

# Today's outline - April 14, 2020 (part A)

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- Resonant techniques

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Homework Assignment #7:

Chapter 7: 2,3,9,10,11

due Thursday, April 23, 2020

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Final Exam, Tuesday, May 5, 2020 13:00 CDT

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Tell me what time slot you would prefer for your presentation (first come, first served!)

13:00	14:00	15:00	16:00	17:00	18:00
13:20	14:20	15:20	16:20	17:20	18:20
13:40	14:40	15:40	16:40	17:40	18:40

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Send me your presentation in Powerpoint or PDF format before the exam

## Matrix elements for x-ray-electron interaction

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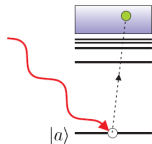
$$\mathcal{H}_I = \frac{e\vec{p} \cdot \vec{A}}{m} + \frac{e^2 A^2}{2m}, \quad \vec{A} = \hat{\epsilon} \sqrt{\frac{\hbar}{2\epsilon_0 V \omega}} \left[ a_k e^{i\vec{k} \cdot \vec{r}} + a_k^\dagger e^{-i\vec{k} \cdot \vec{r}} \right]$$



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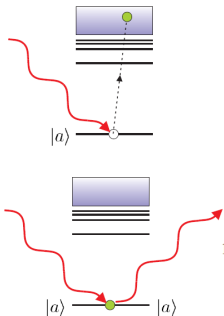


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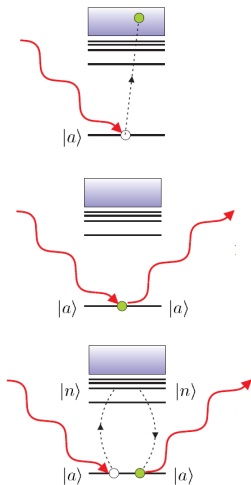
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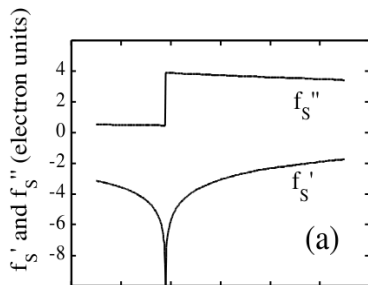


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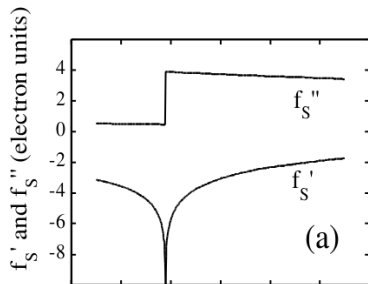
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**Resonant scattering** is a second order process that involves photon annihilation and creation operators, a core electron and an intermediate empty electron state

# Diffraction anomalous fine structure (DAFS)

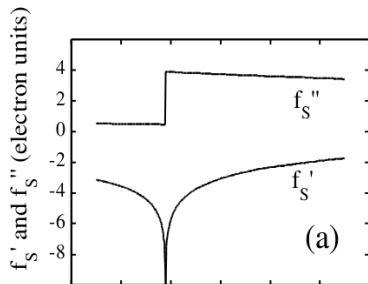


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The simple model of resonant scattering and absorption produce a resonance dip in the real part of scattering factor of an atom at the absorption edge but there is no structure in either for an isolated atom

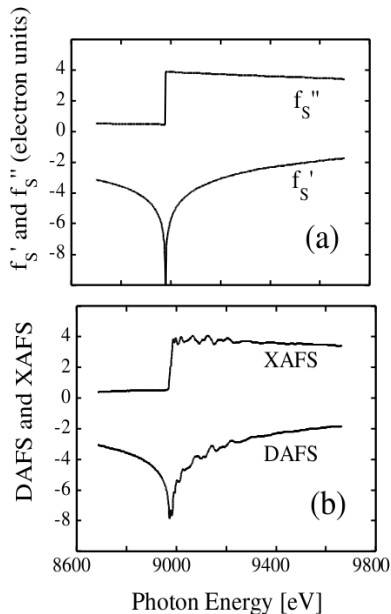
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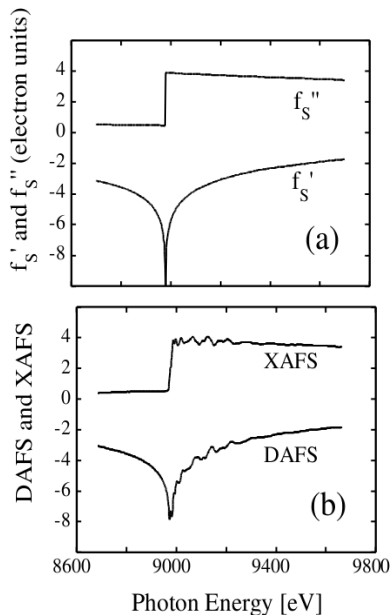
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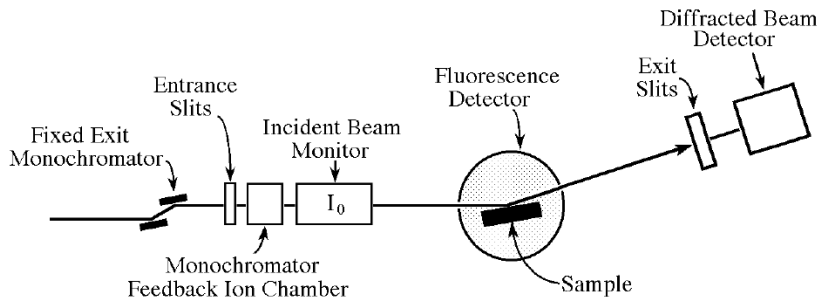
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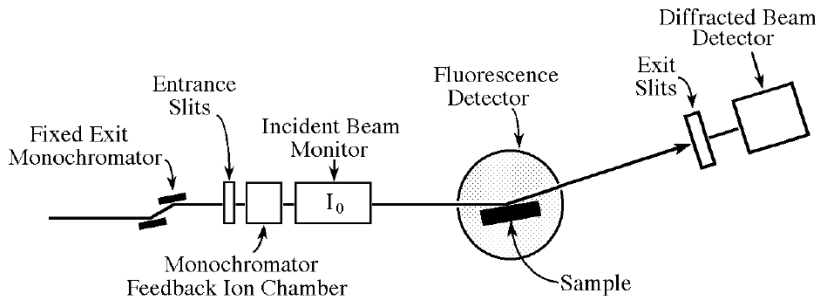
These oscillations can be measured in Bragg reflections contributed to by the atom with the absorption edge and exploited to extract site-specific EXAFS



# The DAFS experiment

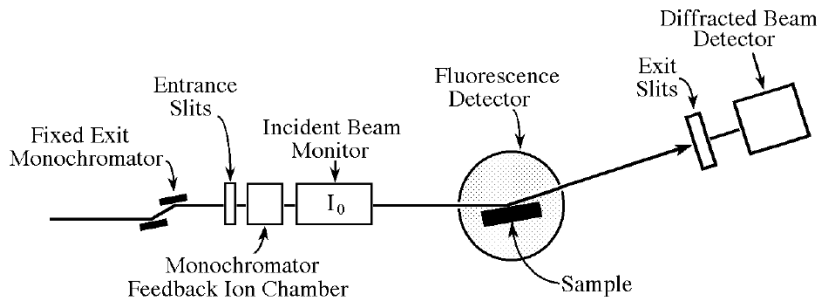


# The DAFS experiment



As the energy is swept through the absorption edge, the angle of the sample and the detector are changed to remain in a Bragg condition.

