Controlling the Electronic and Magnetic Structure of Fe-doped Cobalt Ferrite

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Fe-doped $CoFe_2O_4$ – $Co_{1-x}Fe_{2+x}O_4$

Inverse spinel crystal structure

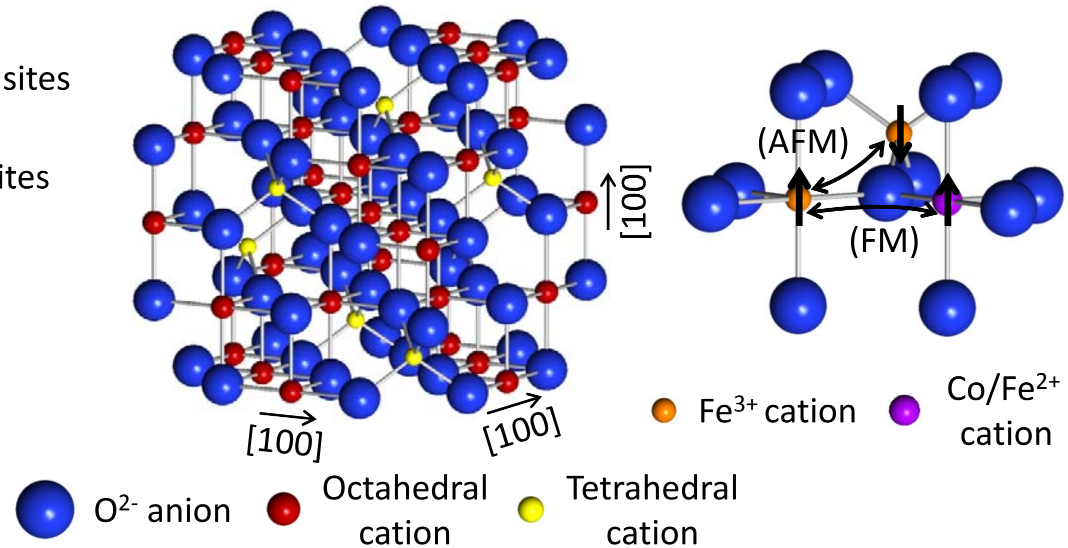
- Fe^{3+} cations mixed between octahedral sites and tetrahedral sites
- Co/Fe^{2+} cations located on octahedral sites

Ferrimagnetic

- Octahedral and tetrahedral sites are antiferromagnetically aligned
- T_c ~ 800 K

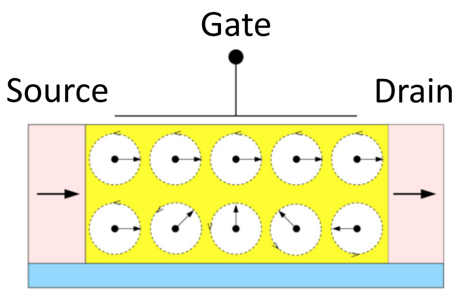
Mobile charges

- Fe^{2+} cation has loosely bound electron that can hop to Fe^{3+} cations



Why do we want to control the electronic and magnetic properties?

Spintronics - SpinFET



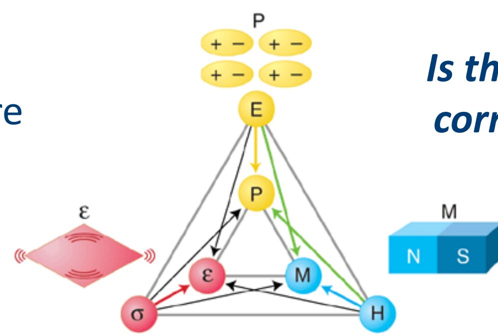
I. Zutic et al., Rev. Mod. Phys. **76**, 323 (2004)

Source and drain require

- Large spin polarization
- Small conductivity mismatch with the semiconductor

Can we tune the conductivity of $Co_{1-x}Fe_{2+x}O_4$?

Multiferroics



Is the magnetic structure correlated with changes in the electronic structure?

