UCDAVIS

Spectroscopic and Nuclear Magnetic Resonance Studies of Screening in Compressed Novel Magnets: Rare Earth and Fe-based Compounds

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1. Overview- High Pressure and Strongly Correlated Electrons
2. NMR Relaxation and AF Order Near a Quantum Critical Point
3. Spin-Orbit Coupling and Strong Correlations in Osmate Double Perovskites
4. Resonant Inelastic Xray Scattering: Ce $\rightarrow$ Pr
5. Al-27 NMR in a Diamond Anvil Cell

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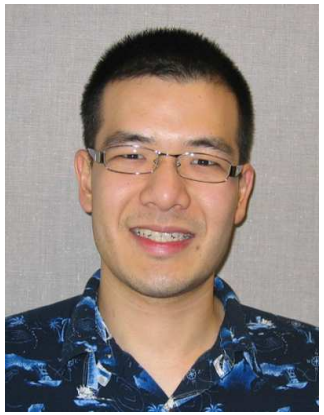

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1. Overview- High Pressure and Strongly Correlated Electrons

Interactions between electrons are origin of many interesting quantum phases

- Ferromagnetism (F) and Antiferromagnetism (AF)
- Mott Insulators (MI)
- Charge Ordering (CO) - e.g. striped and nematic phases
- Superconductivity (SC)

Interplay between phases increasingly important in modern materials science.

- Cuprates and Iron-Pnictides have AF-MI parent compounds.
  Exhibit SC and CO when chemically doped.
- Ba_2NaOsO_6 Ferromagnetic Mott Insulator (this project)
- Heavy Fermion '115' systems
  AF, SC, even coexisting AF+SC phases (this project)

Pressure tunes the ratio of electron interaction to kinetic energies.

Knob to go from one quantum phase to another.

2. NMR Relaxation and AF Order Near a Quantum Critical Point

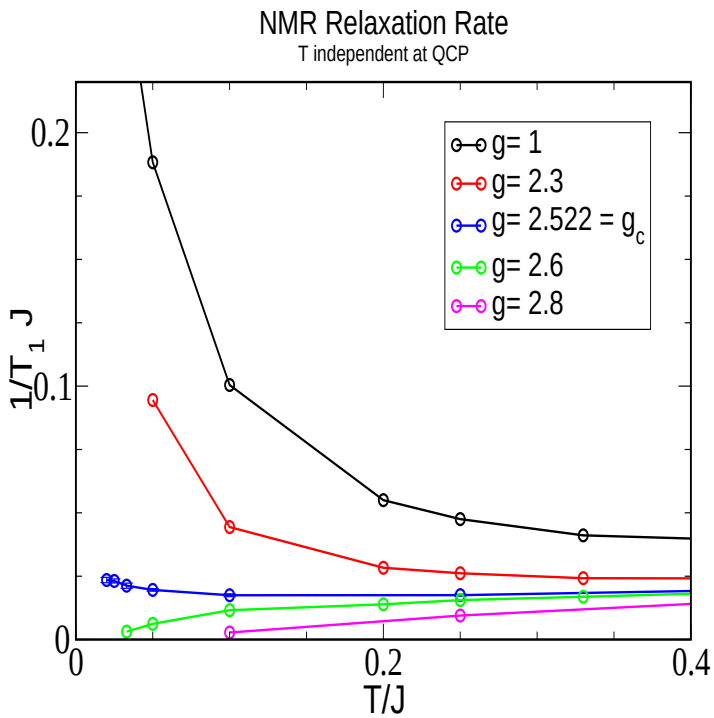
Quantum Monte Carlo on Bilayer Heisenberg Hamiltonian

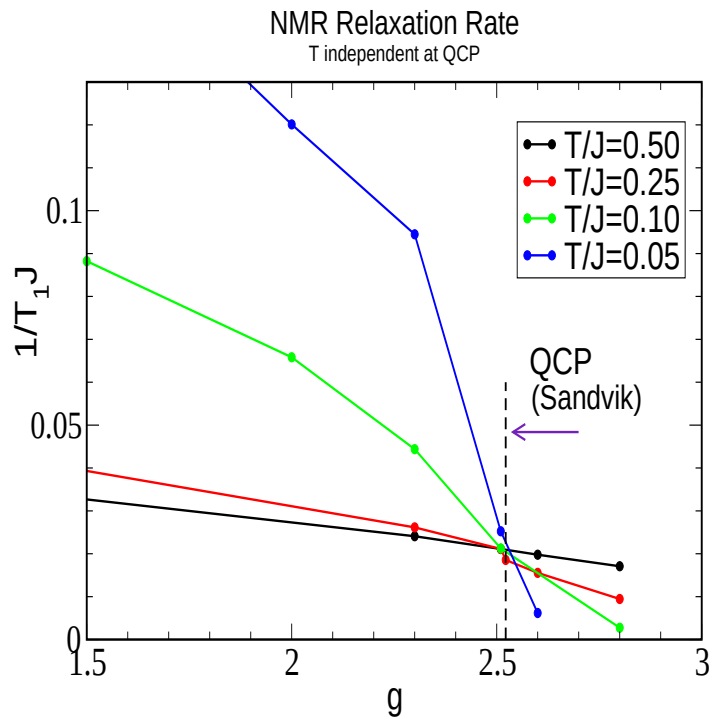
(Strong Coupling Limit of Periodic Anderson Model)

