μSR study of the magnetic state in hole and electron doped Sr$_2$IrO$_4$

S. Tsunoda, K. Horigane$^1$, H. Okabe$^2$, K. Machida, M. Akimitsu$^1$, K. Kawashima$^3$, R. Horie$^1$, K. Kobayashi, A. Koda$^2$, R. Kadono$^2$, and J. Akimitsu$^1$

Graduate School of natural Science, Okayama University, Okayama 700-8530, Japan
$^1$Research Institute for Interdisciplinary Science, Okayama University, Okayama 606-8502, Japan
$^2$Institute of Materials Structure Science/J-PARC Center, KEK, Ibaraki 319-1106, Japan
$^3$IMRA Material R&D Co., LTD., Aichi 448-0032, Japan

*E-mail: k-horigane@okayama-u.ac.jp
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We performed a muon spin relaxation (μSR) study of a lightly hole-doped (K) and electron doped (La) doped Sr$_2$IrO$_4$ system. In the electron doping case, the fraction of long-range order is approximately 10%, and the effective Ir moment was 0.053 $\mu_B$, which is substantially smaller than that of Sr$_2$IrO$_4$ (0.4 $\mu_B$). However, the ZF-μSR time spectra of hole-doped Sr$_{1+\delta}$K$_{0.05}$IrO$_4$ exhibit a clear sinusoidal oscillation below $T_N$ (= 224 K), and the muon spin precession frequency $f$ is almost the same as that of Sr$_2$IrO$_4$. Moreover, a reduction of the asymmetries of oscillation was observed at temperatures below 150 K. The reduction likely originates from the ordered magnetic moment at the apical oxygen, suggesting that hole carriers were introduced into the apical oxygen.

**KEYWORDS:** Ir oxide, superconductivity, μSR method

1. Introduction

The 5$d$ transition-metal compounds have been attracting intensive attention in recent years because their strong spin–orbit coupling leads to novel physical properties. For instance, Sr$_2$IrO$_4$ ($T_N$ = 240K) is a novel $J_{\text{eff}} = 1/2$ Mott state induced by relativistic spin–orbit coupling and Coulomb repulsion $U$ [1]. Theoretically, Sr$_2$IrO$_4$ was predicted to be a high-temperature superconductor when doped with carriers because it strongly resembles the cuprates in crystal structure, electronic structure, and magnetic coupling constants [2]. Because of the similar Mott physics between cuprates and iridates, Sr$_2$IrO$_4$ is a good candidate for exploring unconventional high-$T_C$ superconductivity by carrier doping. Recently, our group have investigated the substitution effect for Sr$_2$IrO$_4$ to confirm the influence of band filling control of the Mott insulating state. We synthesized a hole doping sample of Sr$_{2-x}$K$_x$IrO$_4$ and an electron doping sample of Sr$_{2-x}$La$_x$IrO$_4$ [3,4]. From the magnetic susceptibility data, the absolute magnetic moment, and Néel temperature, $T_N$, of Sr$_{2-x}$La$_x$IrO$_4$ decrease with increasing La doping. However, the absolute magnetic moment and $T_N$ of Sr$_{2-x}$K$_x$IrO$_4$ are approximately constant with K substitution. These facts suggest that electron carriers are effectively introduced into the IrO$_2$ layer. To understand these differences from a microscopic perspective, we conducted ZF- and LF-muon spin relaxation (μSR) measurements in hole- and electron-doped Sr$_2$IrO$_4$. 

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2. Experimental details

We performed μSR measurements on polycrystalline samples of Sr$_{2-x}$La$_x$IrO$_4$ ($x = 0.05$) and Sr$_{2-x}$K$_x$IrO$_4$ ($x = 0.045$). The detailed synthesis procedure is described in Refs. 3 and 4. The actual composition for the K site was analyzed using energy-dispersive X-ray spectrometry. The magnetic transition temperatures of our samples were determined by magnetic susceptibility to be 190 K (La, $x = 0.05$) and 220 K (K, $x = 0.045$), respectively. ZF- and LF-μSR experiments were performed using the Advanced Research Targeted Experimental Muon Instrument at the S beamline (ARTEMIS) spectrometer [5] with a fly-past chamber at the Material and Life Science Experimental Facility (MLF), J-PARC, Tokai, Japan.