N. A. Spaldin and M. Fiebig, Science **76**, 391 (2005)
W. Eerenstein et al., Nature **442**, 759 (2006)

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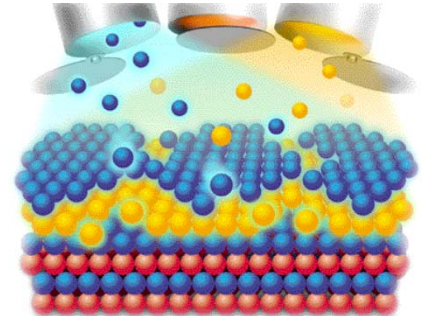
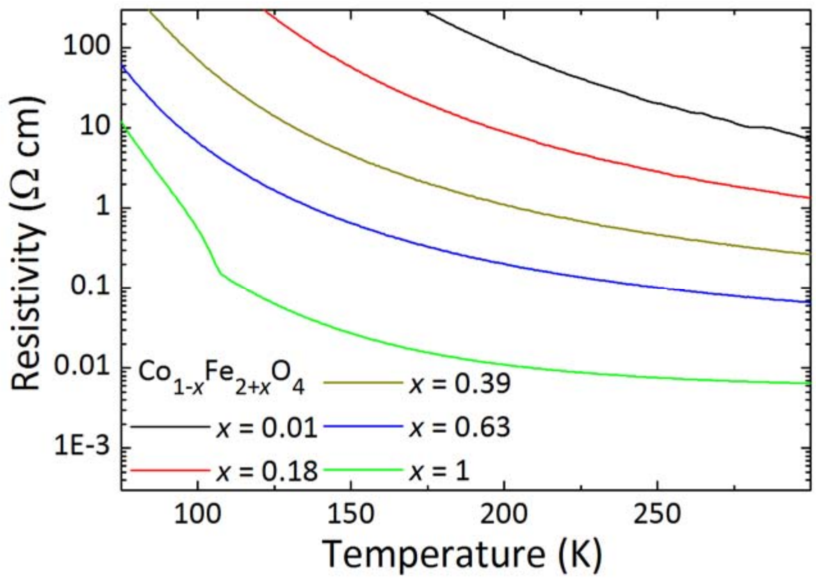
MBE growth and macroscopic properties

Oxide-MBE is a growth technique in which ***crystalline*** thin films are grown by combining evaporated metal atoms with atomic or molecular oxygen flux onto a single-crystal substrate in ultra-high vacuum (UHV)



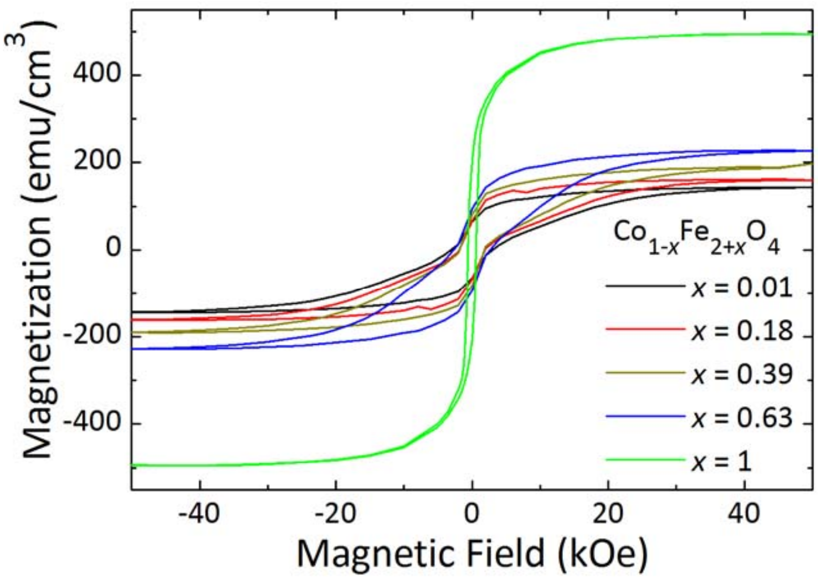
Epitaxial $Co_{1-x}Fe_{2+x}O_4$ thin films were grown with x ranging from 0 to 1 and thicknesses of ~ 20 nm

Electronic Properties



Smooth systematic changes in the resistivity occur with Fe doping

Magnetic Properties



Non-linear increase in the magnetization as Fe doping increases

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Synchrotron spectroscopy

X-ray Absorption (XAS)

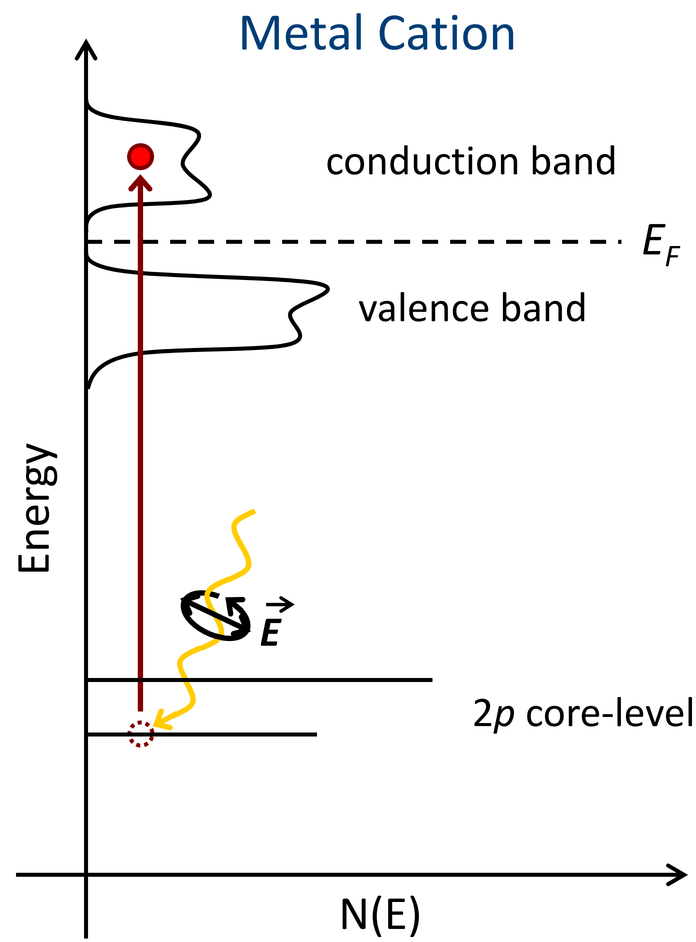
- Requires tunable x-ray source
- Measures multiplets – transitions between $2p^63d^n$ and $2p^53d^{n+1}$ configurations
- Data is modeled using CTM4XAS
  E. Stavitski and F. M F. de Groot, Micron **41**, 687 (2010)

