

Title: Diluted Magnetism in Iridates: Studies of Rh-doped Sr₂Ir₂O₄

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Abstract: The physics of iridium-based 5d transition metal oxides has attracted significant interest due to the potential for exotic magnetic and electronic ground states driven by strong spin-orbit coupling effects. Among the most extensively studied iridates is the layered perovskite Sr₂IrO₄, which was recently proposed as the first experimental realization of a novel $J_{\text{eff}}=1/2$ spin-orbital Mott insulating state. Intriguing similarities between Sr₂IrO₄ and La₂CuO₄, the parent compound of the high-T_c cuprates, have also led to speculation that it may be possible to induce superconductivity in this system through chemical doping. We have investigated the magnetic properties of the doped system Sr₂Ir_{1-x}Rh_xO₄ using a combination of resonant magnetic x-ray scattering (RMXS), resonant inelastic x-ray scattering (RIXS), and x-ray absorption spectroscopy (XAS) techniques. These measurements reveal the effect of Rh-doping on the magnetic structure, phase diagram, and characteristic magnetic excitations of Sr₂IrO₄, and provide fundamental information about the role of quenched Rh impurities.

Acknowledgements

- **University of Toronto:**
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 - Gang Cao (Sample Synthesis)
- **Canadian Light Source:**
 - Yongfeng Hu (XAS)
- **Advanced Photon Source:**
 - Zahir Islam (RMAXS), Mary Upton, Jungho Kim (RIXS)
- **Funding:** NSERC, Banting Postdoctoral Fellowship Program, NRC, CIHR, Prov. of Sask., WEDC, Univ. of Sask., U.S. Dept. of Energy



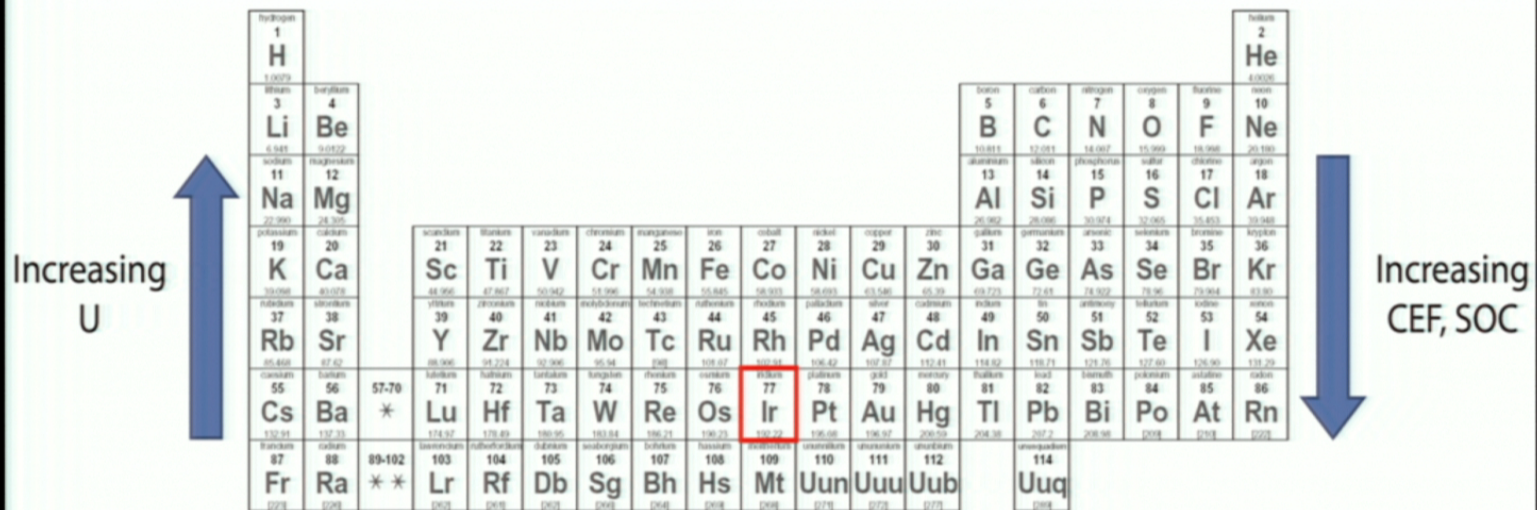
UNIVERSITY OF
TORONTO



A Brief Outline...

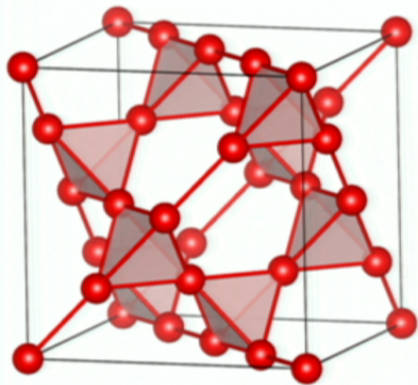
- Introduction – novel physics in spin-orbit coupled iridates
- Sr_2IrO_4 – the $j_{\text{eff}} = 1/2$ spin-orbital Mott insulator
- $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$ – investigating the impact of chemical doping
- Experimental Results:
 - What is the role of Rh dopant ions? (**XAS**)
 - Effect of doping on magnetic structure? (**RMXS**)
 - Effect of doping on magnetic excitations? (**RIXS**)
- Summary and conclusions

Why Study Iridates?

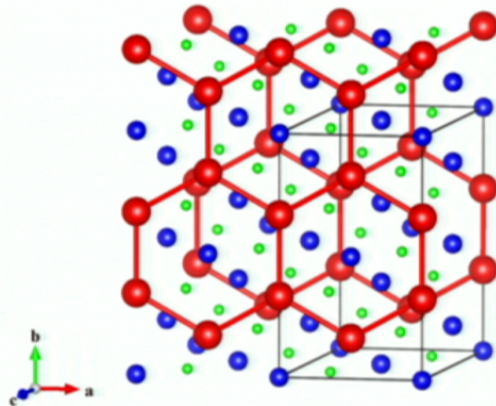


- Interplay between electronic correlations, crystal electric field, and spin-orbit coupling ($U \sim \text{CEF} \sim \text{SOC}$)
- Potential for exotic physics driven by strong SOC ($\sim 0.5 \text{ eV}$)

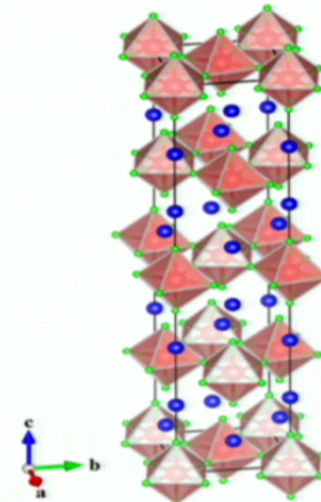
Novel Physics in Iridates



Candidate for Topological Insulator, Weyl Semi-Metal, Metallic Spin Liquid:
 Yang et al, PRB (2010),
 Wan et al, PRB (2011),
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 Nakatsuji et al, PRL (2006)

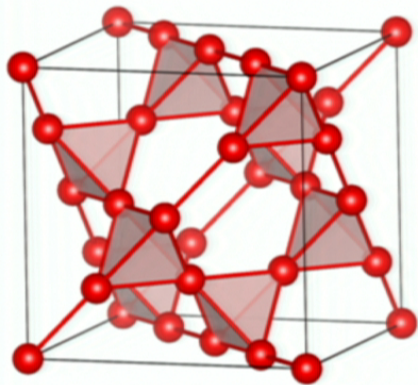


Candidate for Topological Insulator, Kitaev-Heisenberg Model:
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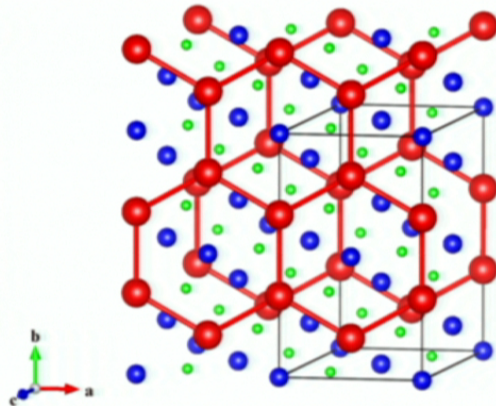


$J_{\text{eff}}=1/2$ spin orbital
 Mott insulator:
 Kim et al, PRL (2008)
 Kim et al, Science (2009)
 Kim et al, PRL (2012)

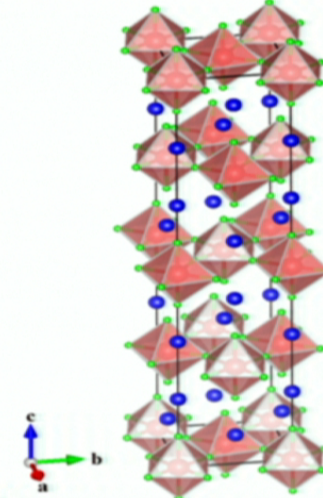
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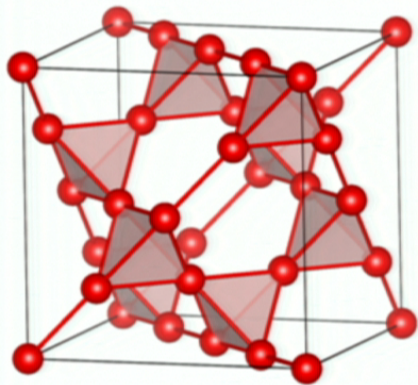


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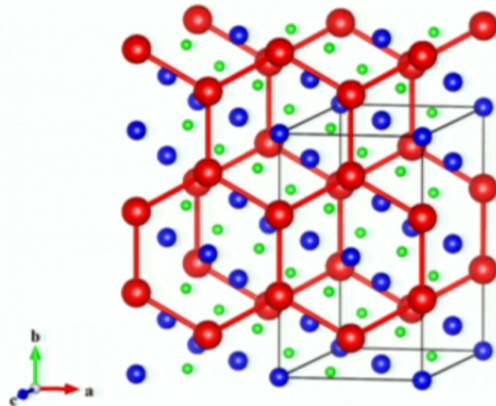