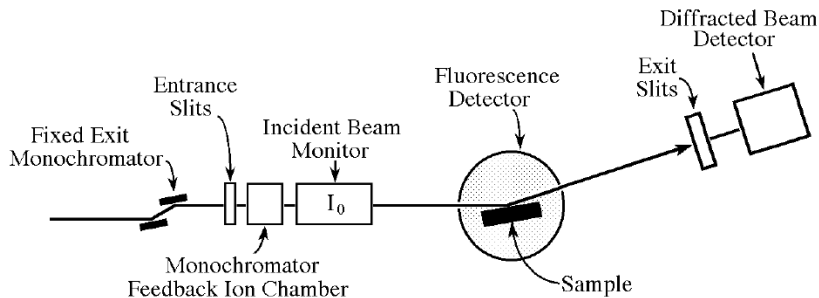
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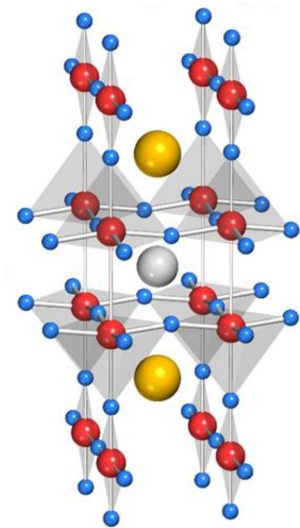


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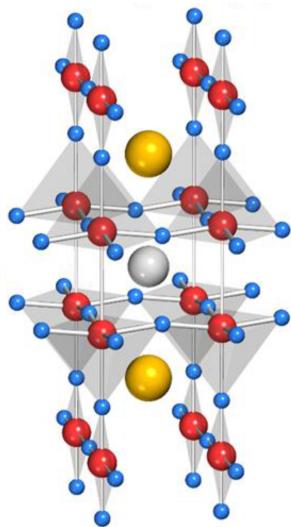
Initially experiments were done on single crystals but now DAFS on powders can be performed

# DAFS of $\text{YBa}_2\text{Cu}_3\text{O}_7$



'Separated anomalous scattering amplitudes for the inequivalent Cu sites in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  using DAFS,' J.O. Cross, M. Newville, L.B. Sorensen, H.J. Straiger, C.E. Bouldin, and J.C. Woicik, *J. Phys.* **C2**, 745-747 (1997).

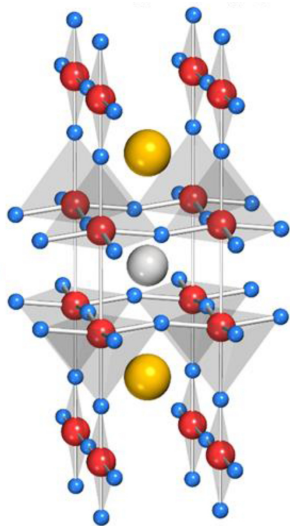
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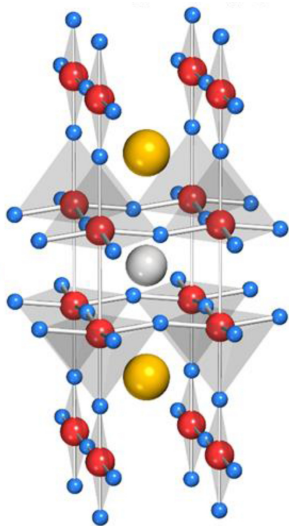


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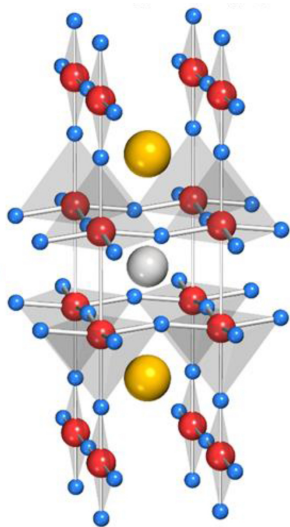
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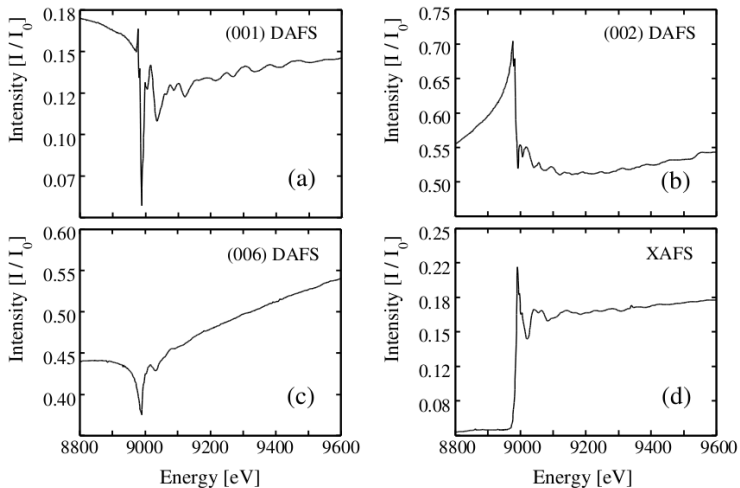
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by measuring the DAFS of multiple (00l) diffraction peaks, it is possible to separate the EXAFS of the two Cu sites