X-ray Magnetic Linear Dichroism (XMLD)

- Uses linearly polarized x-rays to probe unoccupied valence band orbital states
- Absorption only occurs if there are empty states in direction of ***E***
- Can observe characteristics such as anisotropic bonding or aligned magnetic state

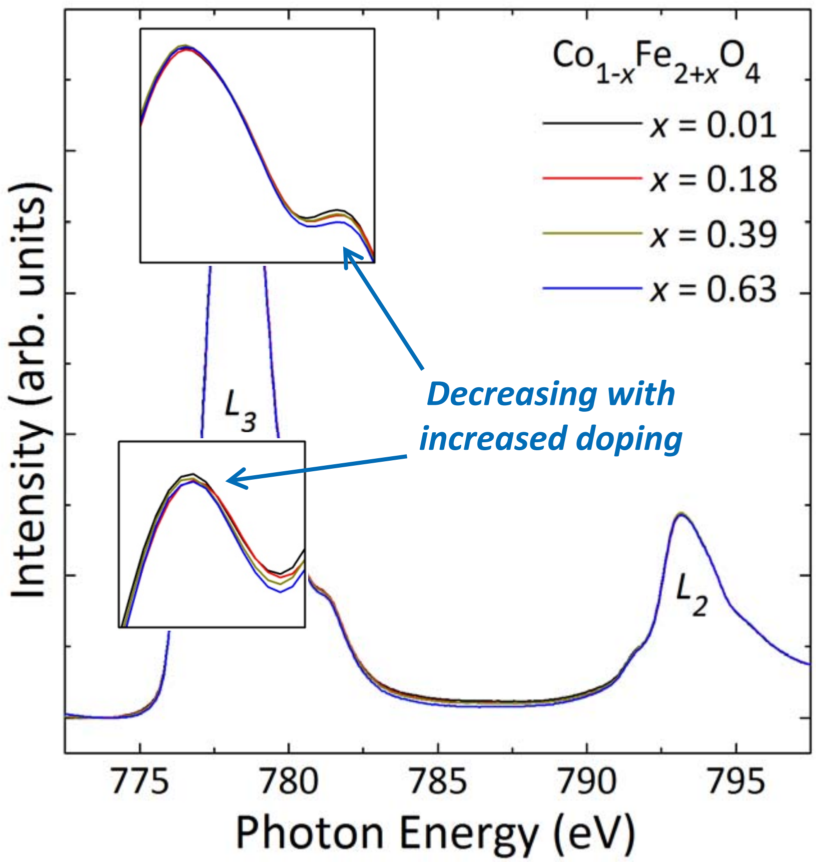
X-ray Magnetic Circular Dichroism (XMCD)

- Uses circularly polarized x-rays to probe spin and orbital moments
- Circularly polarized x-rays have angular momentum which is transferred to electron upon absorption
- Due to spin-orbit coupling, this momentum is transferred to both spin and orbital momentum of electron