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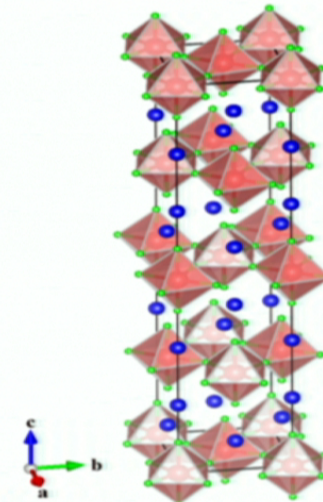
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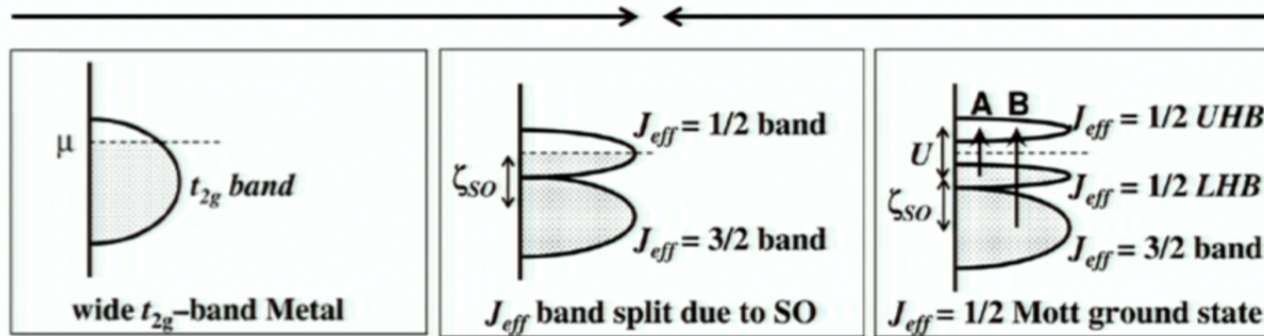
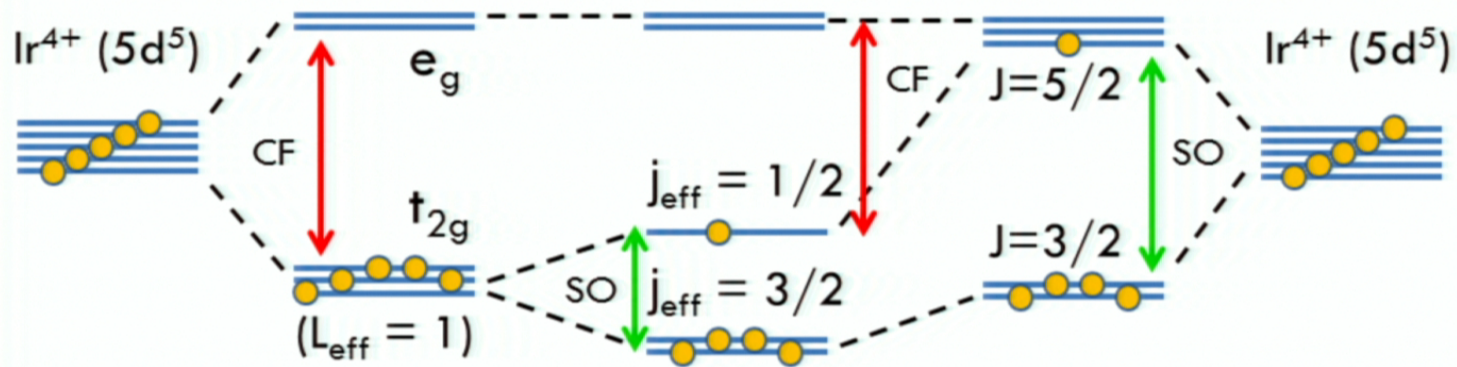
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Sr₂IrO₄: the Spin-Orbital Mott Insulator

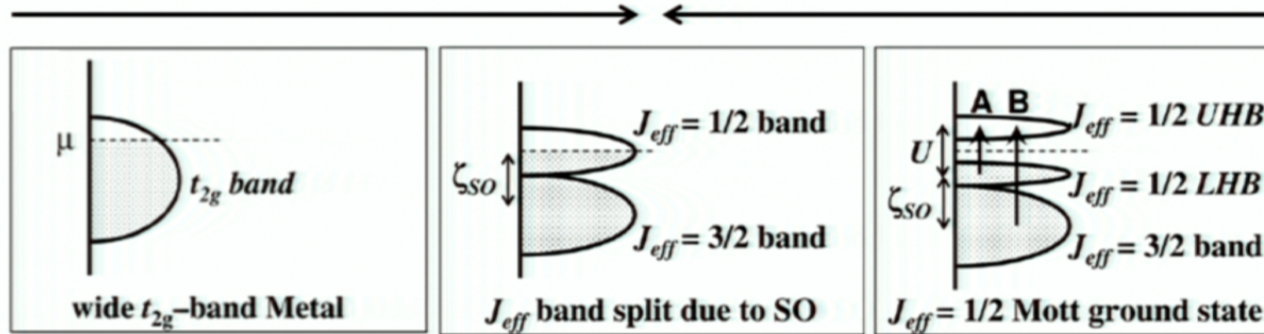
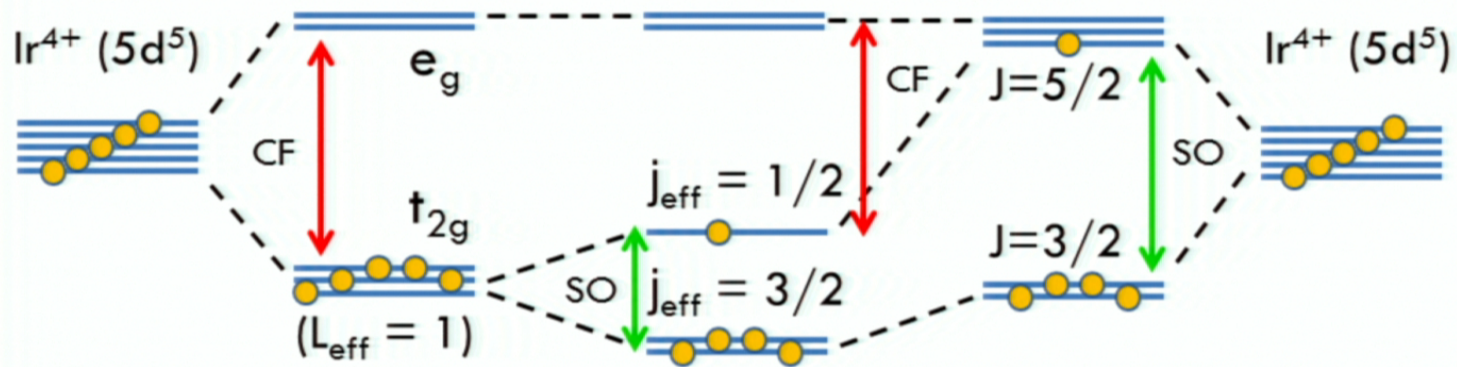
A surprising number of iridates are insulators - why?



B.J. Kim et al, PRL (2008)

Sr₂IrO₄: the Spin-Orbital Mott Insulator

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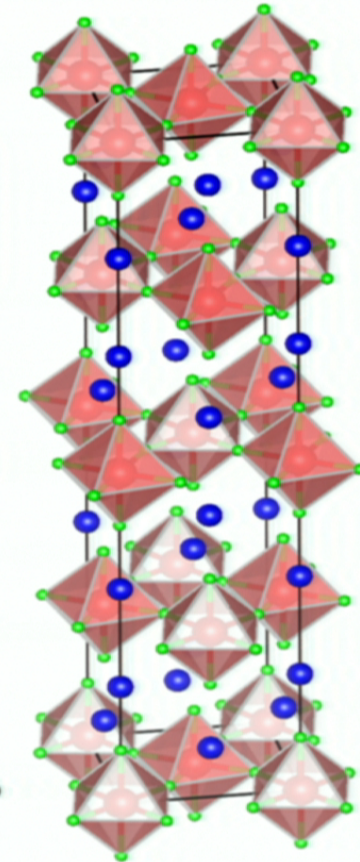
Physical Properties of Sr_2IrO_4

- Member of Ruddlesden-Popper series ($n=1$):



$$\begin{aligned} a &= 5.50 \text{ \AA} \\ c &= 25.80 \text{ \AA} \end{aligned}$$

- Space Group: $I4_1/acd$
- 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 La_2CuO_4 and Sr_2RuO_4
- Possibility of doping-induced superconductivity?
 - Wang and Senthil, PRL (2011)
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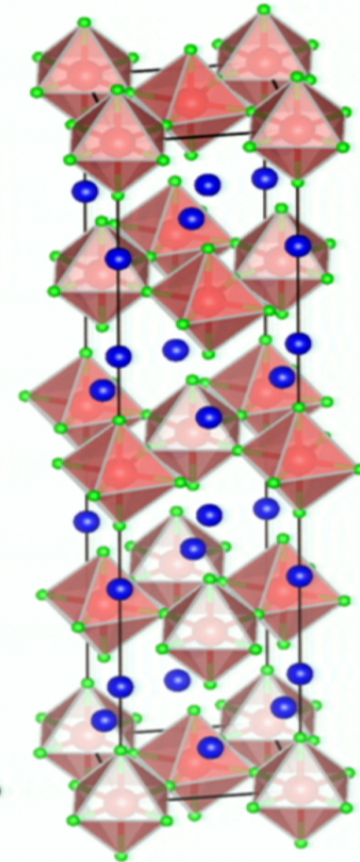
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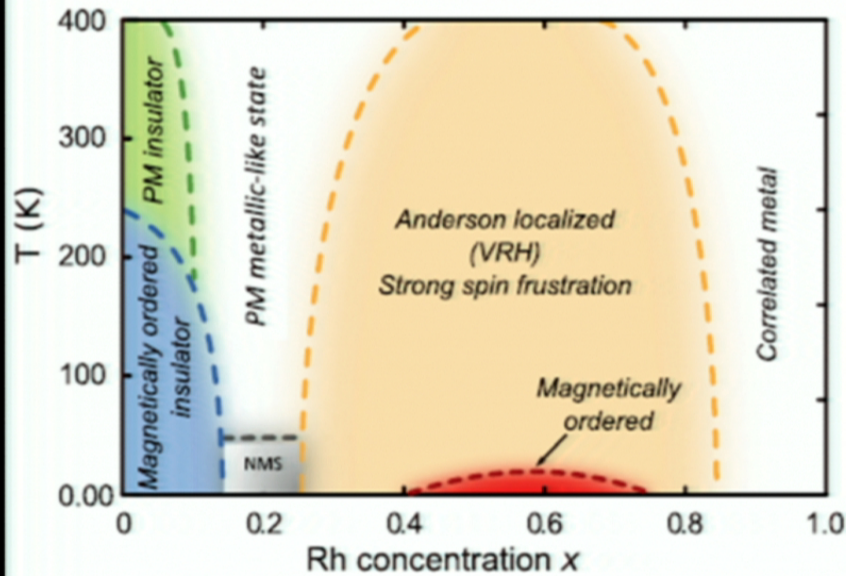
Doping Studies on Sr_2IrO_4

(No superconductivity so far...)