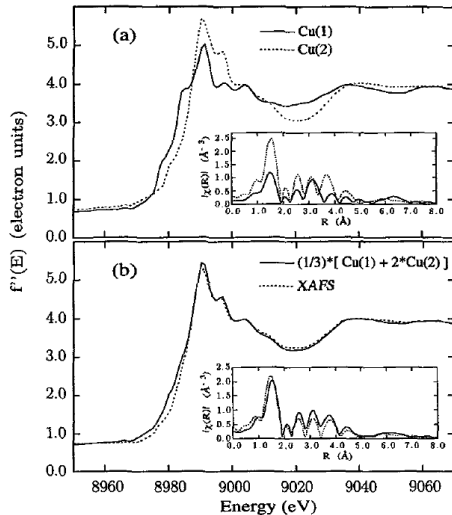
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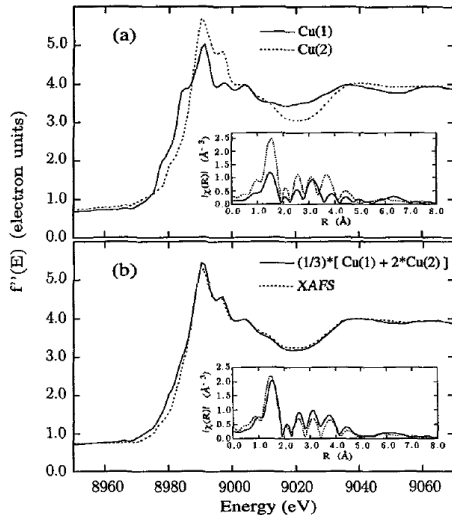
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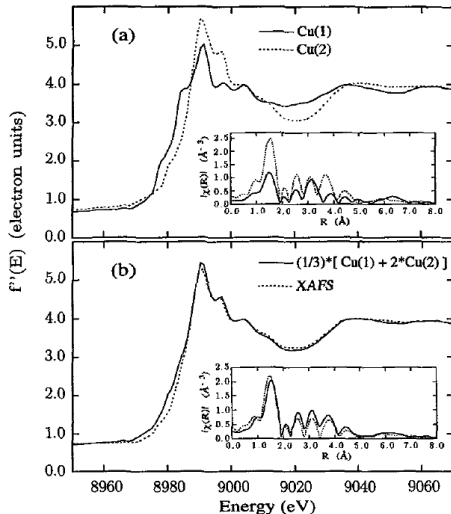
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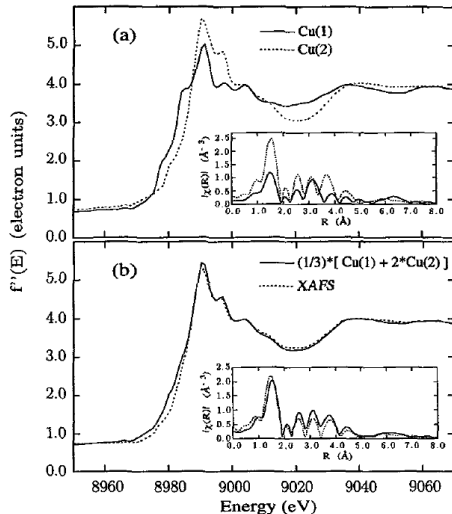


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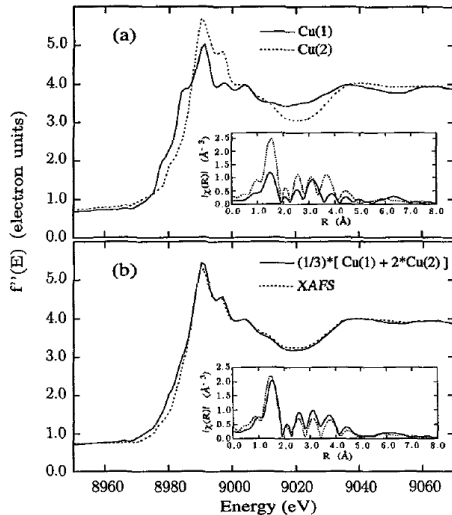
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## DAFS of maghemite $\gamma\text{-Fe}_2\text{O}_3$ shells

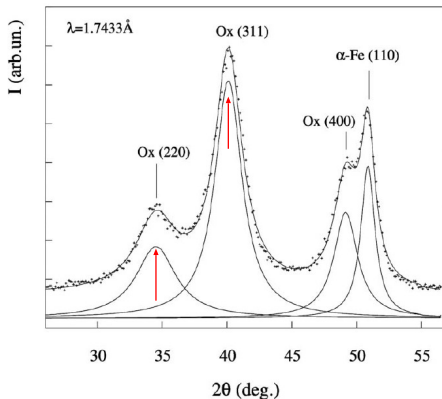
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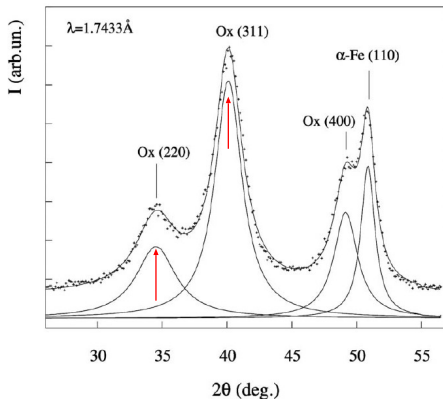


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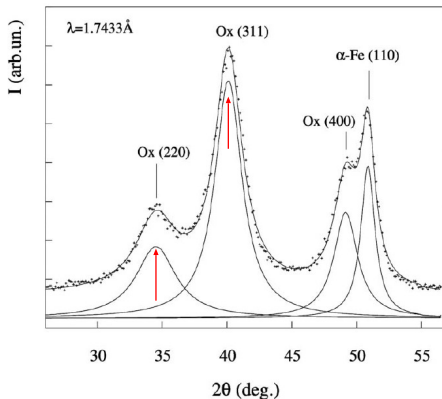
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DAFS on the powder samples has the potential to focus solely on the  $\gamma\text{-Fe}_2\text{O}_3$  to the exclusion of the metallic core by measuring the oscillations in the oxide (220) and (311) reflections



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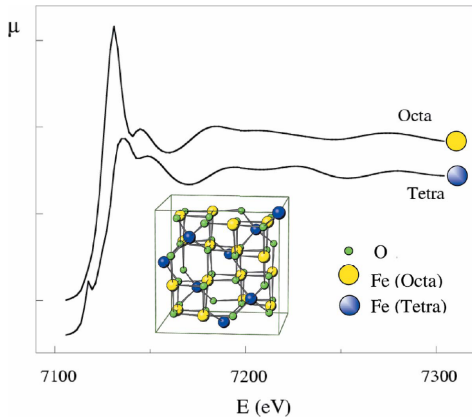
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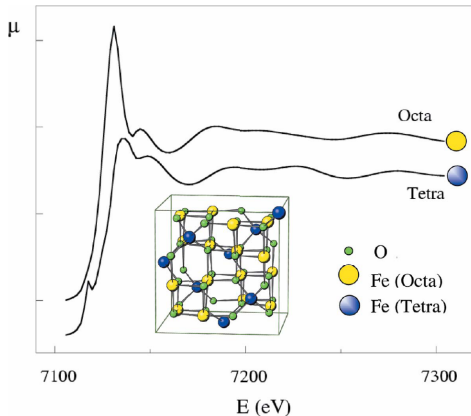