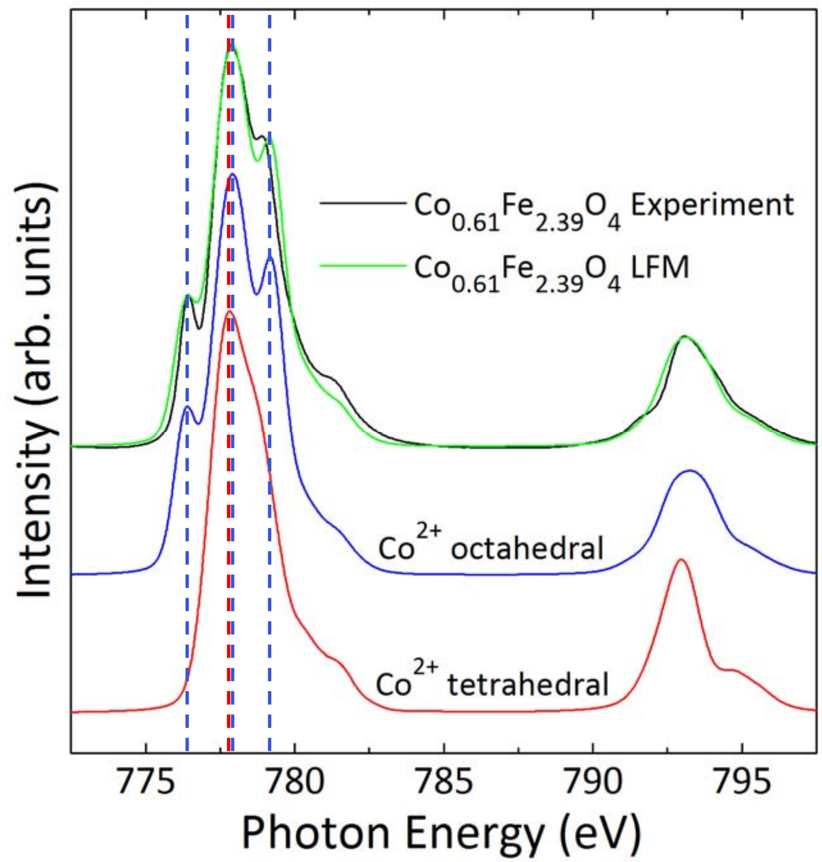


XAS spectra – Co $L_{2,3}$ comparison

Co $L_{2,3}$ Sample Comparison



LFM Calculation



Co^{2+} tetrahedral/octahedral ratio increases with increased doping → Fe^{2+} is preferentially substituting onto the octahedral sites

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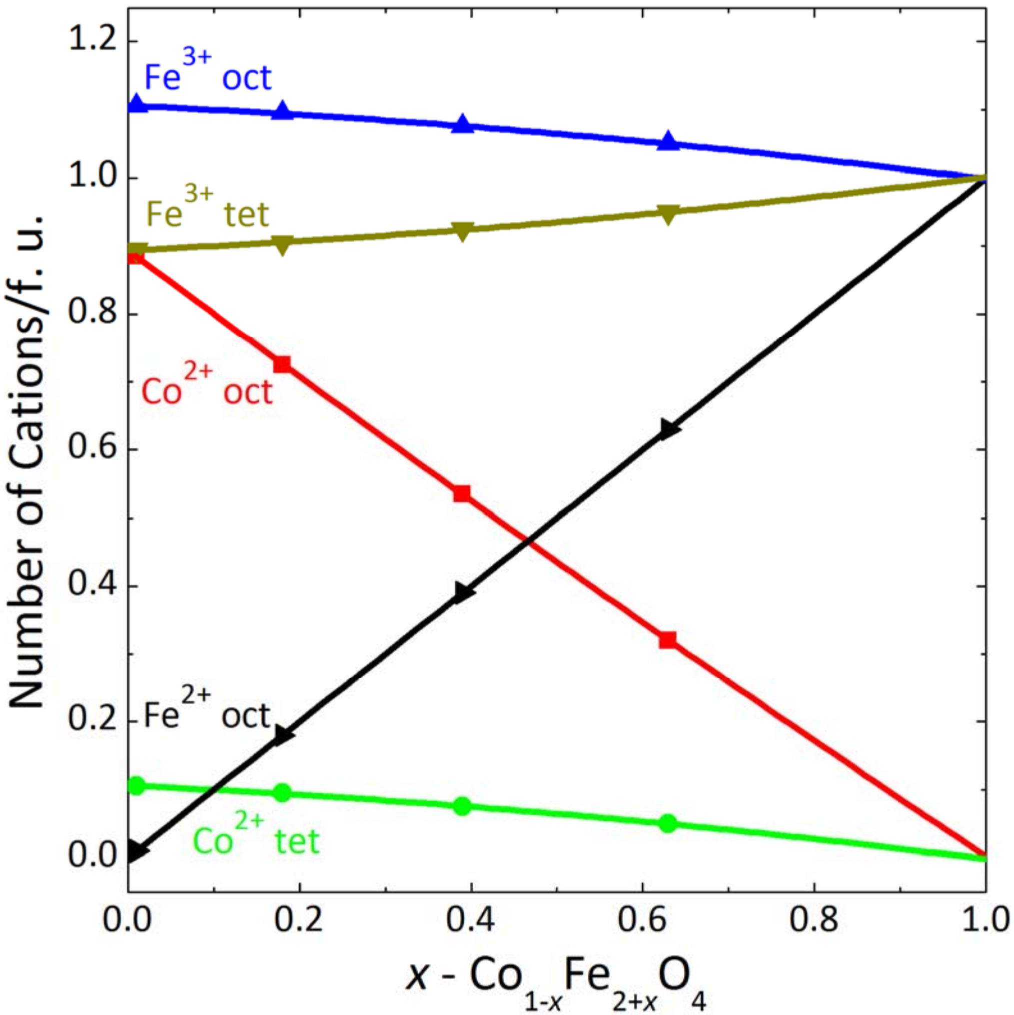
XAS – determining the site occupancy



Fe^{2+} preferentially substitutes for Co^{2+} octahedral cations

- Leads to increase in conductivity

To compensate for Fe^{2+} only residing on octahedral sites, more Fe^{3+} now reside on tetrahedral sites

- Causes crystal structure to become more nearly inverse spinel

Extrapolating data out to $x = 1$ shows that crystal structure becomes fully inverse spinel, as is known for magnetite