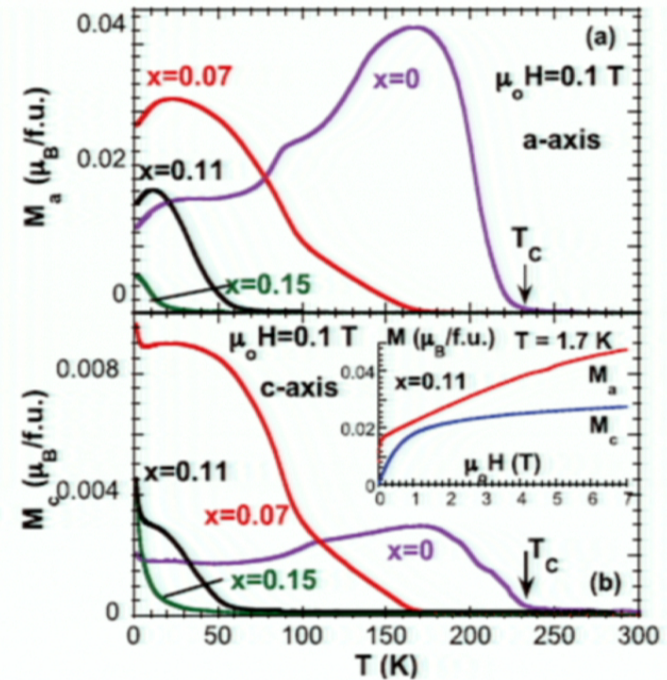
hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 101.07	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57-70 * [138.905]	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	actinium 89-102 * * [227]	lawrencium 103 Lr [260]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [263]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [266]	unbinilium 110 Uun [267]	ununilium 111 Uuu [268]	unununium 112 Uub [269]	unquadrium 114 Uuq [289]										

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

What is the effect of Rh-doping?

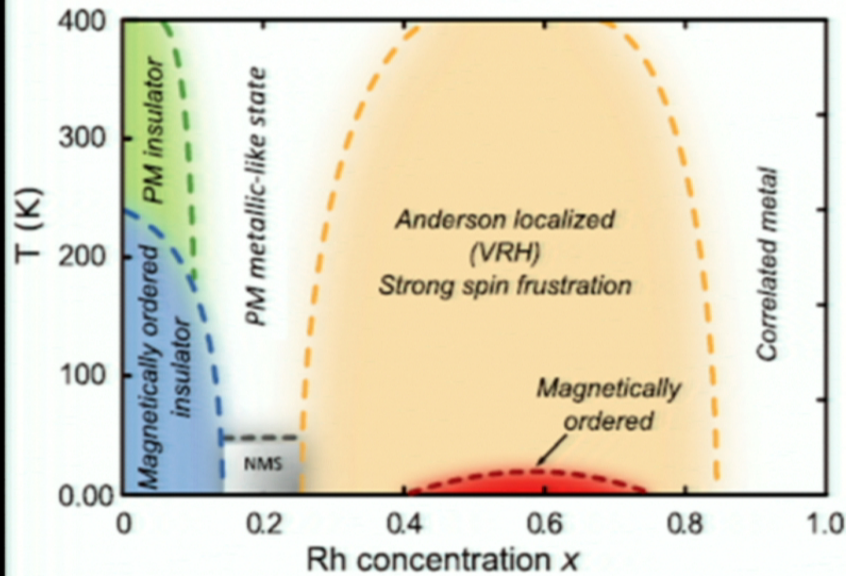


T. Qi et al, PRB (2012)

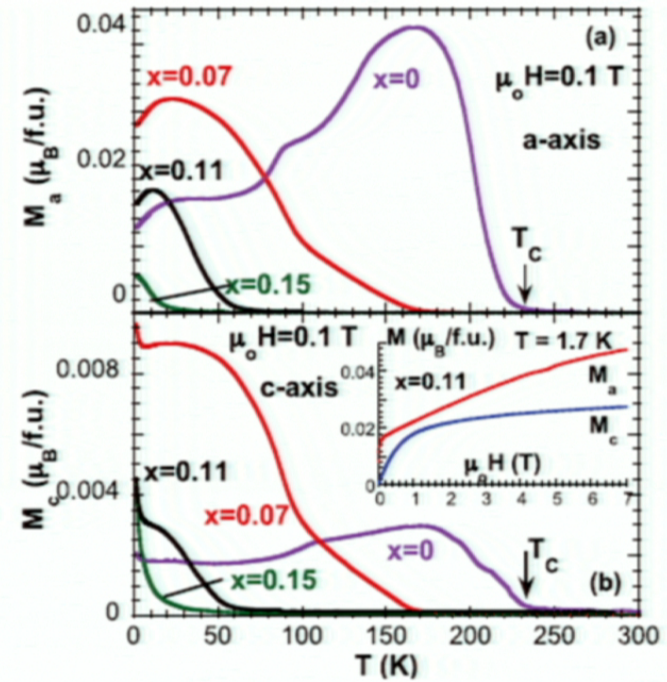


- Rh-doping induces a series of electronic and magnetic phase transitions between Sr_2IrO_4 and Sr_2RhO_4

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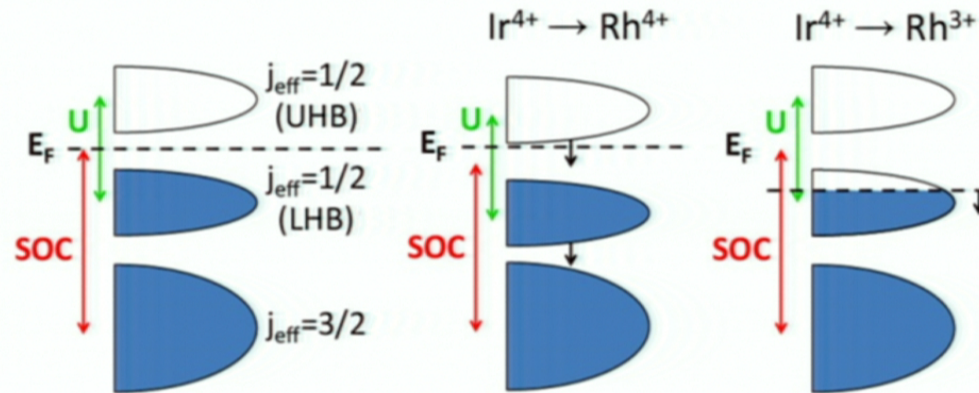


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What is the effect of Rh-doping?

- **Substitute Rh⁴⁺ (4d⁵) for Ir⁴⁺ (5d⁵)?** → isoelectronic doping, tune SOC [Qi et al, PRB (2012), Lee et al, PRB (2012)]

iron 26 55.845	cobalt 27 58.933	nickel 28 58.693
ruthenium 44 101.07	rhodium 45 102.91	palladium 46 106.42
osmium 76 190.23	iridium 77 192.22	platinum 78 195.08

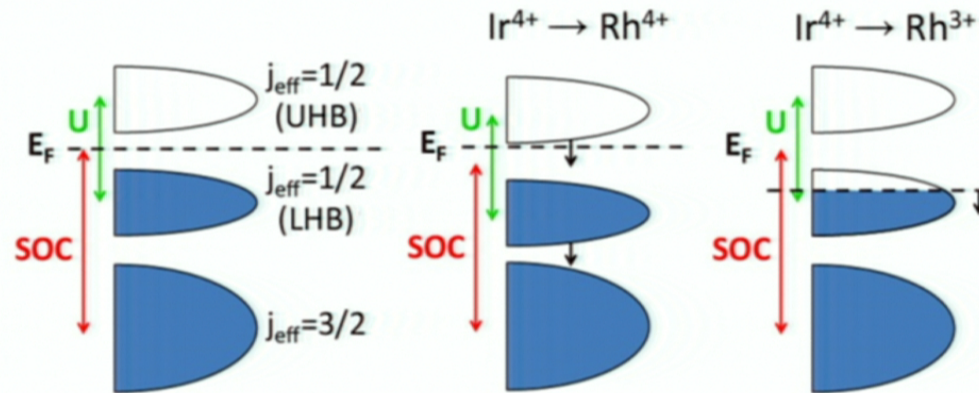


- **Substitute Rh³⁺ (4d⁶) for Ir⁴⁺ (5d⁵)?** → hole doping, tune band filling and SOC [Klein et al, JPCM (2008)/JEM(2009)]

