Single crystal growth and magnetism of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$: tracking the $J = 0$ ground state of Ir$^{5+}$

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Abstract. Single crystals of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ have been successfully grown using hydroxides flux. Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ crystallize in the K$_4$CdCl$_6$-type structure with the space group $R$-3$c$ (No.167). Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ are electrically insulating with estimated activation gaps of 0.68 eV and 0.80 eV, respectively. Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ show paramagnetic behavior down to 2 K. In this work, the observed effective moments, $\mu_{\text{eff}}$, for Sr$_3$NaIrO$_6$ single crystals are 0.31 $\mu_B$ for $H \perp c$ and 0.28 $\mu_B$ for $H \parallel c$, which are much smaller than that of 0.49 $\mu_B$ previously reported for the polycrystalline Sr$_3$NaIrO$_6$ samples. For Sr$_3$AgIrO$_6$ single crystals, a much larger value of $\mu_{\text{eff}} = 0.57 \mu_B$ is observed as compared with Sr$_3$NaIrO$_6$ single crystals. The x-ray absorption spectroscopy and low-temperature specific heat data indicate that the Ir in Sr$_3$NaIrO$_6$ has an almost pure Ir$^{5+}$ valence state, while the Ir in Sr$_3$AgIrO$_6$ is slightly lower than $+5$. The estimated low limits of magnetic impurity Ir$^{4+}$ are about $\sim$1.7\% and $\sim$9.2\% for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively. These magnetic impurities are likely to fully explain the observed $\mu_{\text{eff}}$ values for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ single crystals, supporting the $J = 0$ ground state of Ir$^{5+}$ in Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. 
In 3d transition metal oxides, the valence electrons are strongly correlated and the Hubbard $U$ plays an important role [1–5]. In comparison with 3d electrons, the orbitals of 5d electrons are more extended and the $U$ in the 5d system becomes weaker while the spin-orbit coupling (SOC) becomes much stronger due to their larger atomic number [6,7]. In the strong SOC regime, the SOC can split three $t_{2g}$ orbitals in the octahedral crystal field into an upper $j = 1/2$ doublet and a lower $j = 3/2$ quadruplet [8,9]. For example, in tetravalent iridate Sr$_2$IrO$_4$ (Ir$^{4+}$: 5d$^5$) the SOC-assisted Mott-insulating state is explained with the $J = 1/2$ ground state [9]. Resonant inelastic x-ray scattering measurements on pentavalent osmates (Os$^{5+}$: 5d$^3$) reveal the SOC controlled $J = 3/2$ ground state [10]. In such a scenario, if there are four 5d electrons filling the lower quadruplet, the ground state should be $j = 0$. Long-range magnetic orders reported in Ir$^{5+}$ (5d$^4$) double perovskite oxides Sr$_2$YIrO$_6$ and Ba$_2$YIrO$_6$ with effective moment ($\mu_{\text{eff}}$) of 0.91 $\mu_B$/Ir and 1.44 $\mu_B$/Ir, respectively, raise concerns about the ground state of 5d$^4$ oxides [11,12]. These results have been challenged by other studies reporting that no magnetic order was found in Ba$_2$YIrO$_6$ [13] and Sr$_2$YIrO$_6$ [14] down to ~430 mK. Studies on A$_2$YIrO$_6$ (A = Sr, Ba) and other Ir$^{5+}$ double perovskite oxides generally reveal a weak paramagnetic behavior with small $\mu_{\text{eff}}$ values of 0.19 – 0.63 $\mu_B$/Ir [13–25] which are much lower than the theoretical spin-only $\mu_{\text{eff}} = 2.83$ $\mu_B$/Ir demonstrating a SOC dominated ground state. The origin of these finite magnetic moments is still ambiguous. Quench of the $J = 0$ state for Ir$^{5+}$ due to IrO$_6$ octahedra distortion in Sr$_2$YIrO$_6$ was proposed by Cao et al [11]. However, this scenario cannot explain the paramagnetic moment observed in cubic Ba$_2$YIrO$_6$ where is no structural distortion, and the studies on Ba$_{2-x}$Sr$_x$YIrO$_6$ studies do not find correlations between $\mu_{\text{eff}}$ values and the degree of structural distortions [19,26]. The existence of magnetic impurities has been suggested by studies in Sr$_2$YIrO$_6$ [14] and Ba$_2$YIrO$_6$ [17]. Fuchs et al. confirmed the existence of Ir$^{4+}$ and Ir$^{6+}$ magnetic defects which are responsible for the magnetism in Ba$_2$YIrO$_6$ [18]. The antisite disorder in double perovskites has also been suggested to play an important role [16,20]. Laguna-Marcos et al suggest that the Ir$^{4+}$
and Ir\(^{5+}\) magnetic impurities may locate in the antisite disorder region [20]. Condensation of \(J = 1\) trilpon excitations of \(5d^4\) oxides is also a possible source for the observed magnetic moments [27,28]. Chen et al. proposed that the condensation is unlikely in \(\text{Sr}_2\text{YIrO}_6\) and \(\text{Ba}_2\text{YIrO}_6\) with the ideal crystal structure, but the antisite disorder between \(\text{Y}^{3+}\) and \(\text{Ir}^{5+}\) can break down the local nonmagnetic singlets [16]. Recent studies on \(A_2\text{BIrO}_6\) (\(A = \text{Ba, Sr}; B = \text{Lu, Sc}\)) also support the \(J = 0\) ground state for these \(\text{Ir}^{5+}\) oxides and indicate the magnetic signals are from extrinsic sources, such as magnetic impurities and antisite disorder [21].