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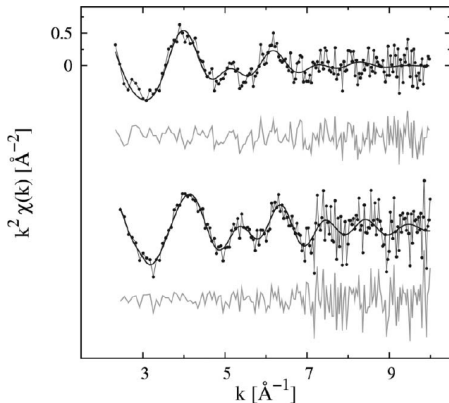
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The EXAFS fits of the two sites correspond closely to the nominal structure of maghemite with some observed oxygen vacancies



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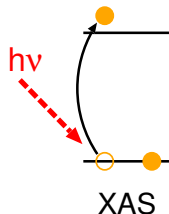
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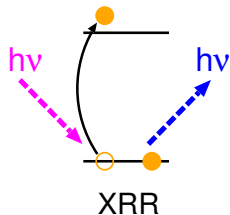
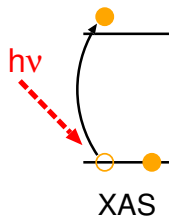
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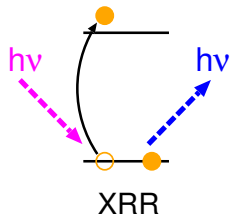
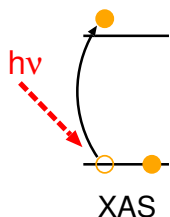


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X-ray Raman is a similar process which produces a photoelectron but is an inelastic scattering process with an outgoing photon of lower energy

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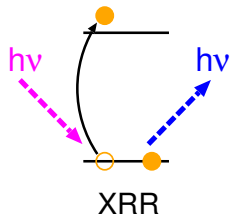
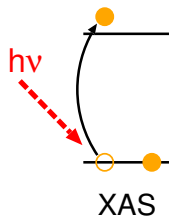
The x-ray absorption event consists of the absorption of a photon and production of a photoelectron

X-ray Raman is a similar process which produces a photoelectron but is an inelastic scattering process with an outgoing photon of lower energy

The incoming x-rays are high energy and the detector is set to measure outgoing x-rays which are at a fixed energy.

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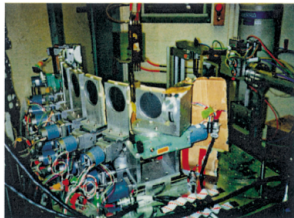
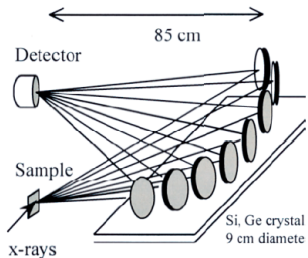


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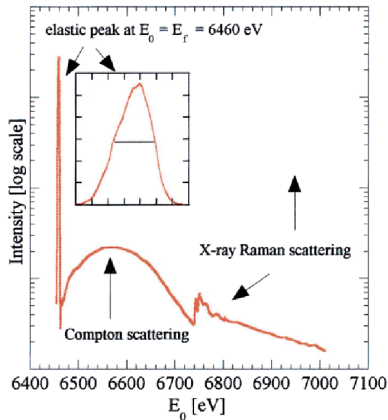
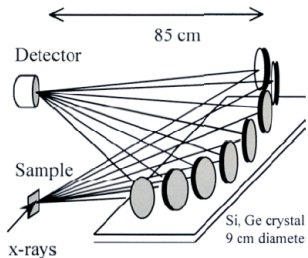
The incoming x-rays are high energy and the detector is set to measure outgoing x-rays which are at a fixed energy. The incoming energy is scanned and the processes detected depend on the difference in energy

# The XRR experiment



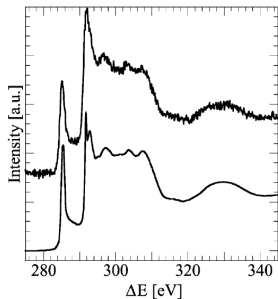
"Bulk-sensitive XAS characterization of light elements: from x-ray Raman scattering to x-ray Raman spectroscopy," U. Bergmann, P. Glatzel, and S. Cramer, *Microchem. J.* **71**, 221-230 (2002)

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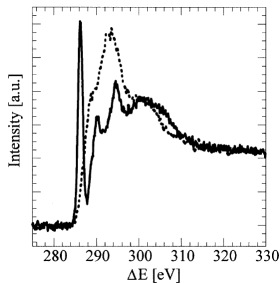
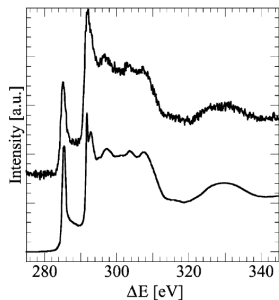
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## Comparison of XRR and XAS on graphite

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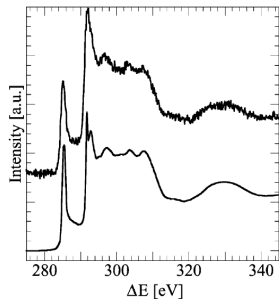
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Aromatic (solid) and  
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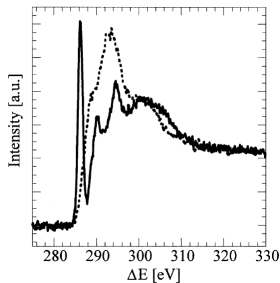
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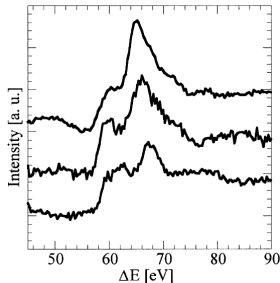
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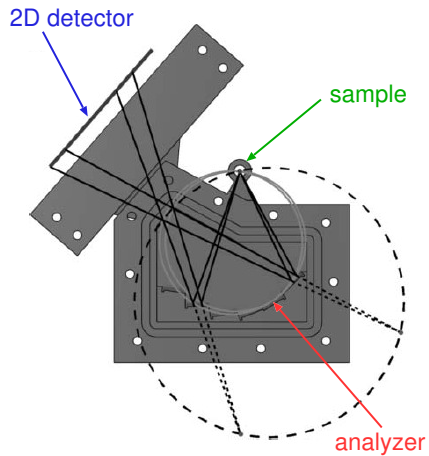
Aromatic (solid) and aliphatic (dashed) carbon K-edge x-ray Raman spectra