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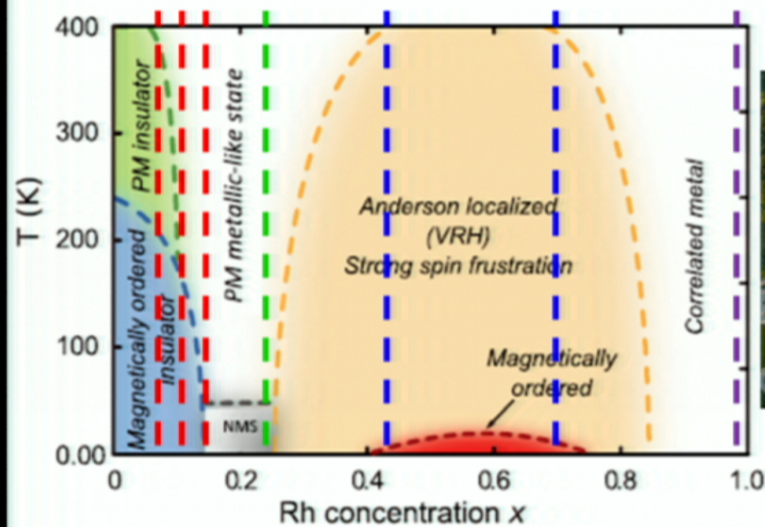
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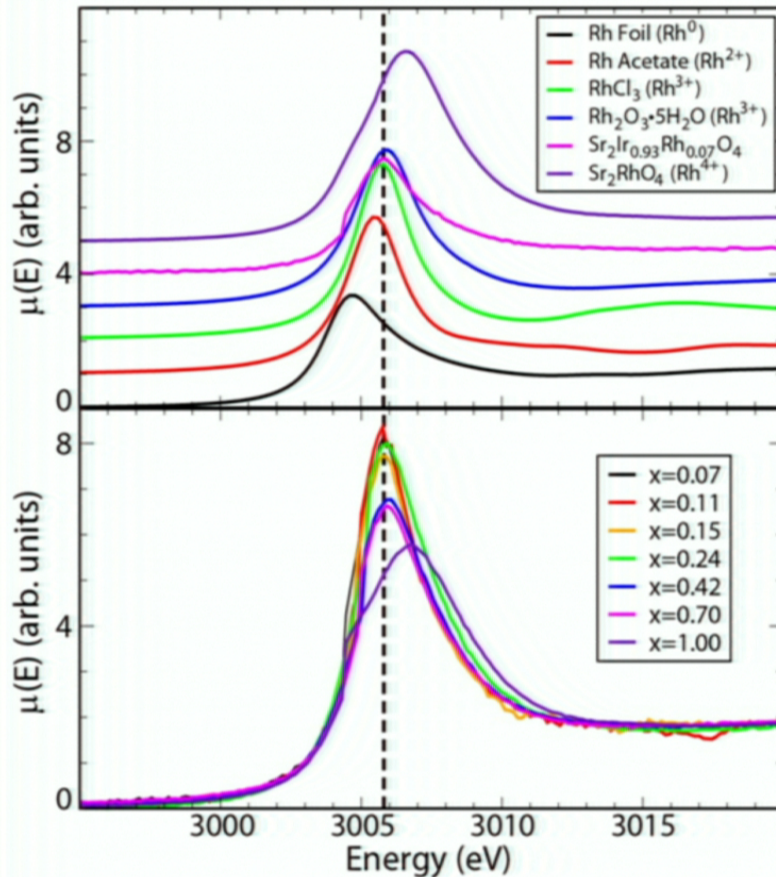
Experimental Details

- 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



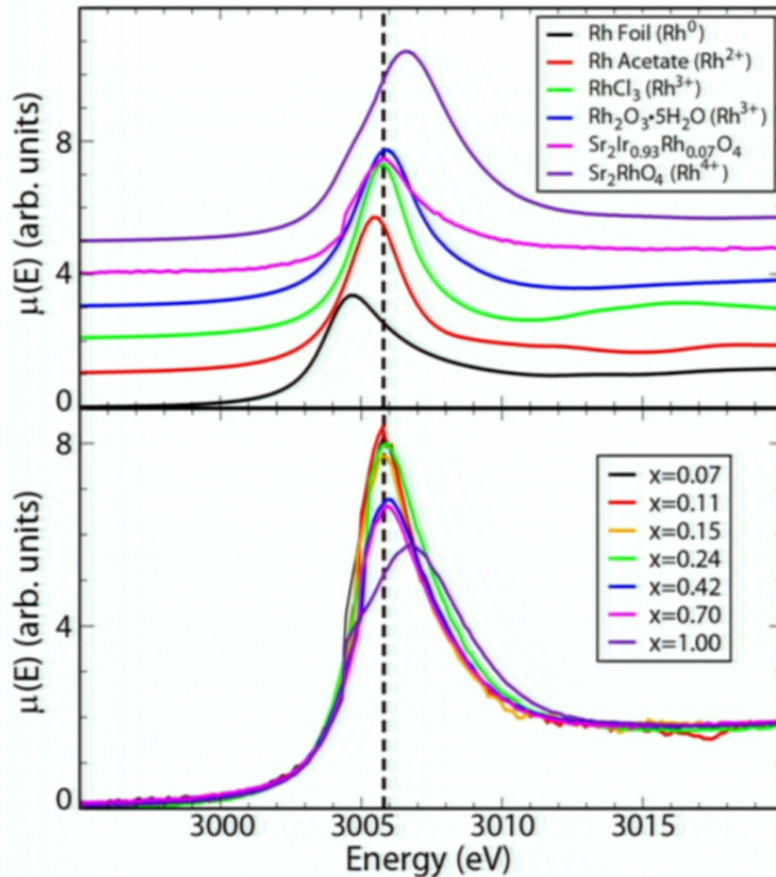
- X-ray Absorption Spectroscopy (**XAS**) – SXRMB at CLS
- Resonant Magnetic X-ray Scattering (**RMXS**) – 6-ID-B at APS
- Resonant Inelastic X-ray Scattering (**RIXS**) – MERIX at APS

XAS: Oxidation State of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



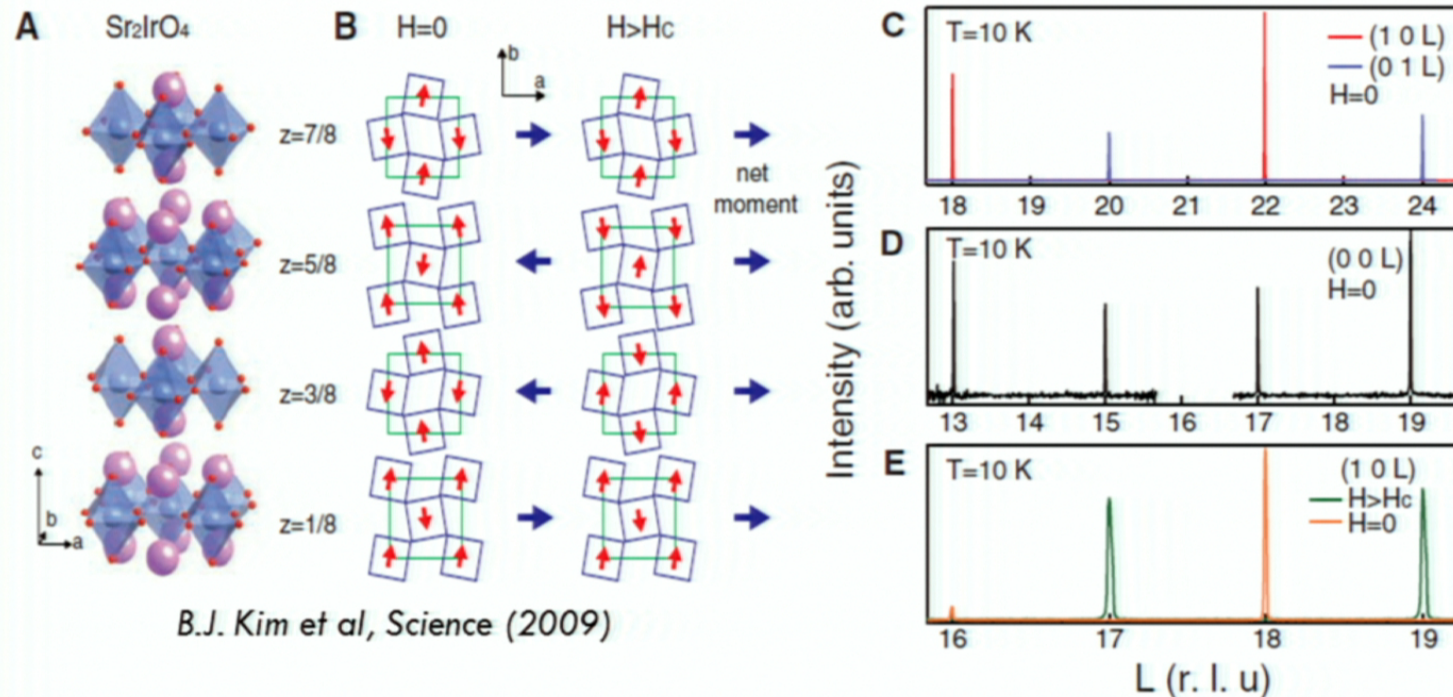
- Compare XAS white-line features at Rh L₃-edge:
- Suggests Rh dopant ions adopt a **Rh³⁺** state for $x = 0.07$ to $x = 0.70$
- $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$ appears to be a hole-doped system

XAS: Oxidation State of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



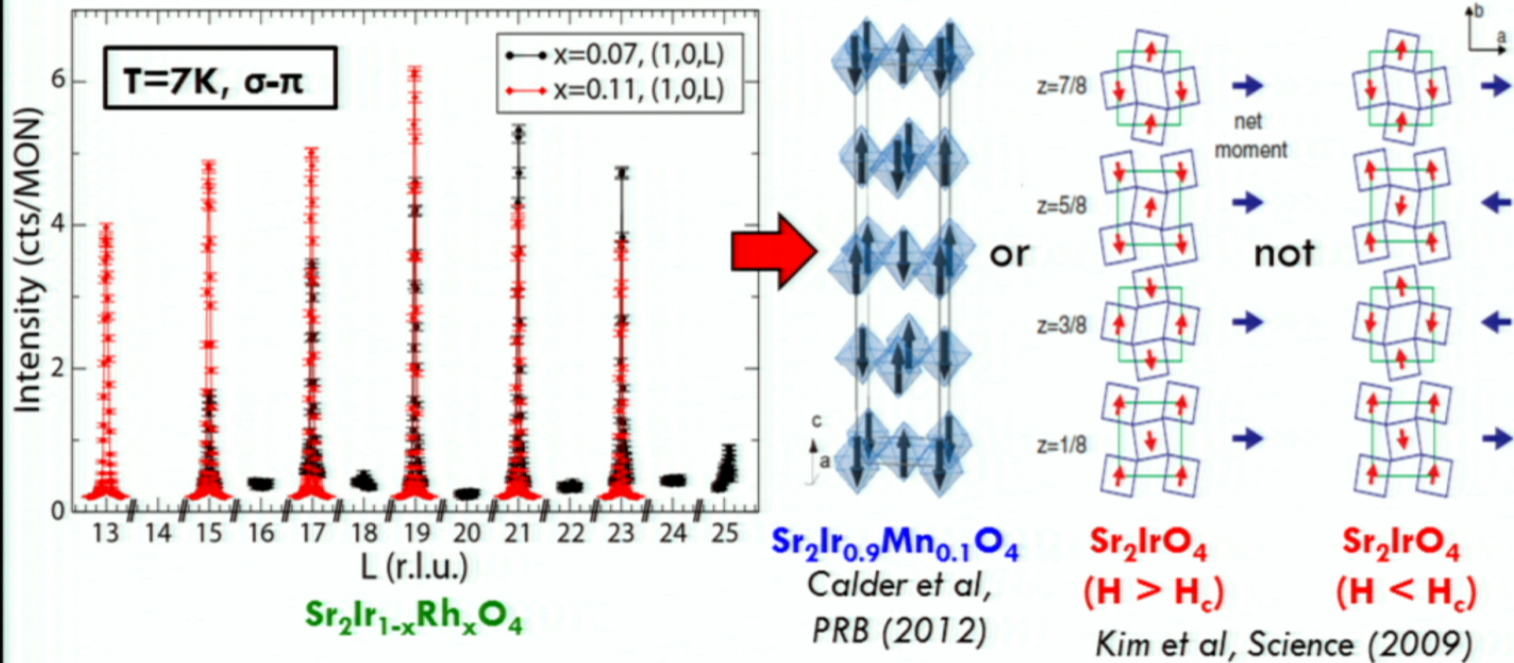
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RMXS: Magnetic Structure of Sr_2IrO_4