To narrow down the possible explanations, it is better to studies on \(\text{Ir}^{5+}\) oxides with less antisite disorder. Recently, studies on \(K_4\text{CdCl}_6\)-type polycrystalline \(\text{Ir}^{5+}\) oxide \(\text{Sr}_3\text{NaIrO}_6\) have been reported and indicate a possible quantum spin liquid ground state (reported \(\mu_{\text{eff}} = 0.49\ \mu_B/\text{Ir}\) [22]. In comparison with \(\text{A}_2\text{YIrO}_6\) (\(A = \text{Sr, Ba}\)), where the \(\text{Ir}^{5+}\) octahedra are separated by \(\text{Y}^{3+}\) \(\text{O}_6\), the \(\text{Ir}^{5+}\) octahedra are separated with \(\text{Na}^{1+}\) \(\text{O}_6\) octahedra in the \(\text{Sr}_3\text{NaIrO}_6\). The larger charge difference would reduce the antisite disorder between \(\text{Na}^{1+}\) and \(\text{Ir}^{5+}\) in \(\text{Sr}_3\text{NaIrO}_6\) as compared with \(\text{Sr}_2\text{YIrO}_6\) and \(\text{Ba}_2\text{YIrO}_6\). Thus, the \(K_4\text{CdCl}_6\)-type iridate is a good platform to investigate the ground state of \(\text{Ir}^{5+}\) ions. To track the \(J = 0\) ground state for \(\text{Sr}_3\text{NaIrO}_6\), it is better to grow single crystals to minimize any by-phases and lattice defects. In this work, we successfully grow single crystals of \(K_4\text{CdCl}_6\)-type iridate oxides \(\text{Sr}_3\text{NaIrO}_6\) and \(\text{Sr}_3\text{AgIrO}_6\). Magnetic measurements reveal that the \(\mu_{\text{eff}}\) for \(\text{Sr}_3\text{NaIrO}_6\) single crystals is about 0.31 \(\mu_B\) for \(H \perp c\) and 0.28 \(\mu_B\) for \(H || c\) which are smaller than that of 0.49 \(\mu_B\) reported for the polycrystalline \(\text{Sr}_3\text{NaIrO}_6\) [22]. The presence of a few percent of magnetic \(\text{Ir}^{4+}\) impurity is indicated by the analysis of low-temperature specific heat data which is likely to fully explain the observed \(\mu_{\text{eff}}\), supporting the \(J = 0\) ground state of \(\text{Ir}^{5+}\) in \(\text{Sr}_3\text{NaIrO}_6\).

**Experiment**

Single crystal samples of \(\text{Sr}_3\text{NaIrO}_6\) and \(\text{Sr}_3\text{AgIrO}_6\) were both prepared by flux method using \(\text{NaOH-KOH}\) and \(\text{KOH}\), respectively. The \(\text{SrOH} \cdot 8\text{H}_2\text{O}\), \(\text{NaOH}\), \(\text{KOH}\), and \(\text{Ir}\) with a molar ratio of 3:50:40:1 (for \(\text{Sr}_3\text{NaIrO}_6\)) and \(\text{SrOH} \cdot 8\text{H}_2\text{O}\), \(\text{Ag}_2\text{O}\), \(\text{KOH}\),
and Ir with a molar ratio of 3:0.5:40:1 (for Sr$_3$AgIrO$_6$) were weighted, respectively. The mixtures were placed into Al$_2$O$_3$ crucibles with lids, then heated to 873 K in 1 h and annealed for 12 h before cooled to room temperature by stopping the heating. Single crystals were separated by washing with deionized water.

Single-crystal x-ray diffraction measurements were conducted on a Bruker D8 Venture diffractometer at 300K using Mo Kα radiation (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). The crystalline structures were refined by the full-matrix least-squares method on $F^2$ using the SHELXL-2018/3 program.