3. Results and discussion

Figure 1a shows ZF-μSR time spectra of Sr$_{1.95}$La$_{0.05}$IrO$_4$. A stretched exponential relaxation was observed at temperatures above $T_N$ (= 190 K). However, substantial oscillatory signals were observed at temperatures below $T_N$, indicating the existence of a long-range-magnetic order below $T_N$, as determined by magnetic susceptibility measurements. At temperatures below 50 K, the spectral damping becomes faster with decreasing temperature and the spectrum at 3 K shows a shallow dip structure. This result is similar to that for $x = 0.1$ [4] and likely originates from the spin-glass state at low temperatures. To understand the magnetism of this system, we fitted the ZF-time spectra using the following function:

$$ A_{ZF}(t) = A_{osc} \exp(-\lambda t) \cos(\omega t + \varphi) + A_{non} \exp(-\lambda' t)^\beta + A_{bg} (T < 190 \text{ K}) \cdots (1) $$

$$ A_{ZF}(t) = A_{non} \exp(-\lambda' t)^\beta + A_{bg} (T > 190 \text{ K}) \cdots (2) $$

where $A_{osc}$, $A_{non}$, and $A_{bg}$ (= 0.04) are the positron decay asymmetries of oscillation, nonoscillation, and background components, respectively, $\lambda$ and $\lambda'$ are the corresponding relaxation rates, $\beta$ is the stretched exponent, $\omega$ is the muon spin precession frequency (= $2\pi f_i = \gamma_i B_i$ with $\gamma_i = 2\pi \times 135.53$ MHz/T and $B_i$ being the local field at the muon site), and $\varphi$ is the initial phase of precession. We estimated the volume fraction of the long-range ordered state using the best-fit values of asymmetries ($A_{osc}$, $A_{non}$, and $A_{bg}$) and found a substantial fraction of long-range order (~10%) shown in Fig. 1b. Curve-fitting of the frequency by the power law $f(T) = f_0 (1 - T/T_N)^\nu$ yielded $f_0 \approx 0.4$ MHz ($B = 29.3$ G). This value is much smaller than that of Sr$_2$IrO$_4$ (217 G) determined via previous μSR measurements [6]. Fig. 1c shows the temperature dependence of $\beta$. A gradual decrease of $\beta$ from 1 to 0.6 appears at approximately 190 K, corresponding to $T_N$. Then, $\beta$ remains approximately 0.6 from 190 K to 50 K. This value of $\beta$ is likely associated with a short-range magnetic Griffiths phase reported in previous μSR measurements [4]. As the temperature is lowered further (below 50 K), $\beta$ reaches approximately 1/3—a typical value in dilute spin-glass systems [7,8].
Fig. 1 (a) Temperature dependence ZF-μSR time spectra for Sr$_{1.95}$La$_{0.05}$IrO$_4$. Solid lines represent the fitting results obtained using Eqs. (1) and (2). (b) Temperature dependence of the partial asymmetry $A_{osc}$, $A_{non}$. The inset shows the temperature dependence of the muon spin precession frequency. (c) The stretching exponent $\beta$. The dotted line indicates $T_{N}$. (d) LF-μSR time spectra recorded at 3.4 K. We also estimated the Ir moment size of $x = 0.05$ from the results of LF-μSR measurements. Fig. 1d shows the LF-μSR spectra of the $x = 0.05$ sample measured at $T = 3$ K. The LF-μSR spectra display a systematic upward shift with increasing field. On the basis of our previous μSR study [4], the static width of the local fields at the muon sites $\Delta$ was estimated to be 5.30 μs$^{-1}$. Thus, the characteristic field at a muon site was determined as $\Delta/\gamma_{\mu} = 62.2$ G. In Sr$_2$IrO$_4$, the moment size of the $J_{eff} = 1/2$ pseudospin is reduced to 0.4 $\mu$B, as confirmed by previous μSR, RIXS, and neutron diffraction measurements [6,9,10]. On the other hand, the effective Ir moment size of Sr$_{2-x}$La$_x$IrO$_4$ $|\mu_{Ir}|$ was determined as 0.053 ($x = 0.05$) $\mu$B. This value is about eight times smaller than that of Sr$_2$IrO$_4$ and consistent with the previous magnetic susceptibility measurements [4]. Thus, the decrease of the Ir moment is attributed to the effects of electron doping by La substitution.