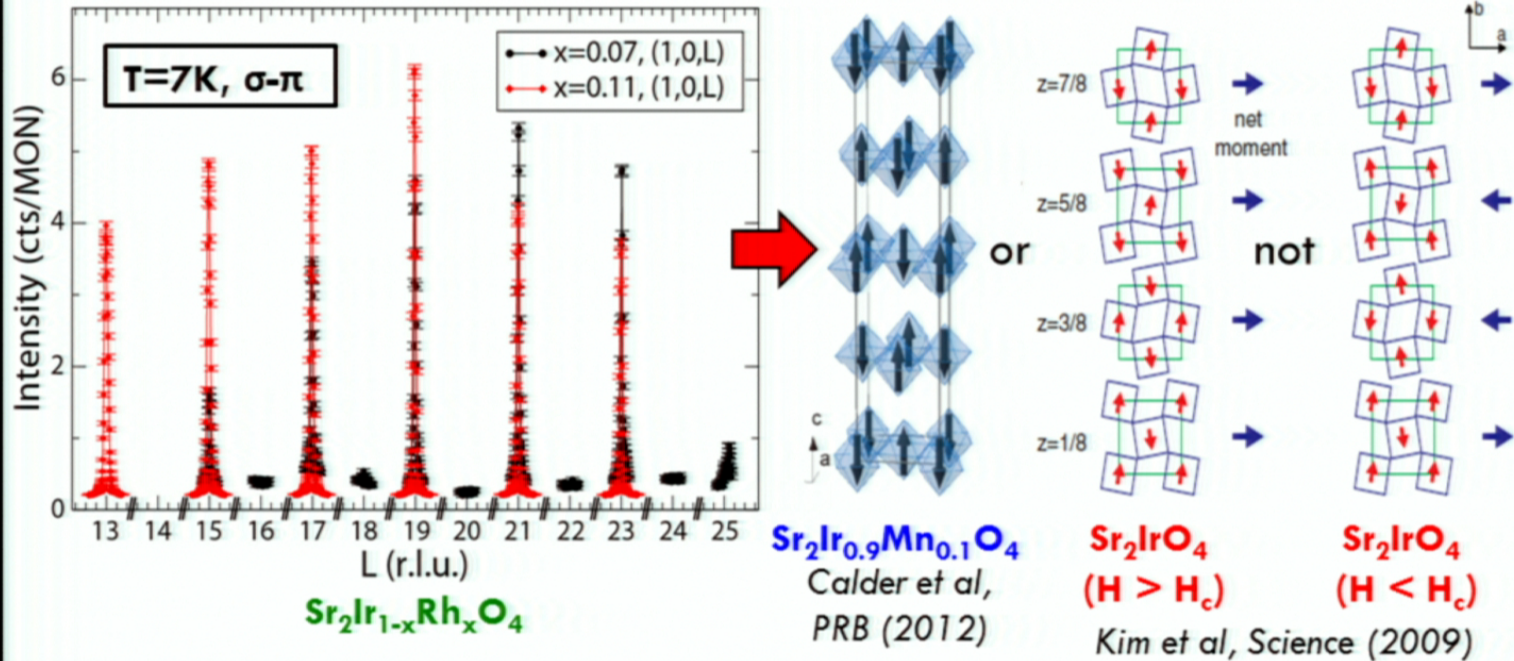
- Parent compound displays canted AF ground state
- Field-induced magnetic phase transition above $H_C \sim 0.25$ T

Magnetic Structure of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



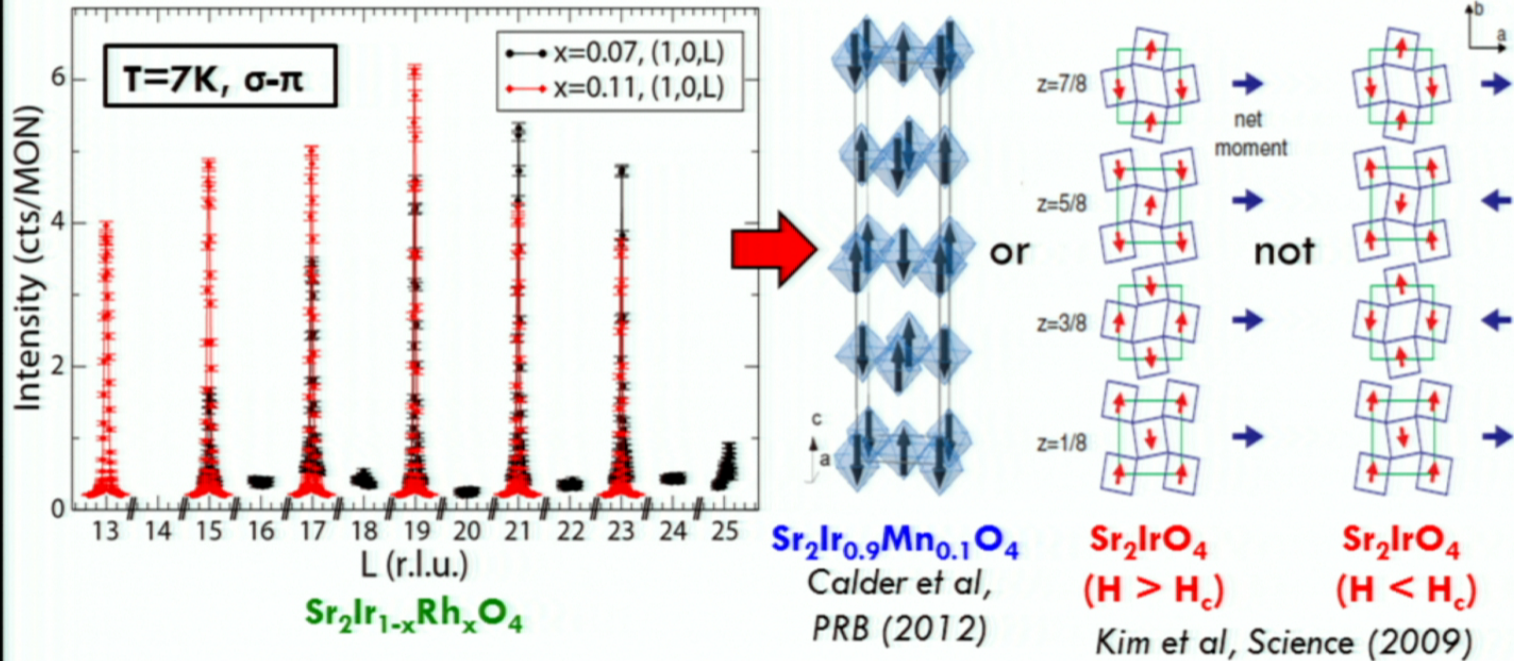
- Magnetic Bragg peaks observed at $(0,1,L)/(1,0,L)$ for $L=\text{odd}$
- No magnetic peaks for $(0,0,L), (1,1,L), (1/2,1/2,L),$ or $(1/2,0,L)$
- Doping-induced change in magnetic structure for $x \leq 0.07$