Single crystals of selected samples were used for magnetic susceptibility ($\chi$), longitudinal resistivity $\rho$, specific heat, and x-ray absorption spectroscopy (XAS). The magnetic properties were measured under different applied magnetic fields in Field-Cooling (FC) and Zero-Field-Cooling (ZFC) modes using SQUID-VSM device in a magnetic properties measurement system (MPMS). Isothermal magnetization (M-H) was measured at several fixed temperatures. These transport measurements (both resistivity and specific heat) were measured by a physical property measurement system (Quantum Design inc) using the standard DC four-probe technique and a thermal relaxation method, respectively. XAS spectra at the Ir-L$_3$ edges were studied at the Taiwan Light Source (TLS) beamline 17C of the National Synchrotron Radiation Research Center (NSRRC).

RESULTS AND DISCUSSION

Single crystals for Sr$_3$NaIrO$_6$ with dimensions of ~2mm×0.3mm×0.3mm and Single crystals for Sr$_3$AgIrO$_6$ with ~0.3mm×0.3mm×0.3mm were obtained as shown in Figs. 1(c) and 1(d), respectively. Analysis of the room temperature SCXRD data confirms that Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ crystallize in the K$_4$CdCl$_6$-type structure with the space group $R-3c$ (No.167). The refined lattice parameters were $a = 9.6408(3)$ Å, and $c = 11.5508(5)$ Å for Sr$_3$NaIrO$_6$ and $a = 9.5996(3)$ Å, and $c = 11.9032(6)$ Å for
Sr₃AgIrO₆. Detailed crystallographic data obtained from the SCXRD were summarized in Table I. The crystallographic information files for Sr₃NaIrO₆ and Sr₃AgIrO₆ are attached in the Supplemental Material [29].

Table I. Crystallographic and structure refinement data for Sr₃AgIrO₆ and Sr₃NaIrO₆.

| Chemical formula | Sr₃AgIrO₆ | Sr₃NaIrO₆ |
|-----------------|----------|----------|
| Formula weight  | 658.94 g/mol | 574.05 g/mol |
| Radiation       | Mo Kα, 0.71073 Å | Mo Kα, 0.71073 Å |
| Temperature     | 300 K | 300 K |
| Crystal system  | Trigonal | Trigonal |
| Space group     | R-3c | R-3c |
| Unit cell dimensions | a = 9.5996(3) Å | a = 9.6408(3) Å |
|                  | c = 11.9032(6) Å | c = 11.5508(5) Å |
| Volume          | 949.95(8) Å³ | 929.76(7) Å³ |
| Z               | 6 | 6 |
| Density(calculated) | 6.911 g/cm³ | 6.152 g/cm³ |
| Absorption coefficient | 49.048 mm⁻¹ | 47.117 mm⁻¹ |
| No. of reflections | 5112 | 6376 |
| No. independent reflections | 265 | 261 |
| No. observed reflections | 256 | 256 |
| F (000)         | 1716 | 1500 |
| Theta range for data collection | 4.21 to 28.29° | 4.23° to 28.36° |
Goodness of fit 1.265 1.118
R1 (I > 2σI) 0.0230 0.0103
ωR2(I > 2σI) 0.0735 0.0258
R1 (all data) 0.0237 0.0106
ωR2(all data) 0.0740 0.0261

Weighting scheme

\[ w = \frac{1}{\sigma^2 F_o^2 + (0.0423 P)^2} + 38.8002P \]
Where \( P = \frac{(F_o^2 + 2F_e^2)}{3} \)

Refinement software SHELXL-2018/3

Table II. Refined atomic positions and temperature parameters for Sr₃NaIrO₆.

| atom | x   | y   | z   | Occupancy | U_eq (Å²) | Site |
|------|-----|-----|-----|-----------|-----------|------|
| Ir1  | 2/3 | 1/3 | 5/6 | 1         | 0.00379(9)| 6b   |
| O1   | 0.4882(2) | 0.3102(2) | 0.7336(2) | 1         | 0.0075(4) | 36f  |
| Sr1  | 0.3090(1) | 1/3 | 7/12 | 1         | 0.0069(1) | 18e  |
| Na1  | 2/3 | 1/3 | 7/12 | 1         | 0.0090(6) | 6a   |

Table III. Refined atomic positions and temperature parameters for Sr₃AgIrO₆.

| atom | x   | y   | z   | Occupancy | U_eq (Å²) | Site |
|------|-----|-----|-----|-----------|-----------|------|
| Ir1  | 2/3 | 1/3 | 1/3 | 1         | 0.0061(3) | 6b   |
| O1   | 0.6896(7) | 0.5138(6) | 0.2373(4) | 1         | 0.0099(10)| 36f  |
| Sr1  | 0.6896(1) | 2/3 | 5/12 | 1         | 0.0094(3) | 18e  |
| Ag1  | 2/3 | 1/3 | 1/12 | 1         | 0.0230(5) | 6a   |
Figure 1. Crystal structures of Sr$_3$AgIrO$_6$(Sr$_3$NaIrO$_6$) view along (a) [110] and (b) [001] directions. (c) and (d) shows optical photos of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ single crystals, respectively.

