A critical point in Sr$_{2-x}$IrO$_4$ and less distorted IrO$_6$ octahedra induced by deep Sr-vacancies

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Abstract

For the Sr$_{2-x}$IrO$_4$ system, recent work pointed out the abnormal electronic and magnetic properties around a critical point. Here, to understand Sr-vacancy effect on spin-orbit coupled Mott insulator Sr$_2$IrO$_4$, the electronic structure and local structure distortion for Sr$_{2-x}$IrO$_4$ system have been investigated by x-ray absorption spectroscopy (XAS). By comparing the intensity of white-line features at the Ir $L_{2,3}$-edge x-ray absorption near-edge spectroscopy (XANES), we observe a sudden rise of the branching ratio in the vicinity of the critical point. Further analysis on the Ir $L_3$-edge extended x-ray absorption fine structure (EXAFS) and calculated data demonstrated that the abrupt enhancement of the branching ratio is intimately related
to the less distorted IrO$_6$ octahedra induced by deep Sr-vacancies, which in turn alters the relatively strength of the spin-orbit coupling (SOC) and crystal electric field (CEF) that would dictate the abnormal behavior of electronic and magnetic structure near the critical point.

Keywords: Sr$_2$IrO$_4$; x-ray absorption spectroscopy; a critical point; local structure
1. Introduction

The 5$d$ transition metal oxides (TMOs) have been the topic of intense research in recent years due to their numerous intriguing phenomena [1, 2]. Because of the large atomic mass associated with 5$d$ elements, the strong relativistic spin-orbit coupling (SOC) effect is an important consideration in describing the physical properties of 5$d$ TMOs, and it rigorously competes with other relevant energies, particularly the on-site Coulomb repulsion $U$ and crystal electric field (CEF) interactions arising from the surrounding coordinate environment [3]. Consequently, a variety of exotic quantum phases, including the $J_{\text{eff}} = 1/2$ Mott state [1, 2], superconductivity [4, 5], a topological insulator [6, 7], Weyl semimetal with Fermi arcs [8], are shown and expected in 5$d$ TMOs.

In the case of the most well-known 5$d$ TMOs, the layered Sr$_2$IrO$_4$ known as SOC-related Mott insulator, has been subjected to the most extensive investigations due to its structural and electronic similarities to those of the celebrated La$_2$CuO$_4$ [9]. Sr$_2$IrO$_4$, which has the K$_2$NiF$_4$ structure, is based on Ir$^{4+}$ in IrO$_6$ octahedra [10]. The octahedral CEF splits the 5$d$ bands into $t_{2g}$ and $e_g$ states, and the $t_{2g}$ manifold splits into two effective angular momentum energy levels (a doublet $J_{\text{eff}} = 1/2$ and a quartet $J_{\text{eff}} = 3/2$) via the strong SOC [1, 2]. Since the Ir$^{4+}$ ions provide five 5$d$-electrons, four of them fill the lower $J_{\text{eff}} = 3/2$ bands, and one electron partially fills the $J_{\text{eff}} = 1/2$ band where the Fermi level $E_F$ resides. The $J_{\text{eff}} = 1/2$ band is so narrow that even a reduced $U$ is sufficient to open a gap, supporting an insulating behavior [1, 2]. Accordingly, the delicate competition among the various interactions such as the CEF,
SOC and $U$ plays a crucial role in realizing the $J_{\text{eff}} = 1/2$ intriguing physics for Sr$_2$IrO$_4$.

Several theoretical investigations predicted that the unconventional high-temperature superconductivity can be induced by carrier doping in this Sr$_2$IrO$_4$-based system [4, 11-13]. Very recently, experiments on doped Sr$_2$IrO$_4$ have uncovered tantalizing evidence of a Fermi surface split up into disconnected segments (“Fermi arcs”) [14] and a low-temperature gap with d-wave symmetry [15, 16], which are hallmarks of the doped cuprates [17]. However, the true sense of superconductivity has not been found yet, regardless of the electron and hole-doping.