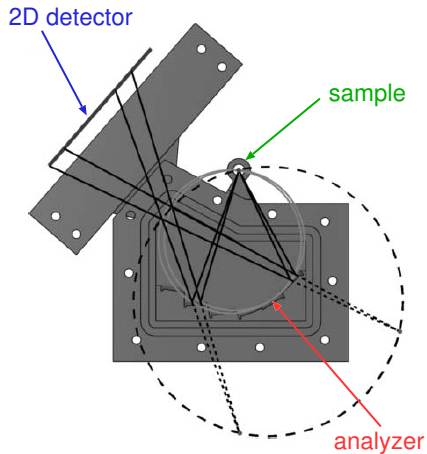
Li K-edge spectra for LiOH·H<sub>2</sub>O (top), Li<sub>2</sub>CO<sub>3</sub> (middle), and Li<sub>4</sub>SiO<sub>4</sub> (bottom).

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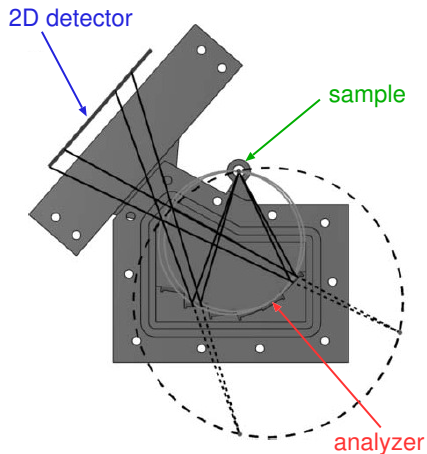


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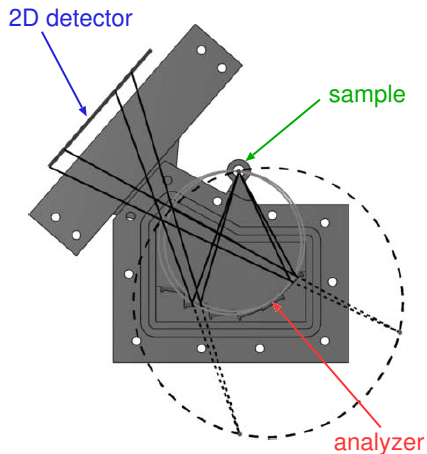
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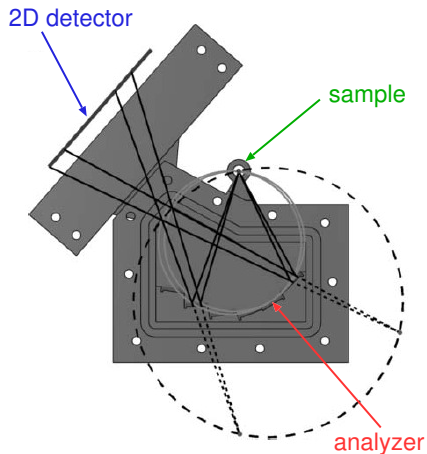


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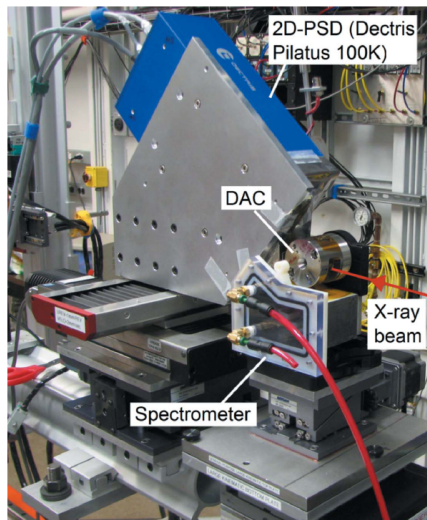
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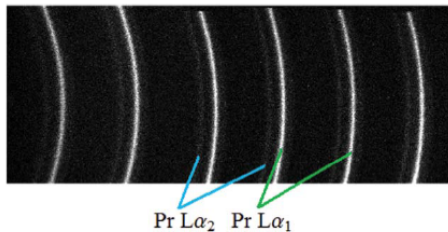
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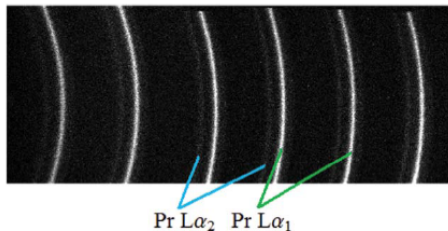
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# XES spectrometer performance



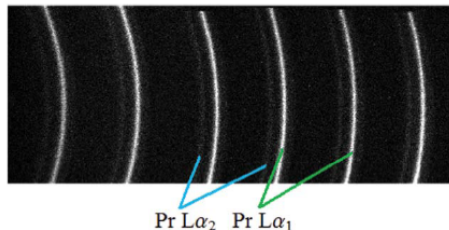


## XES spectrometer performance



The Pr-containing sample is placed in a diamond anvil high pressure cell (DAC) and illuminated with energies near the Pr  $L_3$  edge (5964 eV)

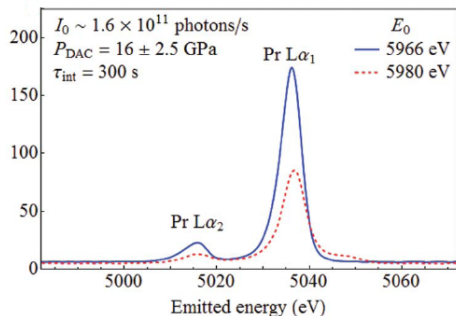
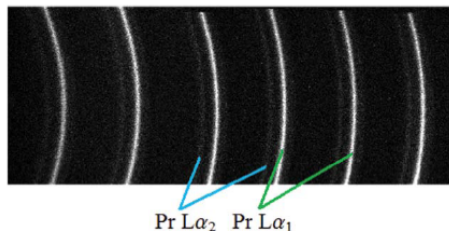
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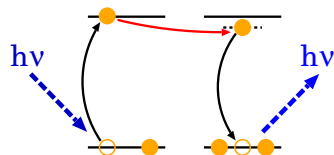


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after integration, the two peaks can be seen to change relative intensities and even position as a function of the incident energy: just at the absorption edge and 14 eV higher