Magnetic Structure of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



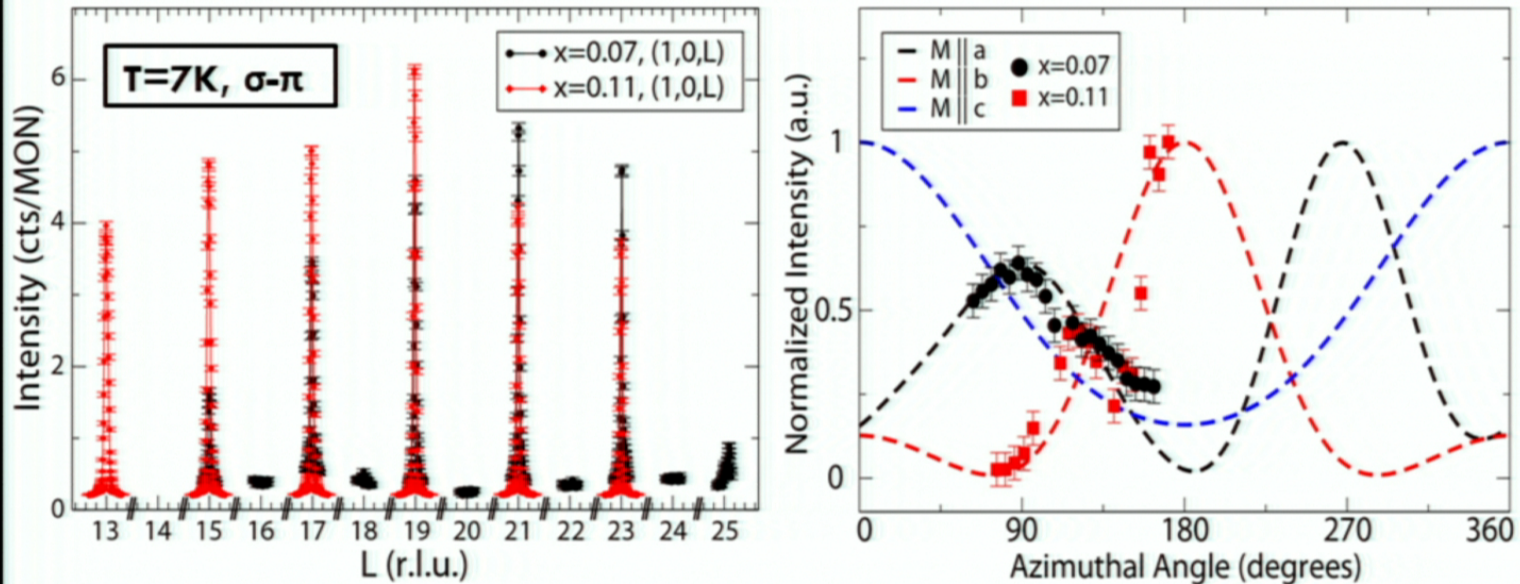
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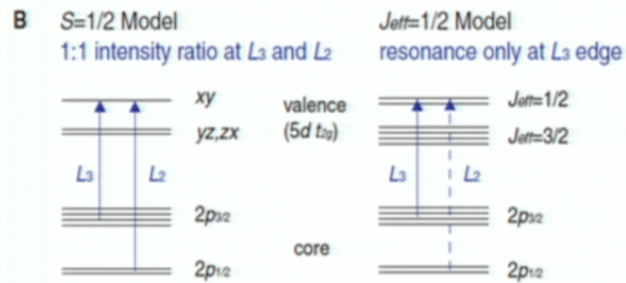
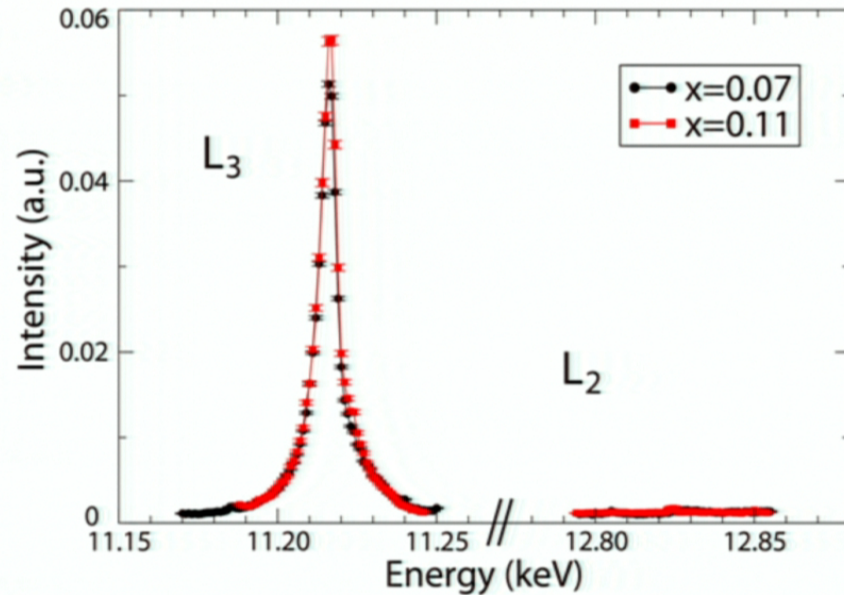
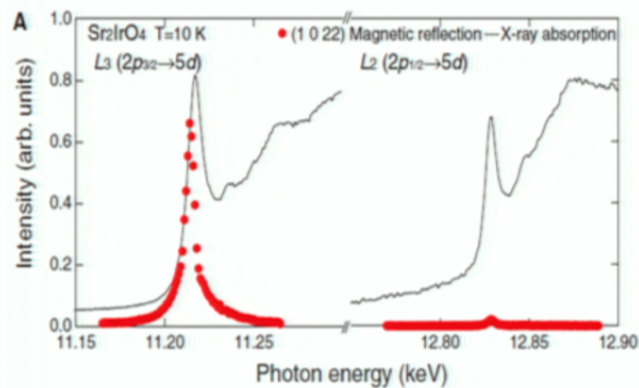
Magnetic Structure of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



- Magnetic structure factor and azimuthal dependence confirm magnetic moments lie within the ab -plane
- Rh-doped Sr_2IrO_4 displays same magnetic structure as Sr_2IrO_4 in applied field ($H > H_c$)

Robustness of the $J_{\text{eff}}=1/2$ State

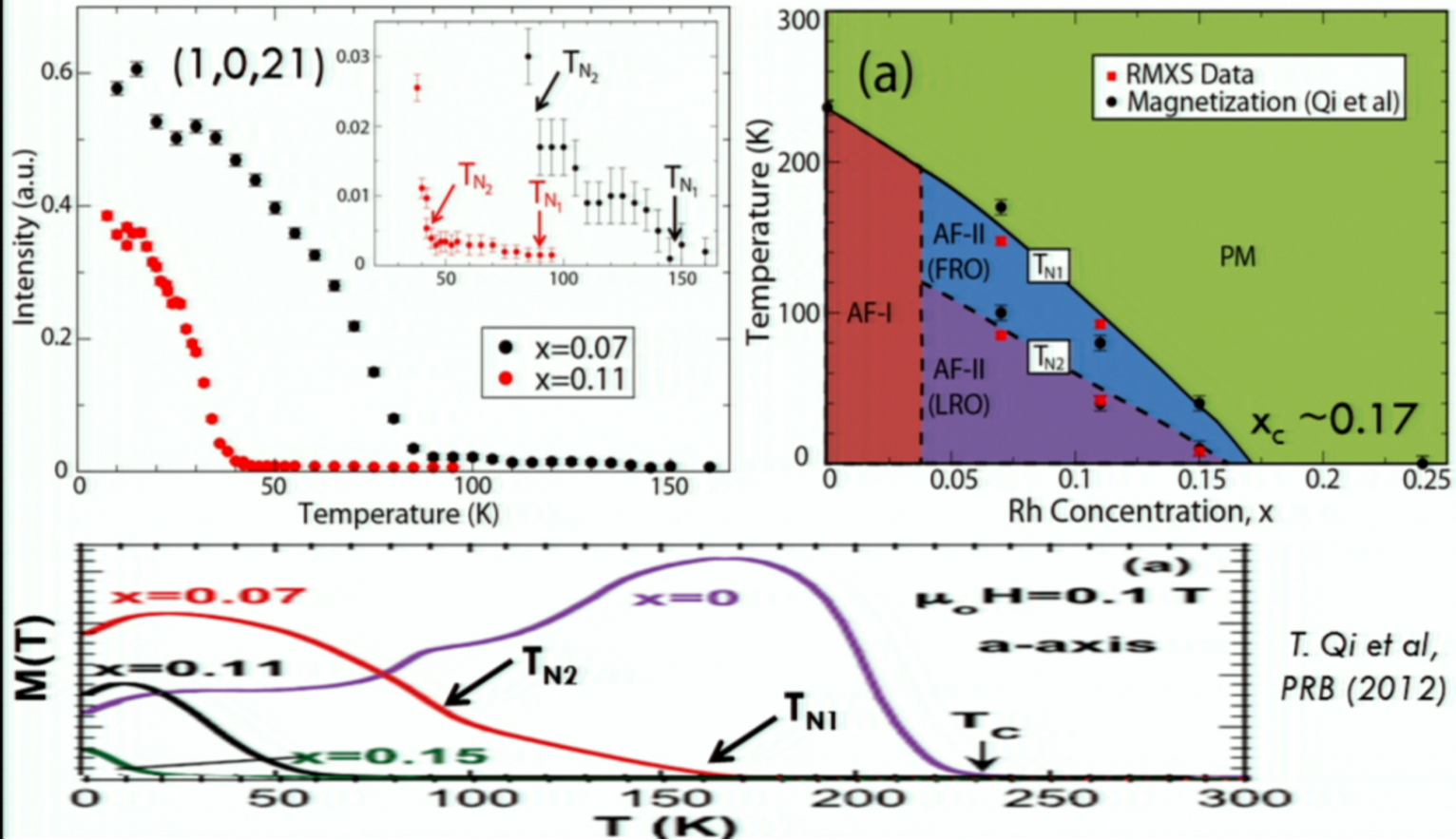
- Large I_{L3}/I_{L2} ratio is a defining signature of the $J_{\text{eff}} = 1/2$ state



B.J. Kim et al, Science (2009)

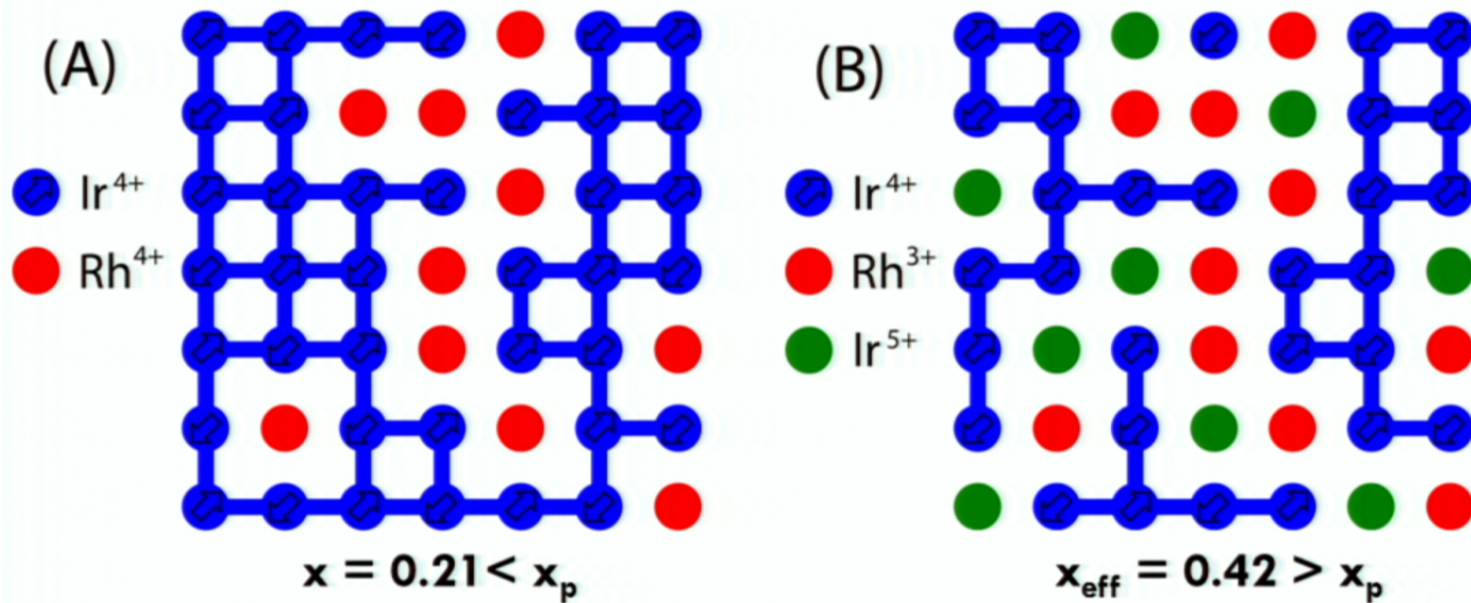
- Minimum intensity ratio for Rh-doped Sr₂IrO₄ is $I_{L3}/I_{L2} > 200$
- Similar result observed in Sr₂Ir_{0.9}Mn_{0.1}O₄ (Calder et al, PRB [2012])