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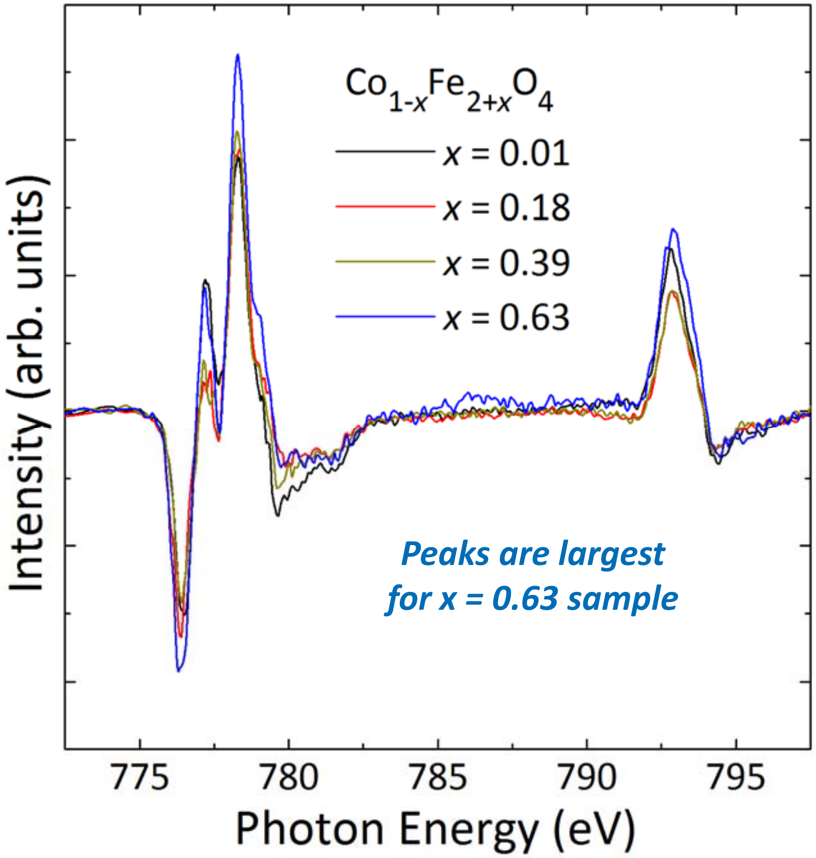
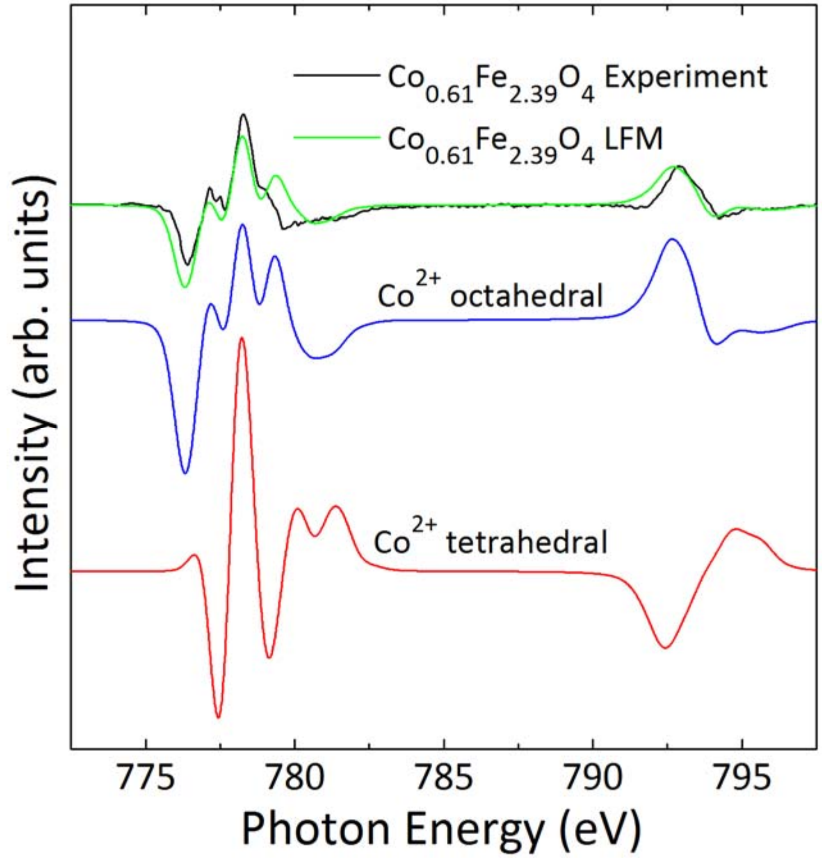
J. A. Moyer et al., Phys. Rev. B **83**, 035121 (2011)