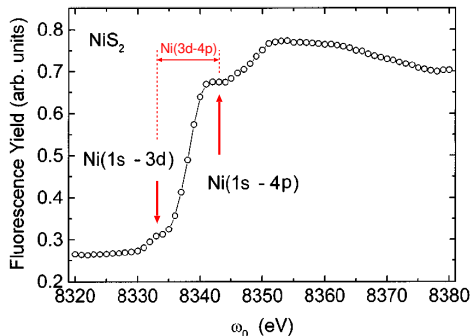
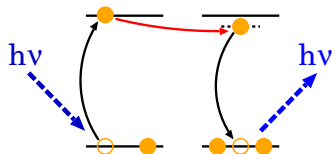
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"Resonant inelastic x-ray scattering," P.M. Platzman and E.D. Isaacs, *Phys. Rev. B* **57**, 11108 (1998)

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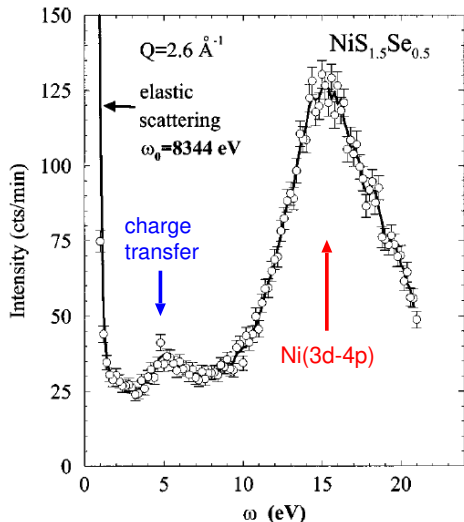


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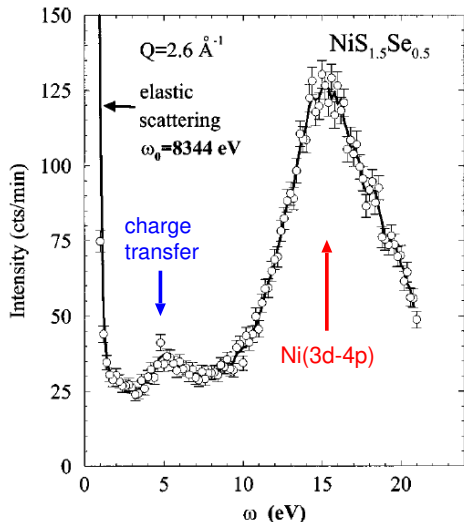


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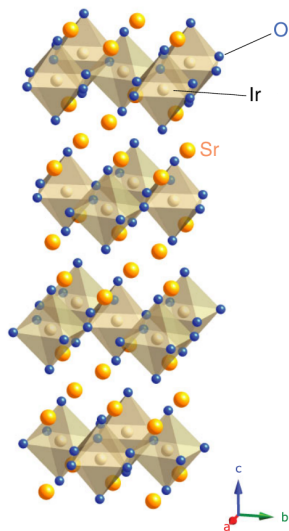
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The RIXS technique can also be used to study a wide variety of electronic excitations as a function of momentum transfer

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# Spin-orbit Mott state in $\text{Sr}_2\text{IrO}_4$

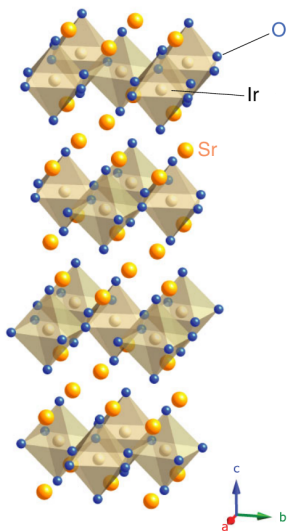


$\text{Sr}_2\text{IrO}_4$  is a structural analog to the high  $T_C$  superconductor  $\text{La}_{(2-x)}\text{Sr}_x\text{CuO}_4$  and to the Fermi liquid metal  $\text{Sr}_2\text{RhO}_4$

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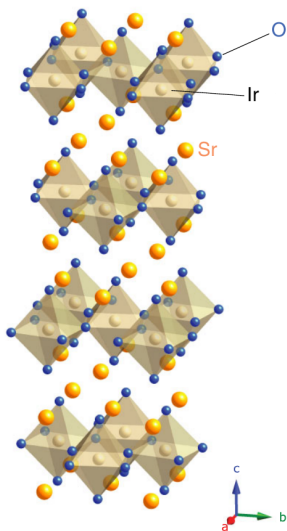


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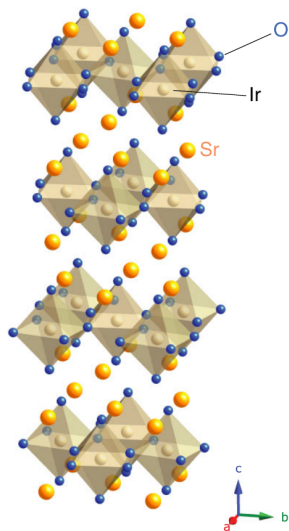
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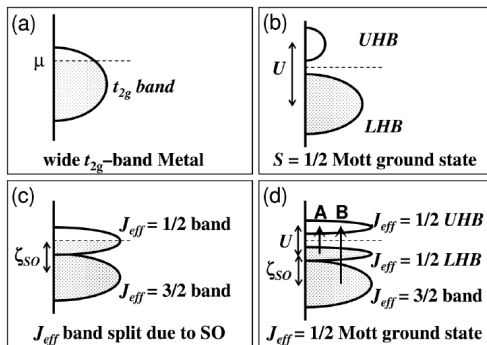
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Starting in 2008, a group from South Korea grew a single crystal of  $\text{Sr}_2\text{IrO}_4$  and published a series of papers that studied its electronic states using resonant x-ray techniques among others

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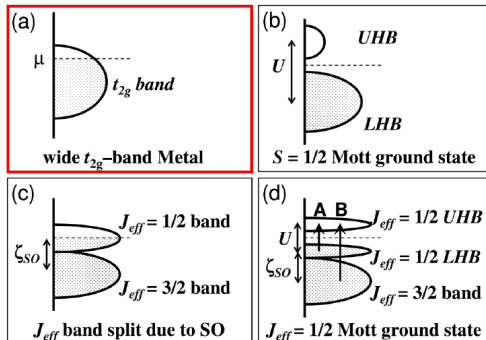
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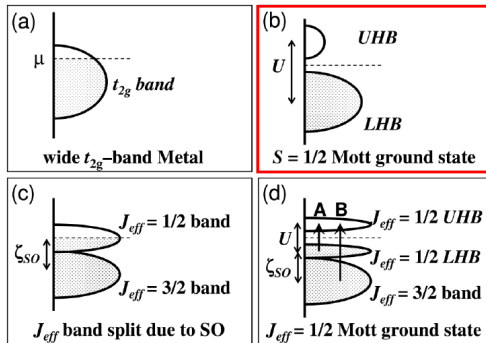