In the crystal structures of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, Na/Ag atoms occupy the 6$a$ site, Ir atoms occupy the 6$b$ site, Sr atoms occupy the 18$e$ site, and O atoms occupy the 36$f$ site (see Table II and Table III). The crystal structure of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO is shown in Figure 1. The IrO$_6$ octahedra are connected with NaO$_6$/AgO$_6$ octahedra through face-sharing, forming one-dimensional chains. During the analysis of single-crystal x-ray diffraction data, we checked the possibility of antisite between Na/Ag and Ir sites and found no indication of antisite disorder. The bond length for Ir–O are 1.984 Å and 1.989 Å for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively. The bond valence sum for Ir ions calculated from the Ir–O bond length is 4.99 and 4.92 for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively, which are close to the nominal Ir$^{5+}$ oxidation states.

It is well known that hard x-ray absorption spectroscopy (XAS) at the 5d elements L edge is highly sensitive to their oxidation states, since the energy position of the strong white line shifts to higher energy by one or more eV if an increase of the valence state of 5d metal ion by one [30–34]. Figure 2 shows the Ir-L$_3$ XAS spectra for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ together with the Ir$^{4+}$ reference La$_2$CoIrO$_6$ and the Ir$^{5+}$ reference Sr$_2$CoIrO$_6$ [35]. The energy position of Sr$_3$NaIrO$_6$ shifts about ~1.3 eV toward
higher energy in comparison with La$_2$CoIrO$_6$, but locates at the same energy as that of Sr$_2$CoIrO$_6$, supporting the Ir$^{5+}$ oxidation state. The energy position of Sr$_3$AgIrO$_6$ is a little lower than those of Sr$_3$NaIrO$_6$ and Sr$_2$CoIrO$_6$, and is about ~1 eV higher than La$_2$CoIrO$_6$, indicating that the oxidation state of Ir ion in Sr$_3$AgIrO$_6$ is little lower than +5. From these XAS spectra we can conclude that the oxidation state of Ir ion in Sr$_3$NaIrO$_6$ are Ir$^{5+}$, but we cannot exclude the presence of a few percent of Ir$^{4+}$ or Ir$^{6+}$ ions [35]. For Sr$_3$AgIrO$_6$, the average Ir oxidation state is little lower than Ir$^{4+}$ and a moderate amount of Ir$^{4+}$ ions is coexisting with the major Ir$^{5+}$ ions.

Figure 2. Ir-L$_3$ XAS spectra of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ in comparison with an Ir$^{4+}$ reference La$_2$CoIrO$_6$ and an Ir$^{5+}$ reference Sr$_2$CoIrO$_6$.

The temperature-dependent resistivity, $\rho(T)$, for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ are shown in Figs. 3(a) and 3(b). The $\rho(T)$ curves show semiconducting behavior. The $\rho$ increases with cooling and is out of range below 250 K and 260 K for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively. The high-temperature data (>320 K) are used to estimate the gap according to the Arrhenius equation, $\rho \propto e^{(E_a/E_kB_T)}$ [see the insets in Figs. 3(a) and 3(b)]. The estimated activation gap, $E_a$, is ~0.80 eV for Sr$_3$NaIrO$_6$ and ~0.58 eV for Sr$_3$AgIrO$_6$. 
Figure 3. The temperature dependence of resistivity for (a) Sr$_3$NaIrO$_6$ and (b) Sr$_3$AgIrO$_6$. The insets show corresponding data fitted with the Arrhenius equation.