XMLD spectra – Co $L_{2,3}$ comparison

Co $L_{2,3}$ Sample Comparison



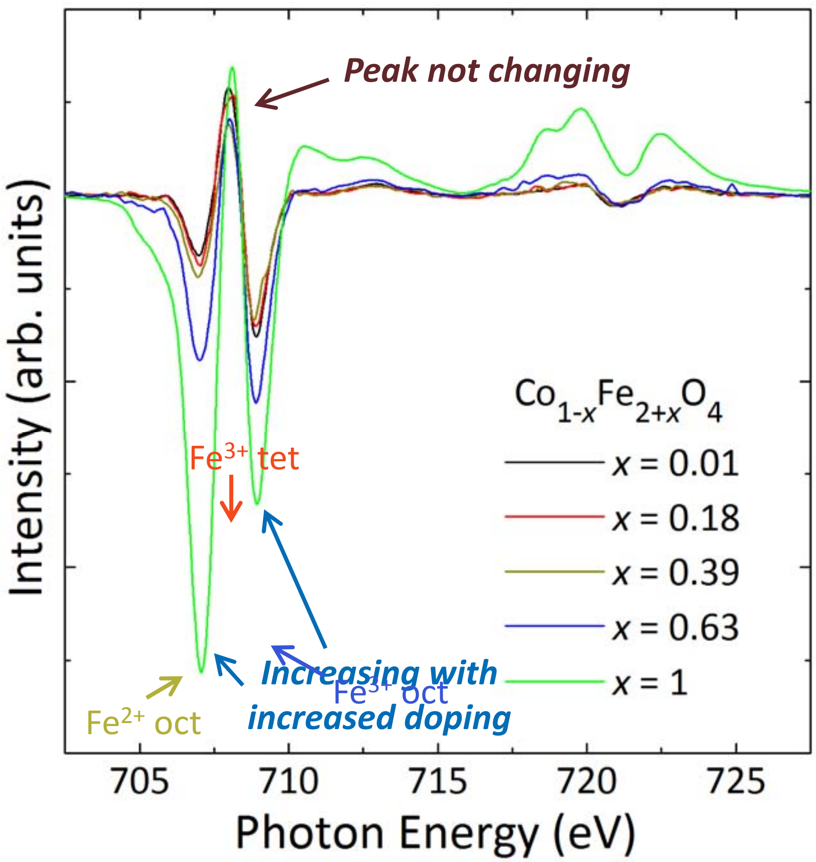
LFM Calculation



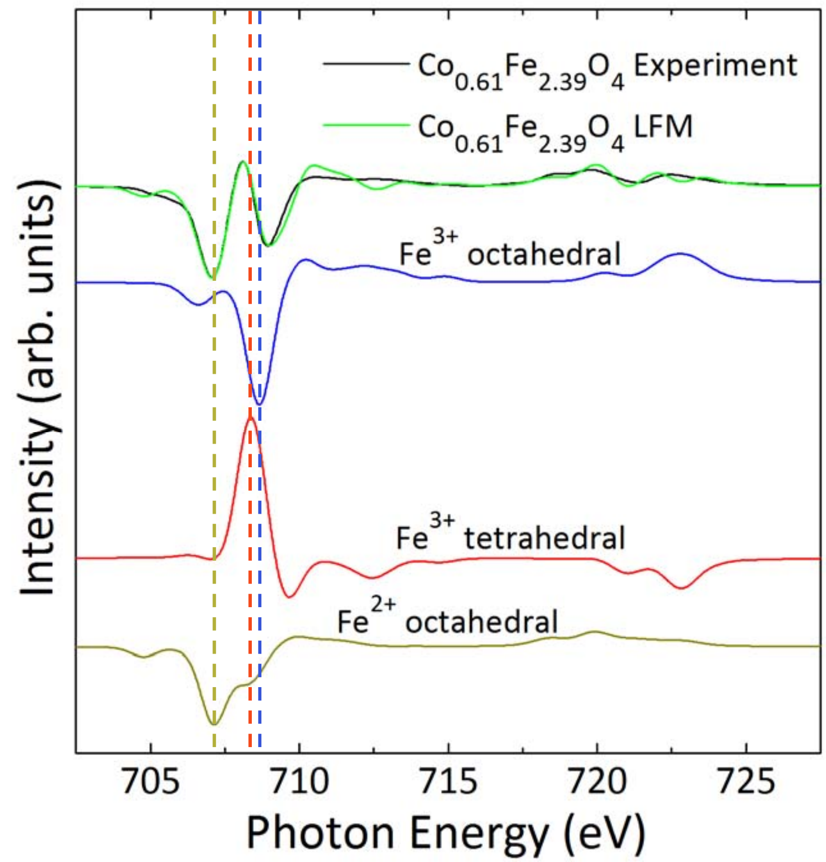
Co^{2+} spins are becoming more aligned as x increases, especially for x = 0.63 sample → Spin canting plays a role in understanding reduced magnetic moment

XMCD spectra – Fe $L_{2,3}$ comparison

Fe $L_{2,3}$ Sample Comparison



LFM Calculation



Magnetic moments of Fe^{3+} octahedral cations increase with increased doping, but this behavior is not duplicated with the Fe^{3+} tetrahedral cations