(a) the unperturbed  $t_{2g}$  triplet has one empty state

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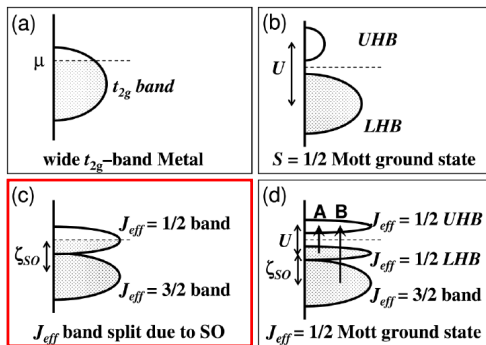
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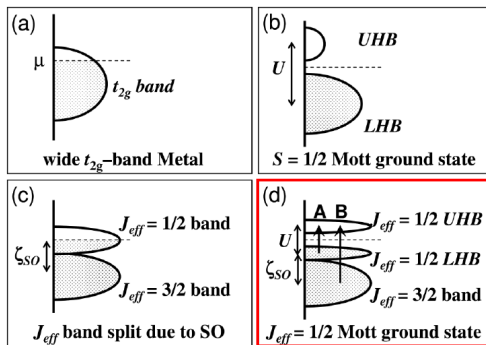
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(d) the Hubbard  $U$  splits the  $J_{eff} = \frac{1}{2}$  into an upper and lower band, creating an insulator

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## Resonant x-ray scattering on $\text{Sr}_2\text{IrO}_4$

Below 240K,  $\text{Sr}_2\text{IrO}_4$  orders antiferromagnetically and with a modest applied field ( $H > 0.3$  T), becomes weakly ferromagnetic

"Phase-sensitive observation of a spin-orbital Mott state in  $\text{Sr}_2\text{IrO}_4$ ," B.J. Kim, H. Osumi, T. Komesu, S. Sakai, T. Morita, H. Tagaki, and T. Arima, *Science* **323**, 1329-1332 (2009).

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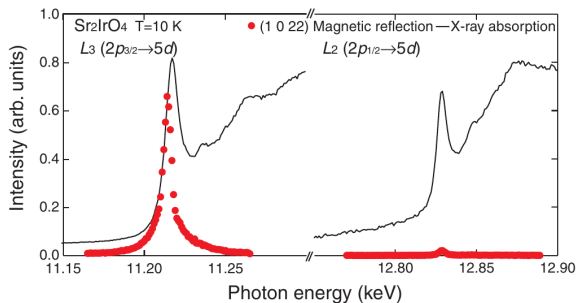
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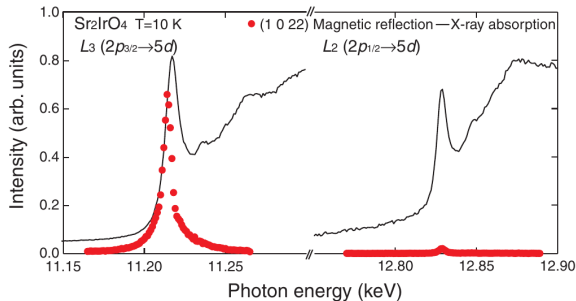
The (1 0 2 2) magnetic reflection (red circles) is enhanced at the L<sub>3</sub> edge but not at the L<sub>2</sub> edge due to interference effects

"Phase-sensitive observation of a spin-orbital Mott state in Sr<sub>2</sub>IrO<sub>4</sub>," B.J. Kim, H. Osumi, T. Komesu, S. Sakai, T. Morita, H. Tagaki, and T. Arima, *Science* **323**, 1329-1332 (2009).

# Resonant x-ray scattering on $\text{Sr}_2\text{IrO}_4$

Below 240K,  $\text{Sr}_2\text{IrO}_4$  orders antiferromagnetically and with a modest applied field ( $H > 0.3$  T), becomes weakly ferromagnetic

Using resonant x-ray scattering, at the  $L_3$  edge of iridium, it is possible to excite the empty upper Hubbard  $J_{\text{eff}} = \frac{1}{2}$  band and enhance the magnetic x-ray scattering

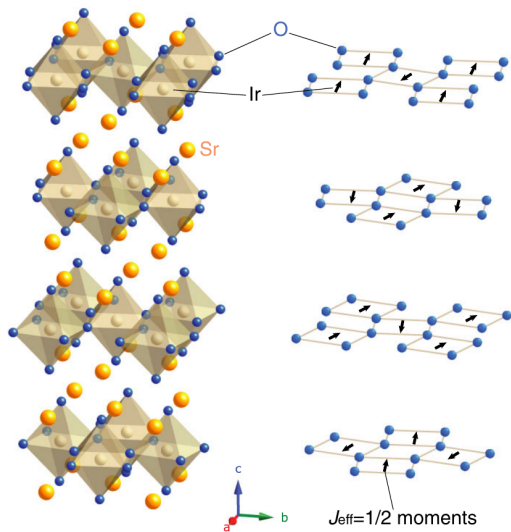


The  $(1\ 0\ 2\ 2)$  magnetic reflection (red circles) is enhanced at the  $L_3$  edge but not at the  $L_2$  edge due to interference effects

This enhancement by a factor of  $100\times$  permits a detailed study of the magnetic structure

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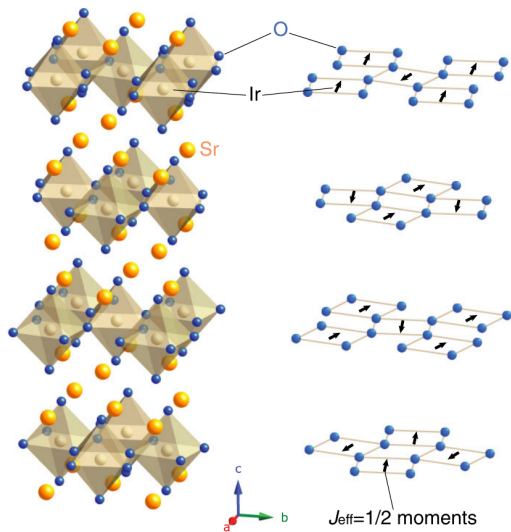
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The insulating antiferromagnetic state of  $\text{Sr}_2\text{IrO}_4$  has canted magnetic moments oriented in the Ir-O planes