Figure 2 shows the ZF-μSR time spectra of hole-doped Sr$_{1.955}$K$_{0.045}$IrO$_4$. Although
the magnetic ordered phase was suppressed by electron doping, the ZF-\(\mu\)SR time spectra of hole-doped \(\text{Sr}_{1.955}\text{K}_{0.045}\text{IrO}_4\) exhibit a clear sinusoidal oscillation at temperatures below \(T_N(\sim 220 \text{ K})\). Such a signal indicates the onset of a relatively homogeneous internal field at muon sites as a result of the long-range magnetic order. To describe the ZF-\(\mu\)SR time spectra, we fitted them using Eq. (1) \((20 \text{ K} < T < 220 \text{ K})\) and Eq. (2) \((220 \text{ K} < T)\). We found a substantial fraction of long-range order \((\sim 70\%)\) at temperatures below \(T_N(= 224 \text{ K})\) (Fig. 3a). The temperature dependence of \(f\) was fitted to the power law. Curve-fitting of the frequency yielded the critical index \(\gamma = 0.217(8)\) and \(f(0) = 2.93(2) \text{ MHz}\), respectively (Fig. 3b). These results are approximately the same as those reported in a previous \(\mu\)SR study of \(\text{Sr}_{2}\text{IrO}_4\) [6]. The effective Ir moment does not change by hole doping; however, we fail to describe the ZF-time spectra below 20K because total asymmetry became large. Recently, Miyazaki et al. reported a \(\mu\)SR study of \(\text{Sr}_{2}\text{IrO}_4\) and found a secondary magnetic phase emerging below \(T_m(\sim 90 \text{ K})\), which originated from the ordered magnetic moment \((\sim 0.03 \mu_B)\) at the apical oxygen [6]. These results suggest that a secondary magnetic phase due to the ordered magnetic moments on the apical oxygen was realized in hole-doped \(\text{Sr}_{1.955}\text{K}_{0.045}\text{IrO}_4\). To describe the time spectra below 20K, we fitted the ZF-time spectra using the following function:

\[
A_{ZF}(t) = A_{1\text{osc}} \exp(-\lambda t) \cos(\omega t + \varphi) + A_{2\text{osc}} \exp(-\lambda t) \cos(\omega t + \varphi) + A_{3\text{non}} \exp(-\lambda' t)^\beta + A_{bg}(T < 20 \text{ K})\cdots (3)
\]

From our analysis, we found that a second frequency \((\sim 4.21(4) \text{ MHz})\) appeared at lowest temperature. This value is consistent with the value assuming a point-like magnetic dipolar moment \((\mu_O)\) placed on the apical oxygen [6]. Therefore, a secondary magnetic phase due to the ordered magnetic moments on the apical oxygen was realized in hole-doped \(\text{Sr}_{1.955}\text{K}_{0.045}\text{IrO}_4\). More interestingly, in the K doping case, we also observed a reduction of \(A_{\text{osc}}\) at temperatures below 150 K whose value is higher than that of \(\text{Sr}_{2}\text{IrO}_4\) \((T_m \sim 90 \text{ K})\). This result suggests that hole carriers due to K substitution may be introduced into not Ir site but the apical oxygen site because \(T_N\) and the effective Ir moment do not change by hole doping. Another possibility is oxygen deficiency because hole carriers are canceled out by tiny amount of oxygen deficiency \((\delta \sim 0.02)\). To clarify the mechanism of hole doping, it is necessary to precisely evaluate the two magnetic phases in \(\text{Sr}_{2-x}\text{K}_x\text{IrO}_4\), which is the focus of further studies that are now in progress.
Fig. 3 Temperature dependence of (a) partial asymmetry $A_{\text{osc}}$, $A_{\text{non}}$, and (b) the muon spin precession frequency in Sr$_{1.955}$K$_{0.045}$IrO$_4$. Partial asymmetry was subtracted the constant background ($A_{\text{bg}} = 0.06844$)

4. Conclusion

We performed a $\mu$SR study in the lightly hole-doped (K) and electron-doped (La) Sr$_2$IrO$_4$ system. ZF-$\mu$SR studies in the La-doped case revealed that a long-range ordered phase (~10%) and short-range magnetic Griffith phase were realized at temperatures below the $T_N$. The effective Ir moment size was 0.053 $\mu_B$, which is substantially smaller than that of Sr$_2$IrO$_4$ (0.4 $\mu_B$), indicating that electrons are introduced into the Ir atoms. However, ZF-$\mu$SR time spectra of hole-doped Sr$_{1.955}$K$_{0.045}$IrO$_4$ exhibit a clear sinusoidal oscillation below $T_N$ (= 224 K) and the muon spin precession frequency $f$ is approximately the same as that of Sr$_2$IrO$_4$. Why the effective Ir moment does not change by hole doping remains unclear. However, we found a possible secondary magnetic phase that emerges at temperatures below 150 K and originates from the ordered magnetic moment at the apical oxygen. This result suggests that hole carriers are introduced into the apical oxygen in Sr$_{2-x}$K$_x$IrO$_4$ system.

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