Fe^{2+} octahedral magnetic moments remain relatively constant for lightly doped films, but increase markedly for $x = 0.63$ and $x = 1$

Can not explain this behavior with the ferromagnetic with spin canting

In agreement with the spin canting model suggested by the XMLD measurements

→ Need to include spin alignments

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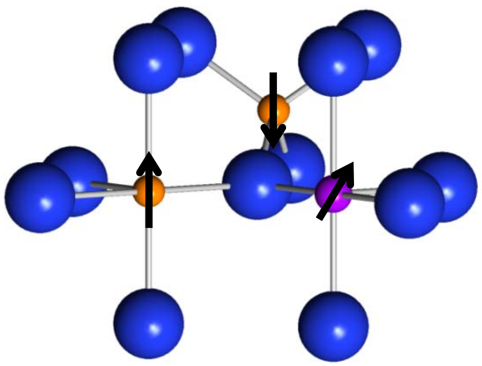
Model of magnetism in Fe-doped $CoFe_2O_4$

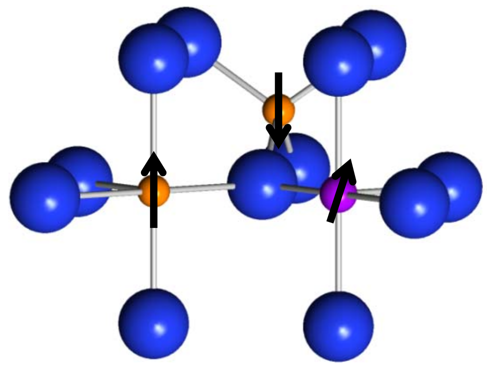
The magnetism of Fe-doped $CoFe_2O_4$ is controlled by two factors:

Spin canting due to spin frustration

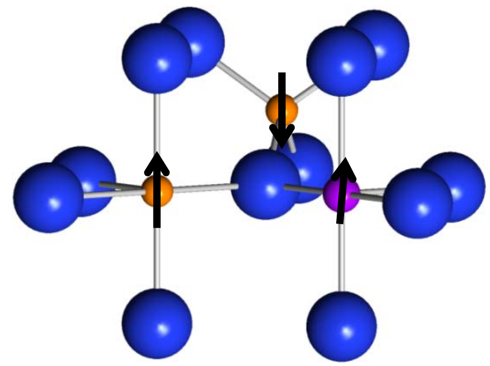
$Co_{0.82}Fe_{2.18}O_4$



$Co_{0.37}Fe_{2.63}O_4$



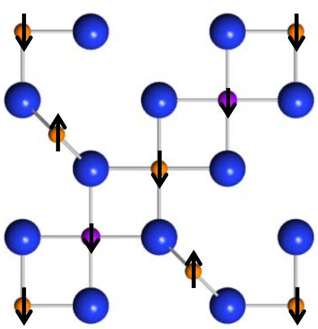
Fe_3O_4



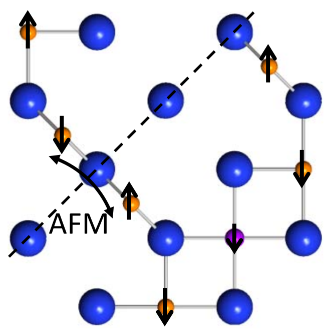
Antiferromagnetic spin alignments

Anti-Phase Boundaries

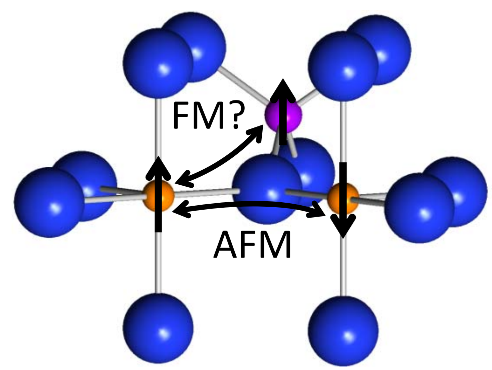
No boundary



Anti-phase boundary



Partially Inverse Spinel Crystal Structure



Fe^{3+} cation   Co/Fe^{2+} cation

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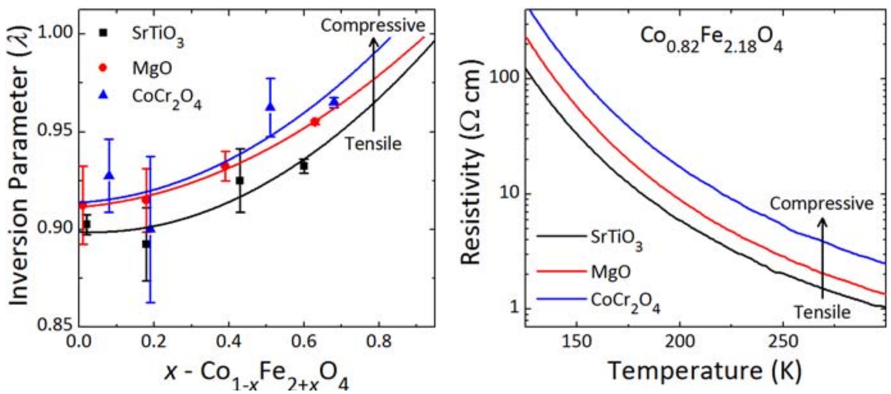
J. A. Moyer et al., Phys. Rev. B **84**, 054447 (2011)