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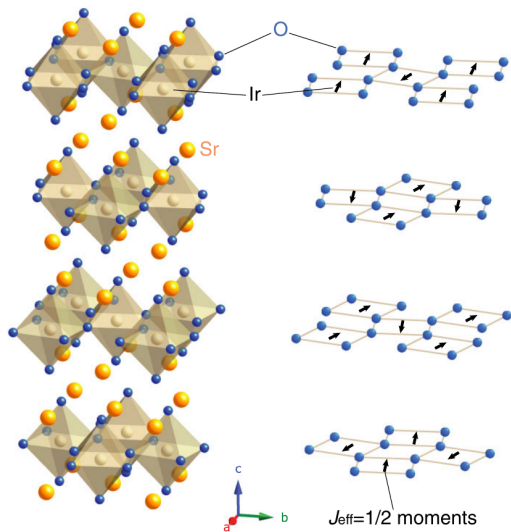


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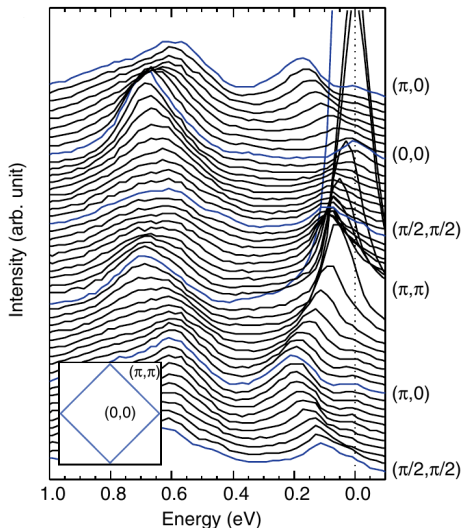
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Energy loss spectra were measured as a function of  $q$  at the Ir L<sub>3</sub> edge

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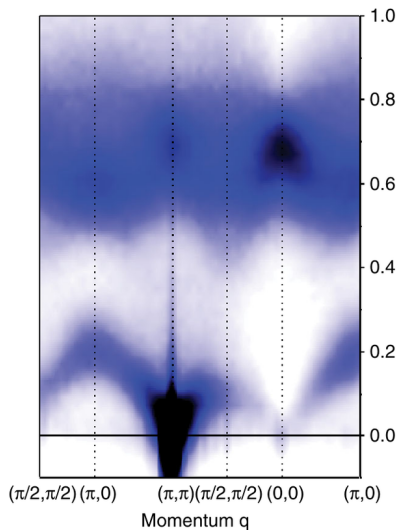


The Bragg peak is clear at energy loss of zero in the  $(\pi, \pi)$  direction

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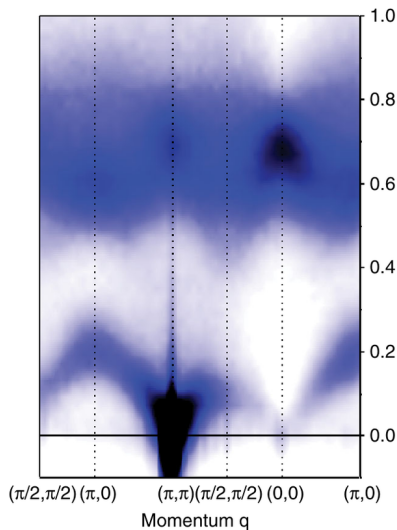


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When lines of constant energy loss are taken through the individual scans and combined to give a contour plot of the excitations the different bands and their shapes as a function of momentum are visible

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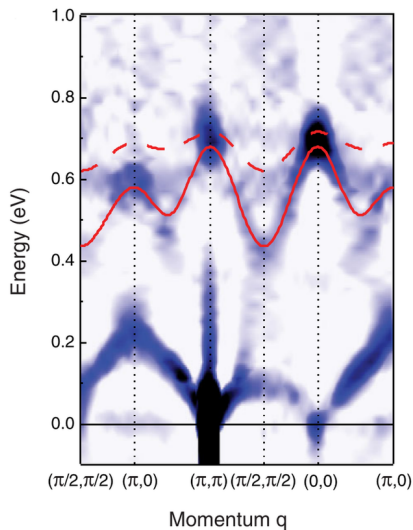
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Taking the second derivative enhances the band structure further

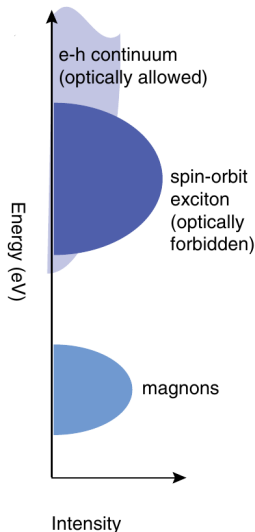
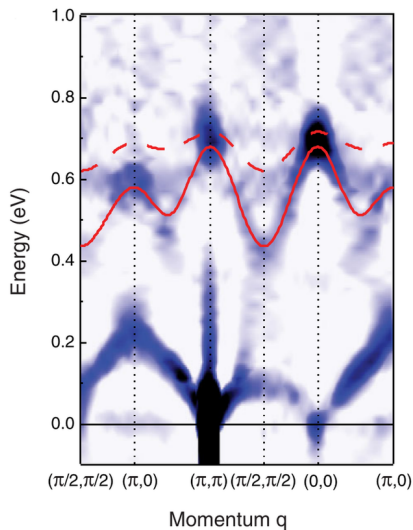
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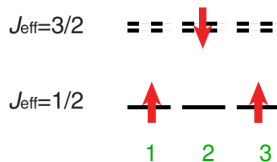
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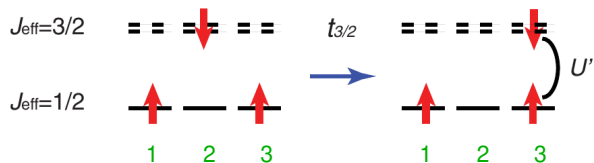


left – a exciton created by RIXS leaves a hole the  $J_{\text{eff}} = \frac{3}{2}$  state on site 2

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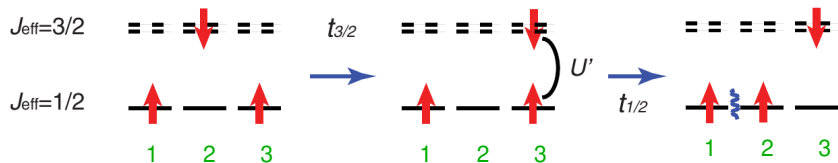
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**center** – the **hole** in the  $J_{\text{eff}} = \frac{3}{2}$  state hops to site **3**

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**right** – the **hole** in the  $J_{\text{eff}} = \frac{1}{2}$  state on site **3** hops to site **2**, completing the exciton hopping process and creating a **magnon**

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