Single crystals of Sr$_3$NaIrO$_6$ are large enough (~2 mm along the c-axis) to measure their anisotropic magnetic properties. The temperature-dependent magnetic susceptibility curves, $\chi(T)$, of Sr$_3$NaIrO$_6$ single crystals measured with magnetic fields perpendicular to the c-axis ($H \perp c$) and parallel to the c-axis ($H \parallel c$) are shown in Figs. 4(a) and 4(b). The ZFC and FC curves are overlapping, and only FC curves are shown. There is no sign of magnetic order down to 2 K. The $\chi(T)$ data above 50 K can be fitted with the Curie-Weiss law, $\chi = \chi_0 + C/(T - \theta_W)$, where $C$, $\theta_W$, and $\chi_0$ are the Curie constant, Weiss temperature, and the temperature-independent component, respectively. For the case of $H \perp c$, the fitting results in a $C$ of 0.012 emu mol$^{-1}$ Oe$^{-1}$ and a $\theta_W$ of -34 K. For the case of $H \parallel c$, a $C$ of 0.008 emu mol$^{-1}$ Oe$^{-1}$ and a $\theta_W$ of 1 K is obtained from the fitting. The $\chi_0$ values for Sr$_3$NaIrO$_6$ are $6.2 \times 10^{-4}$ and $5.4 \times 10^{-4}$ emu mol$^{-1}$ Oe$^{-1}$ for $H \perp c$ and $H \parallel c$, respectively. The $\mu_{\text{eff}}$, calculated from the $C$ is about 0.31 $\mu_B$ for $H \perp c$ and 0.28 $\mu_B$
Regarding the Sr$_3$AgIrO$_6$ single crystals, anisotropic magnetic measurement is not possible due to their small size (~300 μm) and crystal morphology. A total weight of ~19 mg Sr$_3$AgIrO$_6$ single crystals were collected without orientation for magnetic measurement. The $\chi(T)$ curves measured under varied $H$ for Sr$_3$AgIrO$_6$ single crystals without orientation are shown in Fig. 4(c). Only FC curves are shown because the ZFC and FC curves are overlapping. There is no sign of magnetic order down to 2 K. The $\chi(T)$ data above 50 K can also be fitted with the Curie-Weiss law, resulting in a $\chi_0$ of 3.27×10$^{-4}$ emu mol$^{-1}$ Oe$^{-1}$, $C$ of 0.04 emu mol$^{-1}$ Oe$^{-1}$ and a $\theta_W$ of -35 K. The $\mu_{\text{eff}}$ calculated from the $C$ is 0.57 $\mu_B$.

Figure 4. Temperature dependence of magnetic susceptibility and the inverse magnetic
susceptibility for (a) Sr$_3$NaIrO$_6$ ($H \perp c$), (b) Sr$_3$NaIrO$_6$ ($H||c$), and (c) Sr$_3$AgIrO$_6$.

Figure 5. Temperature dependence of specific heat, $C_p$, for (a) Sr$_3$NaIrO$_6$ and (b) Sr$_3$AgIrO$_6$. The insets show the corresponding $C_p/T$ vs $T^2$ curves.

Figure 5 shows the $C_p(T)$ curves of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. There is no indication of magnetic order down to 1.8 K for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. The low-temperature $C_p/T$ vs $T^2$ data, shown in the insets in Figure 5, show rough linear behaviors except for the upturns at the lowest temperatures. The linear parts were analyzed with the approximated Debye model, $C_p/T = \gamma + \beta T^2$, where the $\gamma$ is the electronic specific heat coefficient and the $\beta$ is related to the Debye temperature. Fitting of the linear parts results in a $\gamma = 0.07$ mJ mol$^{-1}$ K$^{-2}$ and $\beta = 2.64 \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$ for Sr$_3$NaIrO$_6$ and $\gamma = 3.0$ mJ mol$^{-1}$ K$^{-2}$ and $\beta = 9.05 \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$ for Sr$_3$AgIrO$_6$. The small $\gamma$ value indicates the vanishing of the density of states, which is consistent with the insulating nature of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. 
The low-temperature $C_p/T$ vs. $T$ curves measured without and with varied magnetic fields are shown in Figs. 6(a) and 6(b) for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively. The $C_p/T$ vs. $T$ curves measured without fields show small anomalies below $\sim$3.5 K. These anomalies shift towards higher temperatures and broaden with increasing applied magnetic fields, suggesting their magnetic origin. To estimate the magnetic contribution ($C_{\text{mag}}$), we subtract the $C_p(T)$ data below 12 K measured under 90 kOe with an estimated lattice contribution $C_{\text{lat}} = \gamma T + \beta T^3$, and the resulted $C_{\text{mag}}/T$ vs. $T$ curves are shown in Figs. 6(c) and 6(d) for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$, respectively. These curves show broad maximums around 3 - 4 K for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. It should be noted that these values may be under-estimated because the entropy below 1.8 K is not counted in these cases. The estimated magnetic entropy ($S_{\text{mag}}$) for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ is about 0.06 J mol$^{-1}$ K$^{-1}$ and 0.33 J mol$^{-1}$ K$^{-1}$, respectively. Assuming these magnetic contributions are from Ir$^{4+}$ impurities, these values are about $\sim$1.7% and $\sim$9.2%, respectively, of the averaged entropy $S_{\text{mag}} = 3.6$ J mol$^{-1}$ K$^{-1}$ reported for the Ir$^{4+}$ double perovskite La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ [36]. These results are consistent with the XAS results that the Ir ions in Sr$_3$NaIrO$_6$ are Ir$^{5+}$ (but cannot exclude the presence of a few percent of magnetic Ir$^{4+}$ or/and Ir$^{6+}$) while a moderate amount of Ir$^{4+}$ ions is coexisting with the Ir$^{5+}$ ions in Sr$_3$AgIrO$_6$. 
The $\mu_{\text{eff}}, \theta_W$, and $\chi_0$ values for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ reported in this work are summarized in Table IV in comparison with other Ir$^{5+}$ oxides crystalizing in double perovskite or K$_4$CdCl$_6$-type structures. The $\chi_0$ summarized in Table IV are of the magnitude of $10^{-4}$ emu mol$^{-1}$ Oe$^{-1}$. The $\chi_0$ reported in this work for Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ single crystals are in the reported range. Except for the large $\mu_{\text{eff}}$ of 0.91 $\mu_B$/Ir and of 1.44 $\mu_B$/Ir once reported for Sr$_2$YIrO$_6$ [11] and Ba$_2$YIrO$_6$ [12], respectively, other studies on Sr$_2$YIrO$_6$, Ba$_2$YIrO$_6$, and the other Ir$^{5+}$ double perovskite and K$_4$CdCl$_6$-type oxides reveal relatively small $\mu_{\text{eff}}$ values of 0.19 – 0.63 $\mu_B$/Ir [13–25]. The $\mu_{\text{eff}}$ values for single crystals of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ in this work are within this range.