As is known to all, material properties are in a close relationship with their atomic structure. Several reports pointed out that carrier doping can alter lattice parameters and further change the electronic and magnetic behaviors of Sr$_2$IrO$_4$ [18-21]. Thus, one of the important issues to be resolved for Sr$_2$IrO$_4$-based system is how carrier doping affect their physical properties in terms of local atomic structure. For instance, Bhatti et al. established a relationship between temperature dependent magnetic property and the structural parameters by means of x-ray diffraction (XRD) measurement on Sr$_2$IrO$_4$ [22]. Furthermore, our pervious investigations suggest the synergistic effect of regular IrO$_6$ octahedra and electron doping that accounts for the transition from a Mott insulator to a conductive state in Sr$_{2-x}$La$_x$IrO$_4$-based system [23]. A more accurate and systematic investigation of local atomic displacements induced by carrier doping is still necessary to better understand the Sr$_2$IrO$_4$ system, that may be beneficial to uncover the potential superconductivity in SOC-related Mott
insulators.

Synchrotron-radiation-based X-ray absorption spectroscopy (XAS) is a well-recognized local experimental technique capable of giving substantial information (i.e. local atomic and electronic structure) for a material [24, 25]. Moreover, Ir $L_{2,3}$-edge XAS can be competent for providing other valuable information (e.g. the strength of SOC) in Ir-based systems [26]. Here, we take the polycrystalline compounds of $\text{Sr}_2\text{IrO}_4$ as the object of our research. As the Sr-vacancies approach $x \sim 0.45$, the properties of the material change suddenly in three aspects [27]: 1) an insulator-metal transition; 2) a sudden drop of the localization temperature and the antiferromagnetic transition temperature, together with an anomalous sign reverse of the Curie-Weiss temperature; 3) a significant structural change probed by both XRD and Raman spectra. All these aspects strongly suggest the existence of a critical point around $x \sim 0.45$ in this system. Therefore, an investigation of the critical point is highly desired and might be a key to achieve the potential superconductivity in $\text{Sr}_2\text{IrO}_4$-based system. In this contribution, detailed investigations of the Sr-vacancy effect at the critical point are probed by a comprehensive analysis of Ir $L_{2,3}$-edge XAS.

2. Experiments and Calculations

Polycrystalline compounds with nominal compositions of $\text{Sr}_{2-x}\text{IrO}_4$ were synthesized by solid-state reaction method as mentioned elsewhere [27]. The samples were well characterized for their phase purity prior to the XAS measurements. We collected both the Ir $L_2$-edge x-ray absorption near edge structure (XANES) and $L_3$-edge extended x-ray absorption fine structure (EXAFS) spectra of $\text{Sr}_{2-x}\text{IrO}_4$ at
room temperature, which occur at energy of 12.824keV and 11.215keV, respectively. The XAS spectra were collected at the BL-14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). Several scans were collected to ensure the spectral reproducibility. The storage ring was working at electron energy of 3.5 GeV, and the maximum stored current was about 250mA. The energy of the incident energy was tuned by scanning a Si (111) double crystal monochromator with energy resolution about $10^{-4}$. Data reduction was performed using the IFEFFIT program package [28].

Density functional theory (DFT) calculations for Sr$_{2-x}$IrO$_4$ system were carried out within the local-density approximation (LDA) including SOC and on-site Coulomb $U$ using OPENMX [29], based on the linear-combination-of-pseudo-atomic-orbitals (LCPAO) method [30]. SOC is treated via a fully relativistic j-dependent pseudopotential in the non-collinear DFT scheme, with 300 Ry of energy cutoff and $11 \times 11 \times 11$ k-grid. For Sr$_{2-x}$IrO$_4$, only one and two of the eight Sr atoms were removed in a unit cell, which correspond to $x = 0.25$ and 0.5, respectively. Atomic positions of the structure have been relaxed until all the force components became smaller than $10^{-4}$ eV/a.u. The on-site Coulomb interaction parameter $U$ is set to 2.0 eV for Ir $d$-orbitals in our LDA + SOC + $U$ calculations.