Magnetic Phase Diagram of $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$



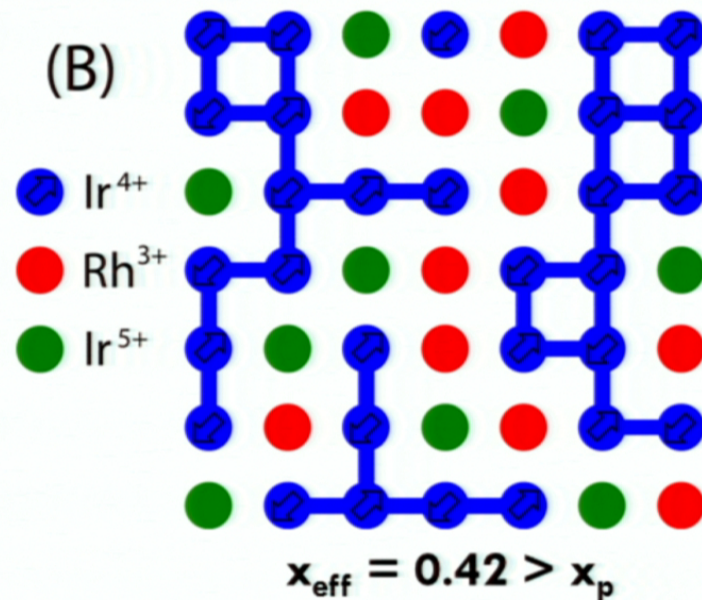
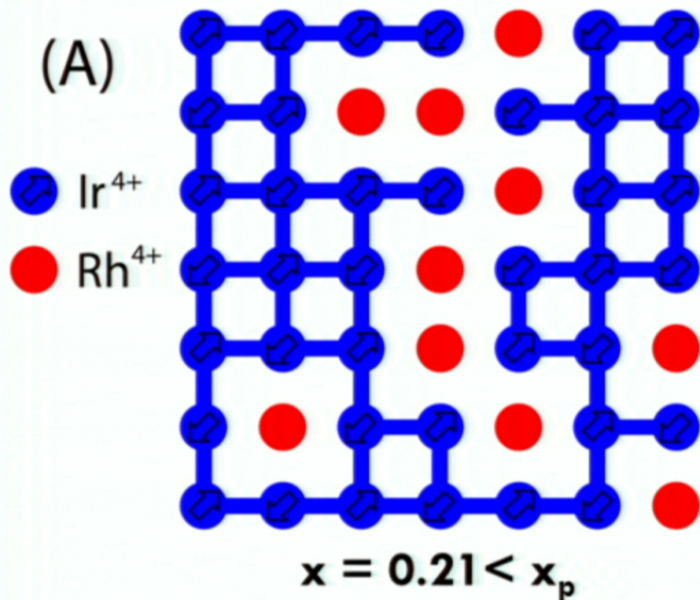
Implications of the Phase Diagram

- 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)]



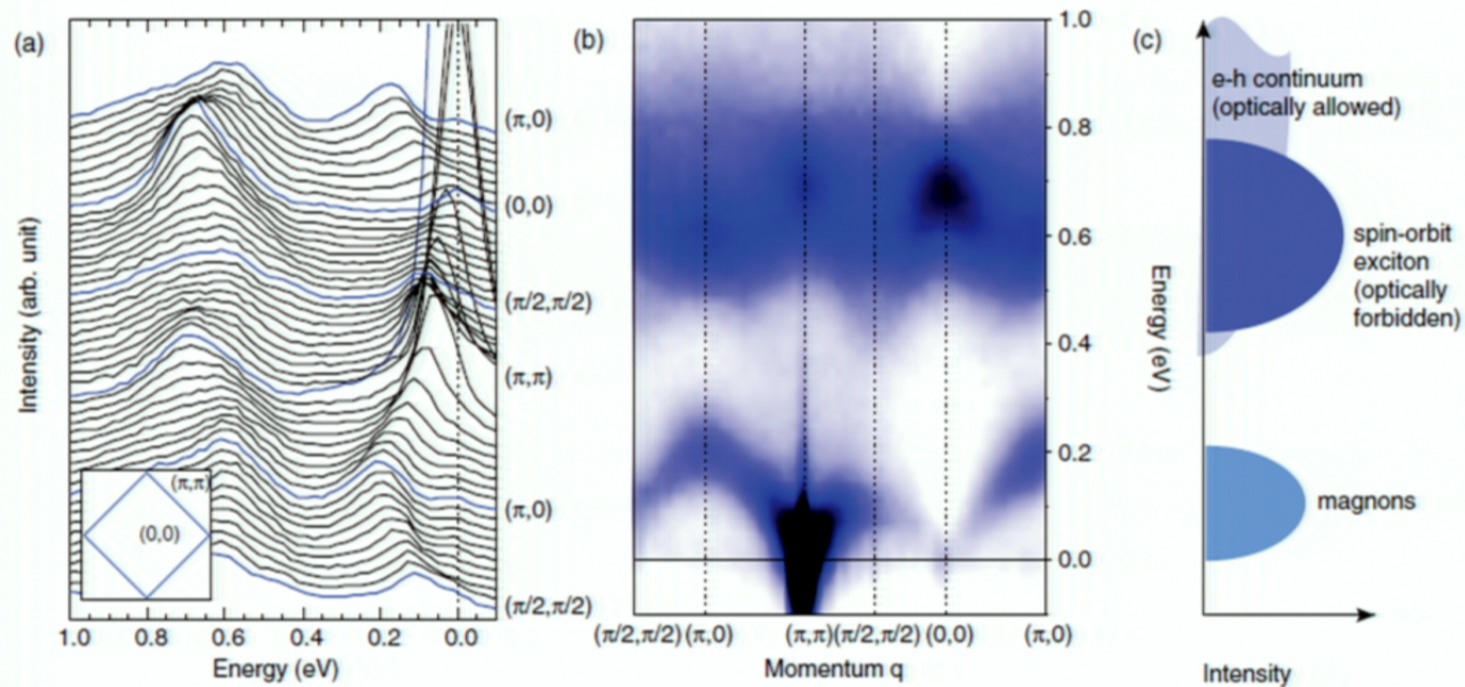
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RIXS: Magnetic Excitations in Sr_2IrO_4

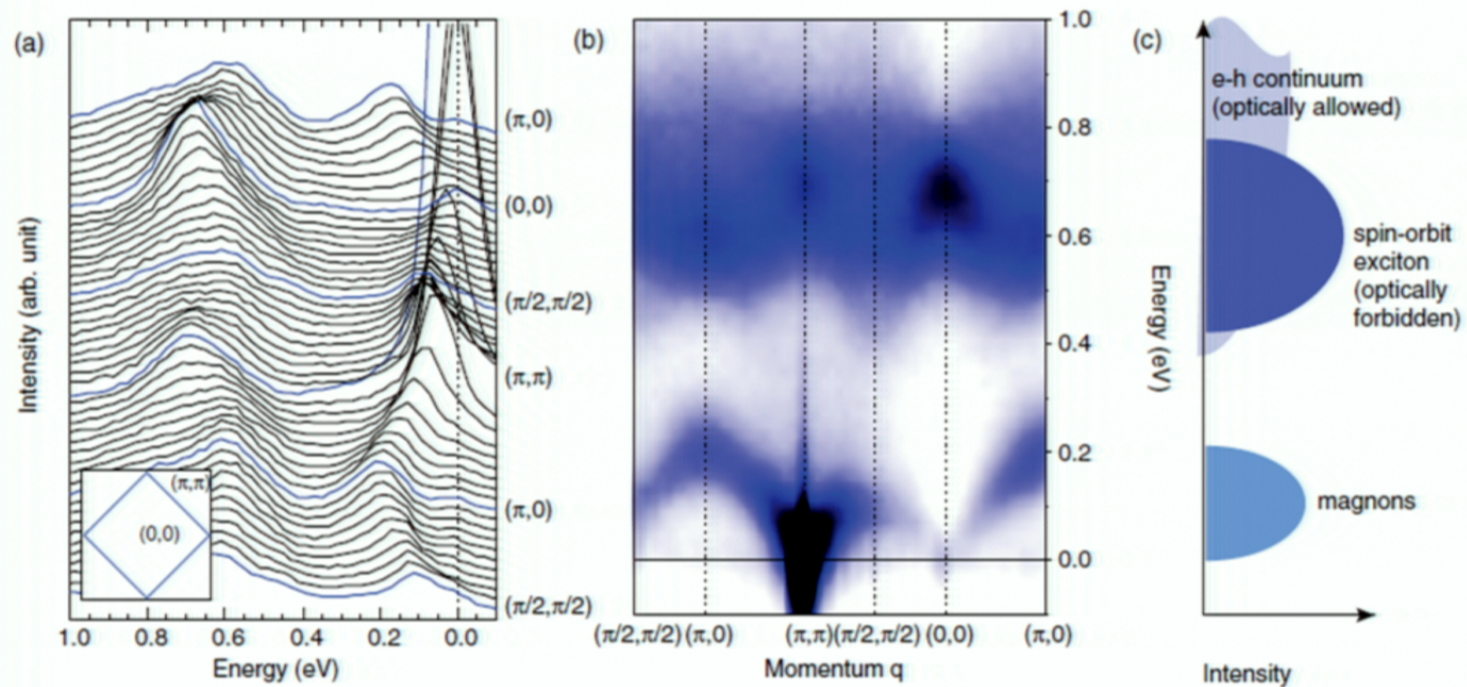
- Ir L_3 -edge RIXS measurements on the parent compound:



