Resonant X-ray Studies of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$: Exploring Magnetism in Doped Iridates

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Introduction – novel physics in spin-orbit coupled iridates

\( \text{Sr}_2\text{IrO}_4 \) – the \( j_{\text{eff}} = 1/2 \) spin-orbital Mott insulator

\( \text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4 \) – investigating the impact of chemical doping

Experimental Results:

• What is the role of Rh dopant ions? (XAS)

• Effect of doping on magnetic structure? (RMXS)

• Effect of doping on magnetic excitations? (RIXS)

Summary and conclusions
Why Study Iridates?

- Interplay between electronic correlations, crystal electric field, and spin-orbit coupling ($U \sim CEF \sim SOC$)
- Potential for exotic physics driven by strong SOC ($\sim 0.5 \text{ eV}$)
Novel Physics in Iridates

Candidate for Topological Insulator, Weyl Semi-Metal, Metallic Spin Liquid:

Candidate for Topological Insulator, Kitaev-Heisenberg Model:
Gretarsson et al, PRL (2013)

\( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \)

\( J_{\text{eff}} = 1/2 \) spin orbital
Mott insulator:
Kim et al, PRL (2008)
Kim et al, Science (2009)
Kim et al, PRL (2012)
The Case for Resonant X-rays

- Iridates are not neutron-friendly materials:
  - Large neutron absorption cross-section
    $[^{191}\text{Ir} \ (37\%): \sigma_{\text{abs}} = 954 \text{ b}, \ ^{193}\text{Ir} \ (63\%): \sigma_{\text{abs}} = 111 \text{ b}]$
  - Absence of large single crystal samples

- But very well-suited to resonant x-rays:
  - Expect large resonant enhancement at Ir L-edges
  - User-friendly hard x-ray energy scale
Sr$_2$IrO$_4$: the Spin-Orbital Mott Insulator

A surprising number of iridates are insulators - why?

Ir$^{4+}$ ($5d^5$) $\rightarrow$ Ir$^{4+}$ ($5d^5$)

$t_{2g}$ ($L_{\text{eff}} = 1$) $\rightarrow$ e$_g$

$J_{\text{eff}} = 1/2$ $\rightarrow$ $J_{\text{eff}} = 3/2$

Ir$^{4+}$ ($5d^5$)

SO $\rightarrow$ t$_{2g}$

$J_{\text{eff}} = 1/2$ $\rightarrow$ $J_{\text{eff}} = 3/2$

Ir$^{4+}$ ($5d^5$)

$SO$ $\rightarrow$ CF

$J = 5/2$ $\rightarrow$ $J = 3/2$

Physical Properties of $\text{Sr}_2\text{IrO}_4$

- Member of Ruddlesden-Popper series (n=1):
  \[ \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \]

- Space Group: $\text{I}4_1/\text{acd}$

- $\text{IrO}_6$ octahedra rotated by $\sim 11^\circ$ w.r.t. $c$-axis

- $J_{\text{eff}} = 1/2$ canted antiferromagnet ($T_N \sim 240 \text{ K}$)

- Similar structure to $\text{La}_2\text{CuO}_4$ and $\text{Sr}_2\text{RuO}_4$

- Possibility of doping-induced superconductivity?
  - Wang and Senthil, PRL (2011)
  - Watanabe et al, PRL (2013)

- $a = 5.50 \text{ Å}$
- $c = 25.80 \text{ Å}$
Doping Studies on Sr$_2$IrO$_4$

(No superconductivity so far...)

- Isoelectronic: Sr$_{2-x}$A$_x$IrO$_4$ ($A = Ba, Ca$), Sr$_2$Ir$_{1-x}$TM$_x$O$_4$ ($TM = Co, Rh?$)
- e$\textsuperscript{-}$-doping: Sr$_2$IrO$_{4-\delta}$, Sr$_{2-x}$La$_x$IrO$_4$, Sr$_2$Ir$_{1-x}$Pt$_x$O$_4$
- Hole-doping: Sr$_{2-x}$K$_x$IrO$_4$, Sr$_2$Ir$_{1-x}$TM$_x$O$_4$ ($TM = Ru, Mn, Fe, Ti, Rh?$)
What is the effect of Rh-doping?

Rh-doping induces a series of electronic and magnetic phase transitions between $\text{Sr}_2\text{IrO}_4$ and $\text{Sr}_2\text{RhO}_4$.
What is the effect of Rh-doping?

- **Substitute Rh$^{4+}$ (4d$^5$) for Ir$^{4+}$ (5d$^5$)?** → isoelectronic doping, tune SOC [Qi et al, PRB (2012), Lee et al, PRB (2012)]

- **Substitute Rh$^{3+}$ (4d$^6$) for Ir$^{4+}$ (5d$^5$)?** → hole doping, tune band filling and SOC [Klein et al, JPCM (2008)/JEM(2009)]
Experimental Details

- Single crystal samples of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$ with $x = 0.07, 0.11, 0.15, 0.24, 0.42, 0.70$, and $1.0$

- X-ray Absorption Spectroscopy (XAS) – SXRMB at CLS
- Resonant Magnetic X-ray Scattering (RMXS) – 6-ID-B at APS
- Resonant Inelastic X-ray Scattering (RIXS) – MERIX at APS
X-ray Absorption Spectroscopy

Anatomy of an X-ray Absorption Spectra:

“White Line”
(2p → 5d)

Edge Step
(2p → Continuum)

Fine Structure

Ir edges:
11.215 keV (L₃)
12.824 keV (L₂)

Rh edges:
3.004 keV (L₃)
3.146 keV (L₂)
XAS: Oxidation State of \( \text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4 \)

