial relaxation rate $1/\tau_0$ increases, indicating that the spin fluctuation of the system increases. In Fig. 2, the $T$ dependences of $1/\tau_0$ and spectral broadening at $T < T_N$ (left panel) are shown for the sample with $100y=2.0$ ($T_c < 5\,\text{K}$). Evidence for the antiferromagnetic (or SDW) transition at $T_N=63\,\text{K}$ found in the figure, is a further support of this idea.

Figure 3 shows the $T$ dependence of $R_{\text{H}}$ of the LaFe$_{1-x}$Co$_x$AsO$_{1-y}$F$_y$ ($x=0.11$) samples. While $R_{\text{H}}$ does not exhibit any correlation with $p$, the behavior changes systematically with $T_N$, which resembles to that of high $T_c$ Cu Oxides. If the magnetic fluctuation is relevant to the observed strong $T$ dependence of $R_{\text{H}}$ as in Cu oxides, the fact that the characteristic temperature of the $R_{\text{H}}$-$T$ curves is smaller by a factor of 2 than that of Cu oxides is important for the consideration of $T_N$ value.

Figure 4 shows NMR Knight shift of $^{75}\text{As}$ reported in our previous paper. Here, combining our new data taken up to $\sim 250\,\text{K}$ for $^{75}\text{As}$ and those of $^{19}\text{F}$, we estimate the chemical shift of $^{75}\text{As}$ by the method shown in the inset and indicate it by the grey broken line. The results show that the contribution to the shift $^{75}\kappa_{\text{spin}}$ vanishes at low temperature in this system with singlet pairing. We also note that the $T$ dependence of $^{75}\kappa$ does not exhibit the two gap nature and can roughly be explained by the simple Yosida function. It is different from the results of ref.14 for PrFeAsO$_{1-x}$F$_x$. We think that this discrepancy arises from that in PrFeAsO$_{1-x}$F$_x$, a possible influence of the Pr moments on the internal field becomes serious.

4. Summary

We have shown that the effect of Co impurities on $T_c$ is weak, which restricts the symmetry and the possible origin of the superconductivity. The observed Knight shift indicates the singlet pairing and it roughly obeys the Yosida function.

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