In comparison with polycrystalline Sr$_3$NaIrO$_6$ (0.49 $\mu_B$/Ir), the observed $\mu_{\text{eff}}$ values for Sr$_3$NaIrO$_6$ single crystal (0.31 $\mu_B$/Ir for $H \perp c$ and 0.28 $\mu_B$/Ir for $H || c$) are reduced. The valence state is also confirmed to be mainly Ir$^{5+}$ in polycrystalline Sr$_3$NaIrO$_6$ [22]. Thus, the reduction of $\mu_{\text{eff}}$ for the single crystal samples may be related to the decrease of by-phases and lattice defects because polycrystalline samples
synthesized by solid-state reactions are difficult to avoid the minute amount of by-phases and usually have more lattice defects than the single-crystal samples.

Though our XAS spectra confirm that the oxidation state of Ir in Sr$_3$NaIrO$_6$ is mainly Ir$^{5+}$, but cannot exclude the presence of a few percent of magnetic Ir$^{4+}$ or/Ir$^{6+}$ ions. Presence of Ir$^{4+}$ and/or Ir$^{6+}$ magnetic defects has been confirmed in Sr$_2$YIrO$_6$ [20], Sr$_2$CoIrO$_6$ [35], and Ba$_2$YIrO$_6$ [18]. Studies on Ir$^{4+}$ double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$ have reported $\mu_{\text{eff}}$ values of 1.71 and 1.42 $\mu_B$, respectively, which are close to the theoretical value of 1.73 $\mu_B$ for Ir$^{4+}$ ($J = 1/2$) [36]. If we assume the observed $\mu_{\text{eff}} \approx 0.3 \mu_B$ for Sr$_3$NaIrO$_6$ single crystals is solely contributed from magnetic Ir$^{4+}$ ($\mu_{\text{eff}} = 1.73 \mu_B$) while Ir$^{5+}$ ions are nonmagnetic ($J = 0$), there are should be about $\sim 3.0\%$ of Ir$^{4+}$ magnetic impurities according to $\mu_{\text{eff}}^2 = (1-x)(\mu_{\text{eff}}^{\text{Ir}^{5+}})^2 + x(\mu_{\text{eff}}^{\text{Ir}^{4+}})^2$. The existence of magnetic Ir$^{4+}$ with a low limit of $\sim 1.7\%$ for Sr$_3$NaIrO$_6$ is suggested from the analysis of low-temperature $C_p(T)$ data, which is not far from the theoretical amount of $\sim 3.0\%$.

In comparison with Sr$_3$NaIrO$_6$, the average valence state of Ir in Sr$_3$AgIrO$_6$ is a little lower than Ir$^{5+}$, indicating the presence of a moderate amount of Ir$^{4+}$ ions. The presence of magnetic Ir$^{4+}$ with a low limit of $\sim 9.2\%$ is estimated for Sr$_3$AgIrO$_6$ by the analysis of the low-temperature $C_p(T)$ data. The observed $\mu_{\text{eff}}$ for Sr$_3$AgIrO$_6$ single crystals is $\sim 0.57 \mu_B$. Assuming the observed $\mu_{\text{eff}}$ of 0.57 $\mu_B$ for Sr$_3$AgIrO$_6$ is solely contributed from magnetic Ir$^{4+}$ while Ir$^{5+}$ ions are nonmagnetic, there should be about $\sim 10.9\%$ of magnetic Ir$^{4+}$ according to $\mu_{\text{eff}}^2 = (1-x)(\mu_{\text{eff}}^{\text{Ir}^{5+}})^2 + x(\mu_{\text{eff}}^{\text{Ir}^{4+}})^2$, which is comparable to the low limit of Ir$^{4+}$ ($\sim 9.2\%$) estimated from $C_p(T)$ data of Sr$_3$AgIrO$_6$ single crystals.