- Compare XAS white-line features at Rh L\(_3\)-edge:
  - Suggests Rh dopant ions adopt a \textbf{Rh}\(^{3+}\) state for \( x = 0.07 \) to \( x = 0.70 \)

- \( \text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4 \) appears to be a hole-doped system
Resonant Magnetic X-ray Scattering

- Beamline 6-ID-B at APS:

RMXS at Ir L$_3$ (11.215 keV) and L$_2$ (12.824 keV) absorption edges

Polarization analysis performed with PG-(0,0,8)/PG-(0,0,10) analyzer crystal
Parent compound displays canted AF ground state

Field-induced magnetic phase transition above $H_C \sim 0.25$ T
Magnetic Structure of \( \text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4 \)

- Magnetic Bragg peaks observed at \((0,1,L)/(1,0,L)\) for \(L=\text{odd}\)
- No magnetic peaks for \((0,0,L), (1,1,L), (1/2,1/2,L)\), or \((1/2,0,L)\)
- Doping-induced change in magnetic structure for \(x \leq 0.07\)
Magnetic Structure of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$

- Magnetic structure factor and azimuthal dependence confirm magnetic moments lie within the $ab$-plane.
- Rh-doped $\text{Sr}_2\text{IrO}_4$ displays same magnetic structure as $\text{Sr}_2\text{IrO}_4$ in applied field ($H > H_c$)
Robustness of the $J_{\text{eff}} = 1/2$ State

- Large $I_{L3}/I_{L2}$ ratio is a defining signature of the $J_{\text{eff}} = 1/2$ state.

- Minimum intensity ratio for Rh-doped $\text{Sr}_2\text{IrO}_4$ is $I_{L3}/I_{L2} > 200$.

- Similar result observed in $\text{Sr}_2\text{Ir}_{0.9}\text{Mn}_{0.1}\text{O}_4$ (Calder et al, PRB [2012]).

Magnetic peaks persist up to $T_{N1}$, dramatic drop in intensity at $T_{N2}$

- Peaks only become resolution-limited below $T_{N2}$, finite magnetic correlation lengths ($\sim 800\text{Å}$) between $T_{N1}$ and $T_{N2}$
Magnetic Phase Diagram of Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$

\[ (1,0,21) \]

\[ x = 0.07 \]
\[ x = 0.11 \]

\[ x_c \sim 0.17 \]

\[ M(T) \]

\[ T_{N1} \]
\[ T_{N2} \]

\[ T_c \]

\[ \mu_0 H = 0.1 \, \text{T} \]

T. Qi et al, PRB (2012)
Implications of the Phase Diagram

- Can magnetic properties be explained using a percolation picture?
- $S=1/2$ square lattice Heisenberg AF has $x_p = 0.407$
- Appears to provide good description of highly doped cuprates
- ex. $\text{La}_2\text{Cu}_{1-x}(\text{Mg,Zn})_x\text{O}_4$ [Vajk et al, Science (2002)]

(A) $\text{Ir}^{4+}$ $\text{Rh}^{4+}$

$x = 0.21 < x_p$

(B) $\text{Ir}^{4+}$ $\text{Rh}^{3+}$ $\text{Ir}^{5+}$

$x_{\text{eff}} = 0.42 > x_p$
Implications of the Phase Diagram

- Why is $x_c < x_p$?
  - Correlations between non-magnetic vacancies – clustering of Rh$^{3+}$ and Ir$^{5+}$ ions
  - Importance of orbital degrees of freedom – effect of dilution stronger than in pure spin-only systems [Tanaka et al, PRL (2007)]
Resonant Inelastic X-ray Scattering

- Beamline 30-ID (MERIX) at APS:
  - RIXS at Ir L₃-edge (11.215 keV)
  - 2m spherical diced Si-(8,4,4) analyzer
  - Energy resolution ~35 meV (FWHM)
RIXS: Magnetic Excitations in Sr$_2$IrO$_4$

- Ir L$_3$-edge RIXS measurements on the parent compound:

J. Kim et al, PRL (2012)
Magnon dispersion is very similar to La$_2$CuO$_4$

Smaller magnetic energy scale

Larger dispersion along zone boundary
RIXS: The Spin-Orbit Exciton

Real space description of the spin-orbiton mode

Hopping process for spin-orbiton mode (hole representation)

J. Kim et al, PRL (2012)
RIXS Measurements on $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$

$Q = (0,0,33), E_i = 11.216$ keV, $T \sim 10K$

Elastic scattering
$t_{2g}$ excitations, 
“spin-orbit exciton”
($J_{\text{eff}} = 3/2 \rightarrow J_{\text{eff}} = 1/2$)

d-d excitations
($t_{2g} \rightarrow e_g$)

Magnon

$J. \text{Kim et al, PRL (2012)}$
Magnetic Excitations in $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$
Orbital Excitations in $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$

- Within the magnetically ordered state ($x < x_c$), orbital excitations exhibit significant dispersion.
- Intensity and dispersion of these modes is dramatically reduced above $x_c$. 
Summary and Conclusions

- $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$ — a doped spin-orbital Mott insulator
- Rh dopants adopt 3+ oxidation state (hole-doping) not 4+ (isoelectronic)
- Doping-induced change in magnetic structure ($x \leq 0.07$)
- Magnetic order suppressed above $x_c \sim 0.17$
- Doping does not appear to disrupt the $j_{\text{eff}}=1/2$ state
- Well-defined magnons and spin-orbit excitons for $x < x_c$
- Magnetic excitations broaden/harden with increasing $x$
- Orbital excitations strongly coupled to magnetic ground state