3. Results and Discussions
Fig. 1. Ir L\textsubscript{2,3}-edge normalized XANES spectra of Sr\textsubscript{2-x}IrO\textsubscript{4}.

The Ir L\textsubscript{2,3}-edge XANES spectra of Sr\textsubscript{2-x}IrO\textsubscript{4} compounds are provided in Fig. 1. The most striking characteristic is the prominent white-line (WL) features which correspond to 2p \rightarrow 5d electronic transitions. From the dipole selection rules, \( \Delta J \) must be equal to 0 or \( \pm 1 \), it follows that for Sr\textsubscript{2}IrO\textsubscript{4}-based system the Ir L\textsubscript{2}-edge will be sensitive to transitions involving 5d\textsubscript{3/2} (i.e. \( J_{\text{eff}} = 3/2 \)) holes, while the L\textsubscript{3}-edge will be related to both 5d\textsubscript{5/2} (upper Hubbard band associated with \( J_{\text{eff}} = 1/2 \) and the CEF \( e_g \) manifolds) and 5d\textsubscript{3/2} final states. Because the WL features are more pronounced at the L\textsubscript{3} edge than the L\textsubscript{2} edge, we can also infer that these unoccupied 5d states are primarily 5d\textsubscript{5/2} rather than 5d\textsubscript{3/2} in nature, consistent with the almost completely filled \( J_{\text{eff}} = 3/2 \) bands in Sr\textsubscript{2}IrO\textsubscript{4} [2]. Furthermore, the integrated intensity of the WL features is proportional to the local density of unoccupied final states (i.e. the population of 5d holes) in the system. From Fig. 1 the integrated intensity of WL features at both
absorption edges grows steadily with increasing the Sr-vacancies, pointing out the increment of Ir-5d holes in Sr$_2$IrO$_4$ compounds. To demonstrate the above discussion, the DFT calculations for Sr$_{2-x}$IrO$_4$ ($x = 0, 0.25$ and $0.5$) were performed. In Table 1, we summarized the number of electrons for each element. It is found that the holes induced by Sr-vacancies are located around all atoms, especially the Ir atoms, in agreement with the result of XANES spectra.

### Table 1

The number of electrons belonging to each atomic species for Sr$_2$IrO$_4$.

|           | Sr$_2$IrO$_4$ | Ir  | Sr  | O  |
|-----------|---------------|-----|-----|----|
| $x = 0$   | 15.91         | 8.46| 6.54|    |
| $x = 0.25$| 15.84         | 8.42| 6.51|    |
| $x = 0.5$ | 15.52         | 8.38| 6.48|    |

The relative strength of the WL features at the $L_3$ and $L_2$ edges (also known as the branching ratio $BR = I_{L_3}/I_{L_2}$) is an important quantity [26], since it is directly related to the expectation value of the angular part of the SOC of 5d states via $BR = (2+r)/(1-r)$, where $r = \langle L \cdot S \rangle / n_h$ and $n_h$ is the average number of 5d holes [31, 32]. For a system with negligible SOC the statistical branching ratio from XANES is 2. To discuss the branching ratio on a quantitative level, the integrated intensity of WL feature at each edge was provided based on the least-squares method as mentioned elsewhere, using a Lorentzian + arctangent fit function [23]. By analysing the XANES spectra, the branching ratio for Sr$_2$IrO$_4$ is $BR = 6.45$, a value which is several
times larger than the statistical one, indicating the presence of extremely large SOC effects. Using $n_h = 5$ we obtain $\langle L \cdot S \rangle = 2.99$ in units of $\hbar^2$, consistent with other reports [26].

![Graph](image)

**Fig. 2.** The branching ratio $I_{L_3}/I_{L_2}$ (a) and $\langle L \cdot S \rangle$ (b) as a function of Sr-vacancy concentrations. (c) A schematic energy diagram of $5d$ level splittings by the CEF and SOC, based on Ref. 2.