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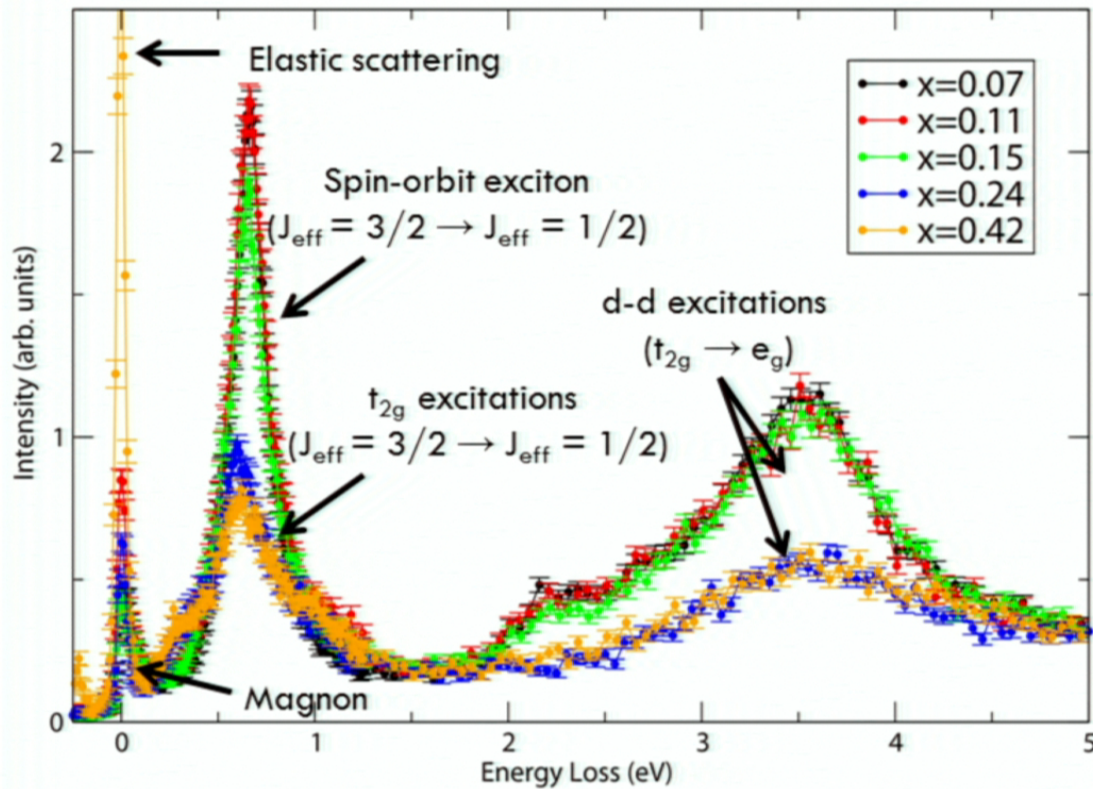
RIXS: Magnetic Excitations in Sr_2IrO_4

- Ir L_3 -edge RIXS measurements on the parent compound:

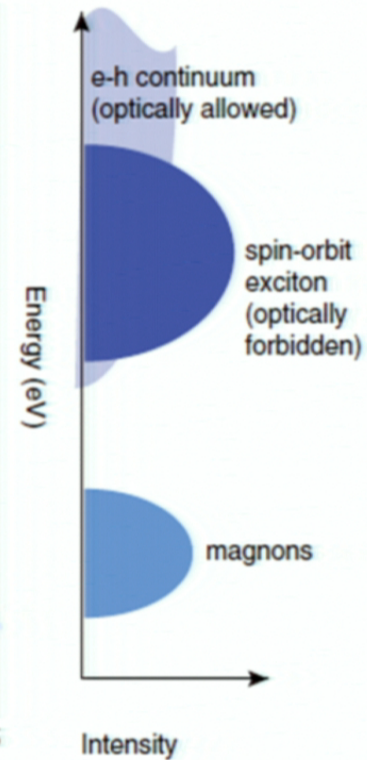


J. Kim et al, PRL (2012)

RIXS Measurements on $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$

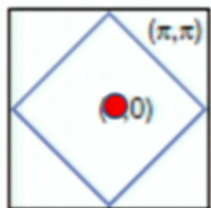
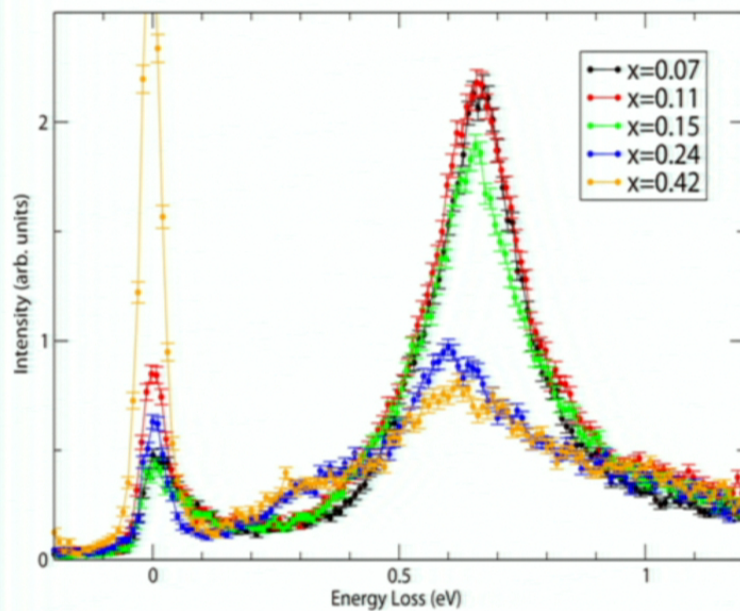


$Q = (0,0,33), E_i = 11.216 \text{ keV}, T \sim 10\text{K}$

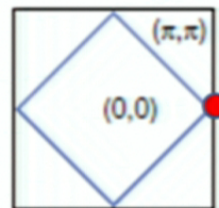
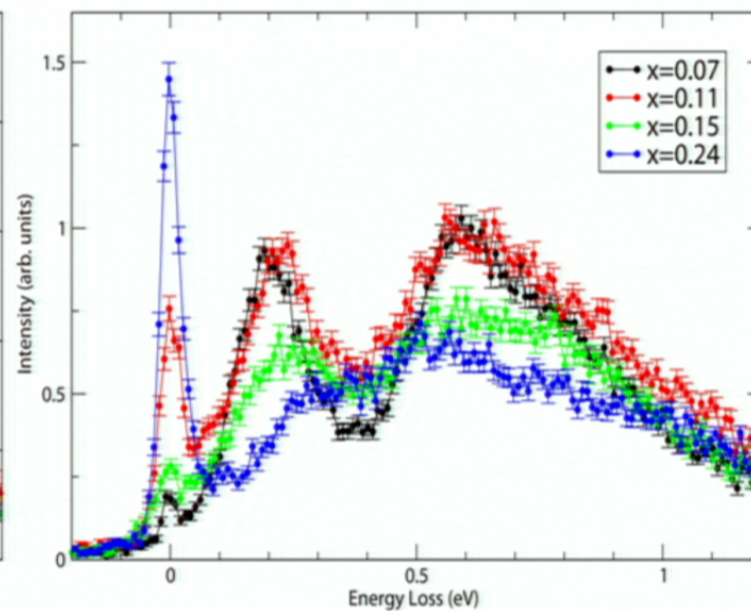


J. Kim et al,
PRL (2012)

Magnetic Excitations in $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$

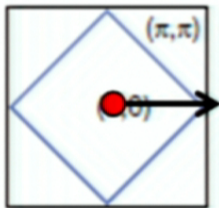
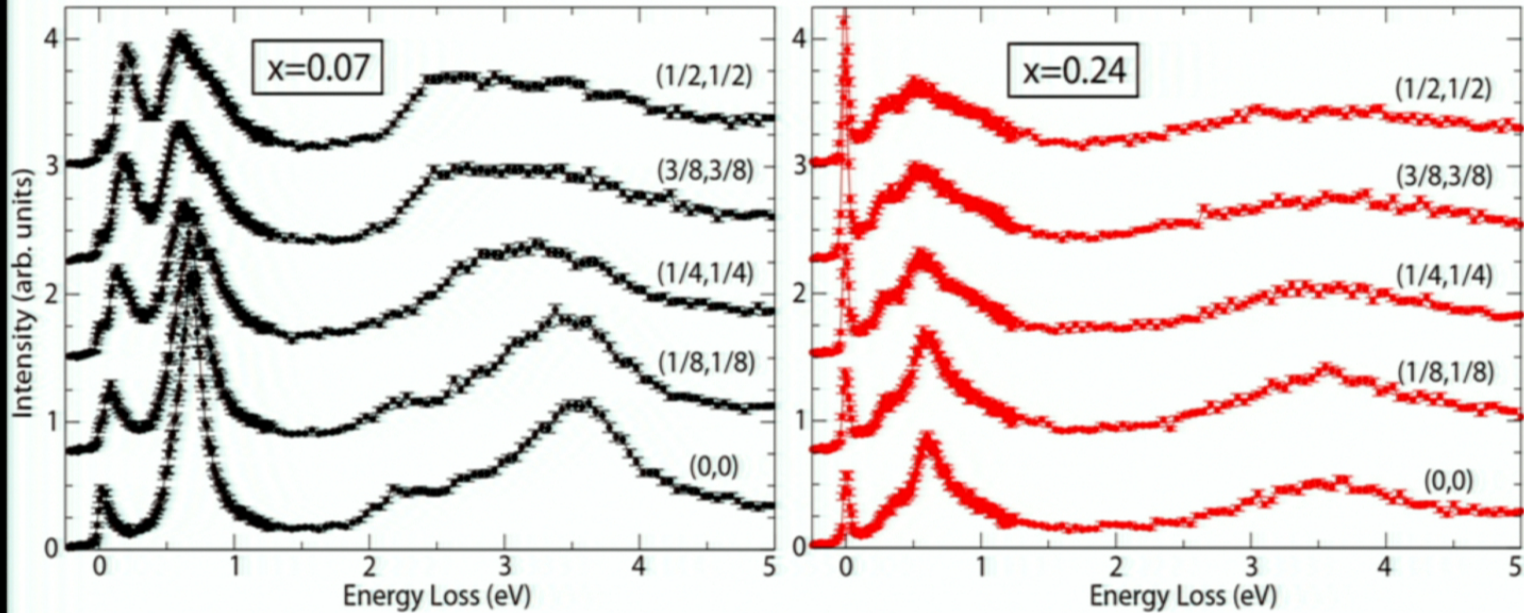


$Q=(0,0,33)$
Zone Center



$Q=(1/2, 1/2, 33)$
Zone Boundary

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