In comparison with A$_2$YIrO$_6$ (A = Sr, Ba), where the Ir$^{5+}$O$_6$ octahedra are separated by Y$^{3+}$O$_6$, the Ir$^{5+}$O$_6$ octahedra are separated by Na$^{1+}$O$_6$/Ag$^{1+}$O$_6$ octahedra along the one-dimensional chain in Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. The much larger charge difference would significantly reduce the antisite disorder between Na$^{1+}$/Ag$^{1+}$ and Ir$^{5+}$ in Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ as compared with Sr$_2$YIrO$_6$ and Ba$_2$YIrO$_6$. Thus, the contributions to the magnetic moment from antisite disorder as discussed for Sr$_2$YIrO$_6$ and Ba$_2$YIrO$_6$ should be much reduced in Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$.  

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From these analyses, the paramagnetic moments observed in \( \text{Sr}_3\text{NaIrO}_6 \) and \( \text{Sr}_3\text{NaIrO}_6 \) single crystals are likely contributed solely by the magnetic \( \text{Ir}^{4+} \), supporting the \( J = 0 \) ground state for \( \text{Ir}^{5+} \). This is consistent with the studies on \( \text{Ir}^{5+} \) double perovskites \( A_2B\text{IrO}_6 \) (\( A = \text{Ba, Sr}; B = \text{Y, Lu, Sc} \)) which support the \( J = 0 \) ground state for \( \text{Ir}^{5+} \) and indicate the magnetic moments are from extrinsic sources [14, 17, 18, 20, 21]. Studies on the layered oxide \( \text{Sr}_2\text{CoO}_3\text{IrO}_6 \) also support the \( J = 0 \) ground state for \( \text{Ir}^{5+} \) and show that the energy gap between the singlet state and the excited triplet state is large [37]. The presence of magnetic \( \text{Ir}^{4+} \) indicates that a small number of oxygen vacancies exist in our \( \text{Sr}_3\text{NaIrO}_6 \) and \( \text{Sr}_3\text{AgIrO}_6 \) single crystals. The possibility of thermodynamic instability of stoichiometric \( \text{Ir}^{5+} \) oxides and a partial reduction of \( \text{Ir}^{5+} \) to \( \text{Ir}^{4+} \) has been suggested by Prof. M. Jansen et al [23].

It should be noted that the \( \theta_w \) values are anisotropic in our anisotropic magnetic measurements on \( \text{Sr}_3\text{NaIrO}_6 \) single crystals. For the polycrystalline \( \text{Sr}_3\text{NaIrO}_6 \), the reported \( \theta_w \) is -23.6 K. For our \( \text{Sr}_3\text{NaIrO}_6 \) single crystals, the \( \theta_w \) is about 1 K for the case of \( H \parallel c \) but is about -34 K for \( H \perp c \), indicating that the magnetic exchange interactions are negligible along the one-dimensional chain (\( H \parallel c \)) and are mainly for interchains (\( H \perp c \)). In the ideal \( \text{Sr}_3\text{NaIrO}_6 \) structure, there is no direct superexchange \( \text{Ir}-\text{O}-\text{Ir} \) path, and the magnetic exchange interactions are mediated by the extended superexchange path \( \text{Ir}-\text{O}-\text{O}-\text{Ir} \) [38, 39]. The nearest \( \text{Ir}-\text{Ir} \) is about 5.78 Å along the chain which is a little bit shorter than the length of 5.89 Å for interchains. But, the nearest \( \text{O}-\text{O} \) distance between nearest \( \text{IrO}_6 \) octahedra along the one-dimensional chain (3.50 Å) is much longer than that of 2.99 Å for interchains, which may responsible for that the magnetic exchange interactions are mainly for interchains in the \( \text{Sr}_3\text{NaIrO}_6 \) single crystals.