As shown in Fig. 2, both the branching ratio and $\langle L \cdot S \rangle$ increase gradually with the increasing Sr-vacancies, while a sudden rise occurs in the deep doping region around $x = 0.45$. This anomalous kink reminds us about the critical point in Sr$_{2-x}$IrO$_4$ system, implying potential changes of the fundamental local atomic structure at the critical point. The $\langle L \cdot S \rangle$ is a property of the local moment, it is mostly determined by the
SOC and the CEF acting on 5d electrons. Note that since XANES probes all empty 5d states, the measured $\langle L \cdot S \rangle$ will be the sum of two contributions (illustrated in Fig. 2(c)): a single hole in the $J_{\text{eff}} = 1/2$ state ($\langle L \cdot S \rangle = 1$) and four holes in the $e_g$-derived states ($\langle L \cdot S \rangle = 4 \times 3 \zeta_{5d} / 10Dq$) [33, 34], where $\zeta_{5d}$ represents the SOC of the 5d states and $10Dq$ is the parameter of octahedral CEF. Therefore, the Sr-vacancies can effectively alter the relative strength of the SOC and CEF, which could be useful to describe the fundamental properties of Sr$_{2-x}$IrO$_4$ system.

It is well known that Ir atoms play a significant role in extremely strong SOC effects of Sr$_2$IrO$_4$-based system, while the cation substitutions can change the strength of SOC [35]. For instance, a substitution of Ir with Ru/Rh would tune the SOC strength from the strong 5d regime to the moderate 4d regime [35]. On the other hand, the substitution at Sr sites (e.g. La-doping) just tunes the band filling, and does not alter the SOC strength [35]. That is to say, only the substitution at Ir sites can significantly tune the SOC strength of the system. Roughly speaking, in our study Sr-vacancies impose negligible effect on the SOC strength, and we neglect the SOC changes in our discussion. Thus we will focus on the CEF effect versus Sr-vacancies.
Fig. 3. (a) Fourier transform magnitudes of $k^3 \chi(k)$ EXAFS signals of Sr$_{2-x}$IrO$_4$ compounds at Ir $L_3$-edge and the contributions of Ir-O1/O2 pairs calculated by FEFF code. The results from the fit of Ir-O1/Ir-O2 bond distances are shown in panel (b). (c) The derived differences between the distances of Ir-O1 and Ir-O2 bonds as a function of Sr-vacancy concentrations. Error bars correlated to the uncertainty value are given.

In the Sr$_2$IrO$_4$-based system, the CEF interaction is arisen from surrounding six oxygen atoms in a nearly octahedral local coordinate environment [10]. The IrO$_6$ octahedron contains two distinct oxygen positions (four basal O1 and two apical O2), which is slightly elongated apically. Therefore, to gain an insight into the local atomic displacements induced by Sr-vacancies, we have undertaken detailed structural study (e.g. the bond distances of Ir-O1 and Ir-O2) by means of the Ir $L_3$-edge EXAFS spectra. The Fourier transform (FT) magnitudes of the EXAFS oscillations providing real space information around Ir atoms are plotted in Fig. 3(a). Note that the positions
of the peaks in the FT are shifted a few tenths of Å from the actual interatomic distances because of the EXAFS phase shift [36]. Obviously, large changes in the FTs of Ir  $L_3$-edge can be seen, indicating the atomic displacements induced by Sr-vacancies.

The EXAFS amplitude depends on several factors and is given by the following general equation [37]:

$$\chi(k) = \sum_j N_j S_0^2 f_j(k, R_j) \exp[-2k^2\sigma_j^2] \exp[-\frac{2R_j}{\lambda}] \sin[2kR_j + \delta_j(k)]$$  \hspace{1cm} (1)

where $N_j$ is the number of neighboring atoms at a distance $R_j$, $S_0^2$ is the passive electron reduction factor, $f_j(k, R_j)$ is the backscattering amplitude, $\lambda$ is the photoelectron mean free path, $\delta_j(k)$ is the phase shift and $\sigma_j^2$ is the correlated Debye-Waller factor.