Further control with strain and thickness

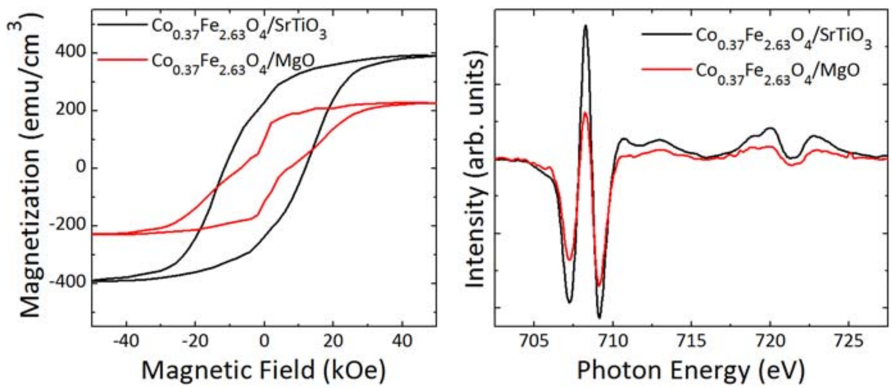
Strain effects on electronic structure



Strain leads to changes in cation site occupancies that are correlated to changes in resistivity

J. A. Moyer et al., Appl. Phys. Lett. **101**, 021907 (2012)

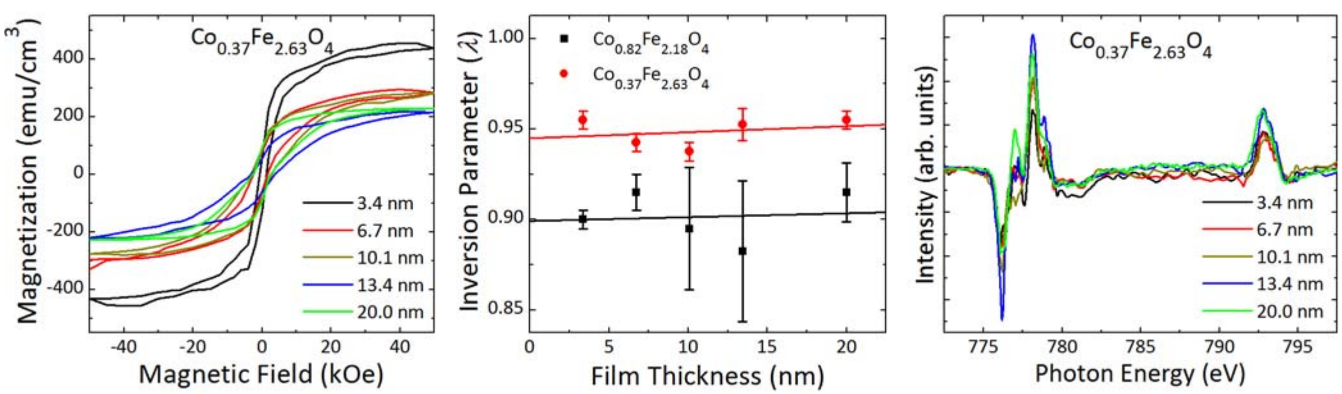
Strain effects on magnetic structure



Increased strain leads to increased moments due to decrease in anti-phase boundary density

J. A. Moyer et al., under review (2013)

Thickness effects on magnetic structure



Increase in saturation magnetization with film thickness is not due to change in site occupancies but a transition to a superparamagnetic state

J. A. Moyer et al., Phys. Rev. B **86**, 174404 (2012)

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Conclusions

- Electronic and magnetic structure of MBE grown Fe-doped $CoFe_2O_4$ is investigated with soft x-ray synchrotron spectroscopies
- Conductivity increases systematically with Fe doping
  - Doped Fe states are Fe^{2+} octahedral cations and have a loosely bound electron that can hop to Fe^{3+} octahedral cations
  - Allows for precise tailoring of its conductivity, a key component for incorporation in spintronic devices
- Magnetic moment increases non-linearly with the Fe doping level
  - Due to a decrease in the spin canting among the divalent cations and a decrease in the anti-ferromagnetic alignments among the trivalent cations
  - Large variation in magnetic moment with doping makes this material promising for use in charge mediated multiferroic devices
- Variations in epitaxial strain lead to changes in the inversion parameter, which is correlated with changes in the resistivity
- Increase in epitaxial strain leads to increases in magnetic moments, possibly due to a reduction in the density of anti-phase boundaries
- Decrease in film thickness results in an increase in magnetic moment
  - Not due to changes in the inversion parameter
  - Accompanied by a decrease in magnetic anisotropy and a likely transition to a superparamagnetic state

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