Table IV. Magnetic properties of \( \text{Ir}^{5+} \) oxides with double perovskite (DP) and \( \text{K}_4\text{CdCl}_6 \) structures.

| Material       | Crystal structure | \( \chi_0 \) \((10^{-4} \text{ emu mol}^{-1} \text{ Oe}^{-1})\) | \( \mu_{\text{eff}} \) (\( \mu_B / \text{Ir} \)) | \( \theta_w \) (K) | Reference |
|----------------|-------------------|------------------------------------------------|---------------------------------|-----------------|-----------|
| \( \text{Ba}_2\text{YIrO}_6 \) | DP                | -                                               | 0.3                             | -10             | [15]      |
Ba$_2$YIrO$_6$ & DP & 4.8 & 0.63 & -5 & [16] \\
Ba$_2$YIrO$_6$ & DP & 5.4 & 0.52 & -4 & [16] \\
Ba$_2$YIrO$_6$ & DP & 5.4 & 0.50 & -8 & [16] \\
Ba$_2$YIrO$_6$ & DP & 5.83 & 0.44 & -8.9 & [13] \\
Ba$_2$YIrO$_6$ & DP & - & 0.31 & - & [17] \\
Ba$_2$YIrO$_6$ & DP & - & 0.48 & -16 & [18] \\
Ba$_2$YIrO$_6$ & DP & -3.9 & 1.44 & -149 & [12] \\
Ba$_{1.26}$Sr$_{0.74}$YIrO$_6$ & DP & 4.4 & 0.64 & -18 & [12] \\
Ba$_{2-x}$Sr$_x$YIrO$_6$ & DP & - & 0.47 & - & [19] \\
Sr$_2$YIrO$_6$ & DP & - & 0.91 & -229 & [11] \\
Sr$_2$YIrO$_6$ & DP & 5.90 & 0.21 & -2.8 & [14] \\
Sr$_2$YIrO$_6$ & DP & - & 0.3 & - & [20] \\
Sr$_{1.6}$Ca$_{0.4}$YIrO$_6$ & DP & - & 0.6 & - & [20] \\
Sr$_2$LuIrO$_6$ & DP & 5.49 & 0.27 & -2.55 & [21] \\
Ba$_2$LuIrO$_6$ & DP & 4.98 & 0.42 & -13.2 & [21] \\
Sr$_2$ScIrO$_6$ & DP & 5.43 & 0.32 & -10.7 & [21] \\
Ba$_2$ScIrO$_6$ & DP & 5.10 & 0.48 & -18.7 & [21] \\
Bi$_2$NaIrO$_6$ & DP & 6.3 & 0.19 & -6.8 & [23] \\
LaSrMgIrO$_6$ & DP & 3.5 & 0.61 & 7 & [24] \\
LaSrZnIrO$_6$ & DP & 3.9 & 0.46 & 1 & [24] \\
Sr$_3$NaIrO$_6$ & K$_4$CdCl$_6$ & - & 0.49 & -23.6 & [22] \\
Sr$_3$LiIrO$_6$ & K$_4$CdCl$_6$ & - & 0.4 & -21 & [25] \\
Sr$_3$LiIrO$_6$ & K$_4$CdCl$_6$ & - & 0.45 & -71 & [25] \\
Sr$_3$NaIrO$_6$ & K$_4$CdCl$_6$ & 6.2 & 0.31($H \perp c$) & -34 This work \\
 & & & 5.4 & 0.28($H || c$) & 1 This work \\
Sr$_3$AgIrO$_6$ & K$_4$CdCl$_6$ & 3.3 & 0.57 & -35 This work \\

**Conclusions**

Single crystals of Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ have been successfully grown using hydroxides flux. Analysis of room temperature SCXRD data found that Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ crystallize in the K$_4$CdCl$_6$-type structure with the space group R-3c (No.167). Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$ are electrically insulating with estimated activation gaps of 0.68 eV and 0.80 eV, respectively. The magnetic results show paramagnetism down to 2 K for both Sr$_3$NaIrO$_6$ and Sr$_3$AgIrO$_6$. In comparison with polycrystalline Sr$_3$NaIrO$_6$ (0.49 $\mu_B$), our Sr$_3$NaIrO$_6$ single crystals display smaller $\mu_{\text{eff}}$ values (0.31 $\mu_B$ for $H \perp c$ and 0.28 $\mu_B$ for $H || c$). The $\mu_{\text{eff}}$ for Sr$_3$AgIrO$_6$ single crystals is about 0.57 $\mu_B$. Combined analyses of the XAS spectra and the low-temperature $C_p(T)$ data indicate that the Ir ions...
are mainly Ir\(^{5+}\) in Sr\(_3\)NaIrO\(_6\) but there is a low limit of \(~1.7\%\) of magnetic Ir\(^{4+}\) ions. For Sr\(_3\)AgIrO\(_6\), the Ir ions are a little lower than Ir\(^{5+}\) and it contains magnetic impurity Ir\(^{4+}\) with a low limit of \(~9.2\%\). The magnetic impurities are likely to fully explain the observed \(\mu_{\text{eff}}\) values for Sr\(_3\)NaIrO\(_6\) and Sr\(_3\)AgIrO\(_6\) single crystals, supporting the \(J = 0\) ground state for Ir\(^{5+}\) in Sr\(_3\)NaIrO\(_6\) and Sr\(_3\)AgIrO\(_6\).

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