In order to obtain quantitative results, we fit the first peak of EXAFS spectra ($R = 1.0 \sim 2.2$ Å) involving contributions of four basal O1 and two apical O2, which were isolated from the FTs with a rectangular window. The range in $k$ space was $3 \sim 15$ Å$^{-1}$ and that in $R$ space was $1.0 \sim 2.2$ Å. For the least-squares fits, average structure measured by diffraction on Sr$_2$IrO$_4$ system is used as the starting model [27]. The backscattering amplitudes and phase shift were calculated using the FEFF code [38]. Only the radial distances $R_j$ and the corresponding $\sigma_j^2$ were allowed to vary, with coordination numbers $N_j$ fixed to the nominal values. The passive electrons reduction factor $S_0^2$ and photoelectron energy zero $E_0$ were also fixed after fit trials on different scans. The number of independent parameters which could be determined by EXAFS is limited by the number of the independent data points $N_{\text{ind}} \sim (2\Delta k \Delta R)/\pi$, 

where $\Delta k$ and $\Delta R$ are respectively the ranges of the fit in the $k$ and $R$ space [37]. In our case, $N_{\text{ind}}$ is 9 ($\Delta k = 12 \text{ Å}^{-1}$, $\Delta R = 1.2 \text{ Å}$), sufficient to obtain all parameters.

As shown in Fig. 3(b), the distances of both Ir-O1 and Ir-O2 pairs increase gradually with the increasing Sr-vacancies, while an obvious kink occurs in the deep doping region. Note that the IrO$_6$ octahedron is slightly elongated apically, and deep Sr-vacancies suddenly decrease the ratio of apical Ir-O2 to basal Ir-O1 distance (illustrated in Fig. 3(c)), indicating less distorted IrO$_6$ octahedra induced by deep Sr-vacancies. Surprisingly, all these structural changes are in coincidence with the existence of the critical point around $x = 0.45$. That is to say, the changes of fundamental atomic structure would be important to describe the properties around the critical point.

![Fig. 4. Total density of states for Sr$_{2-x}$IrO$_4$ system.](image-url)
**Fig. 5.** The ratio of apical Ir-O2 to basal Ir-O1 bond length (a) and the CEF parameter $10D_q$ (b) for Sr$_{2-x}$IrO$_4$ system.

In order to validate the above XAS results, we performed DFT calculations on Sr$_{2-x}$IrO$_4$ system. The total density of states in **Fig. 4** suggests that deep Sr-vacancies turn the Sr$_{2-x}$IrO$_4$ system from a Mott insulator to the metallic state, in agreement with the experimental results [27]. As shown in **Fig. 5**, Sr-vacancies also induce structural changes driving the ratio of apical Ir-O2 to basal Ir-O1 bond length towards the value of 1, suggesting the less distorted IrO$_6$ octahedra. Accordingly, the $10D_q$ parameter decreases suddenly (*i.e.* the weakened CEF) along with the deep Sr-vacancies, consistent with the abrupt enhancement of $\langle L\cdot S \rangle$.

As mentioned above, our results provide experimental and calculated data on the less distorted IrO$_6$ octahedra induced by deep Sr-vacancies; this in turn tunes the relatively strength of the SOC and CEF for Sr$_{2-x}$IrO$_4$ system, which would dictate the
abnormal behavior of electronic and magnetic properties at the critical point.

4. Conclusion

To summarize, we have investigated the Sr-vacancy effect on the spin-orbit coupled Sr$_2$IrO$_4$ probed by Ir $L_{2,3}$-edge XAS. By fitting the white line features of Ir $L_{2,3}$-edge XANES, the sudden enhancement of both the branching ratio and the derived $<L\cdot S>$ were observed in the vicinity of the critical point. Further investigations in terms of local structure showed that the abrupt rise of $<L\cdot S>$ near the critical point is intimately related to the less distorted IrO$_6$ octahedra (i.e. the weakened CEF). So in this contribution we establish the delicate interplay between the critical point and the regular configuration of IrO$_6$ octahedra, hoping this point of view could be beneficial to our understanding of abnormal physics properties in Sr$_{2-x}$IrO$_4$-based system.

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