Quantum Critical Point:

Antiferromagnet to Singlet Transition with increasing Interlayer coupling g

[a] Pure System: NMR relaxation rate is temperature independent at QCP





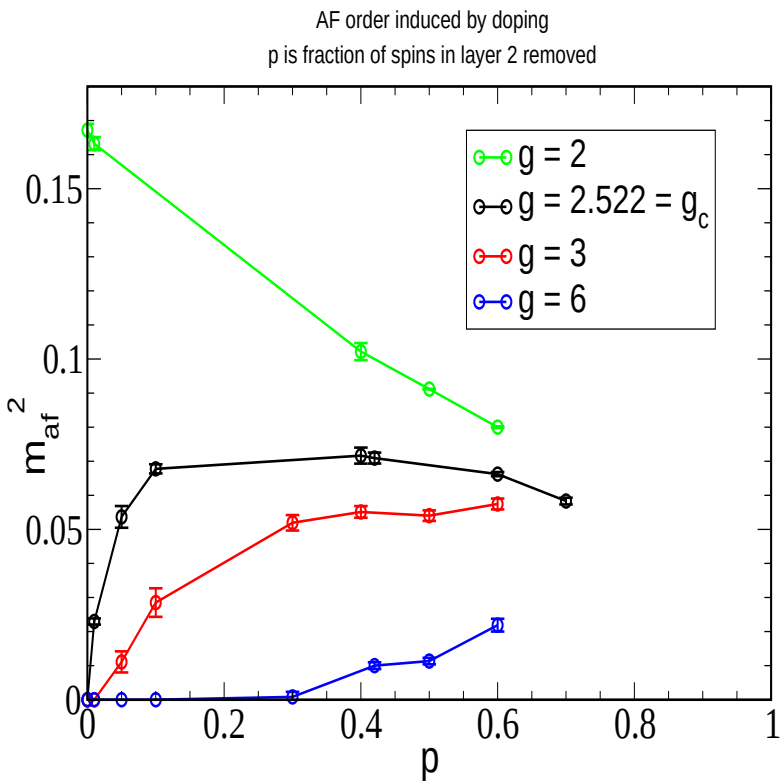
[b] Effect of impurities on AF order

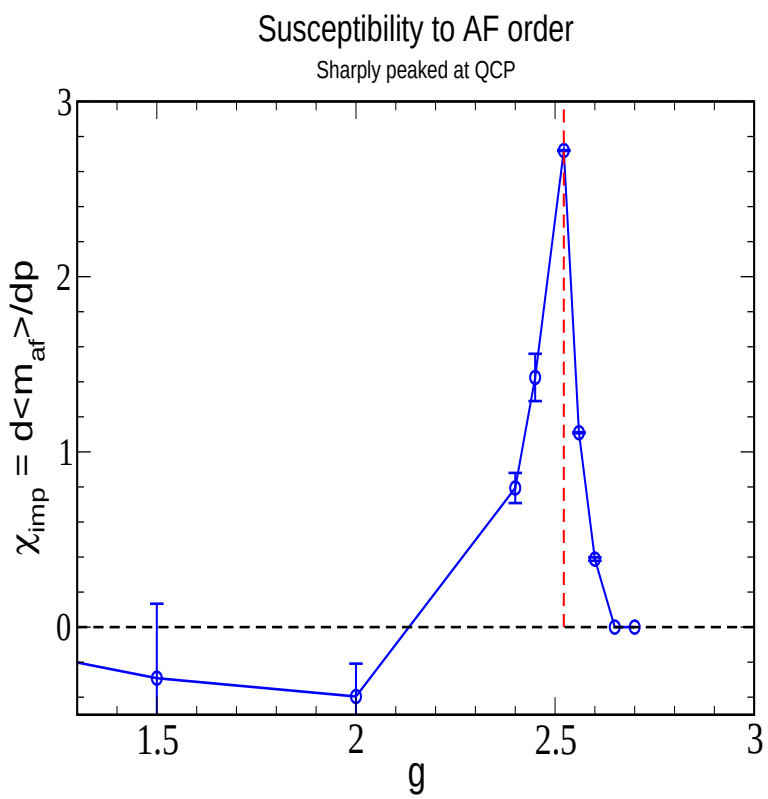
Dope second layer with fraction p of "impurities".

Spin in layer 1 lacks partner: break singlets. (La doping for Ce in $CeRhIn_5$).

Left: AF order is induced.

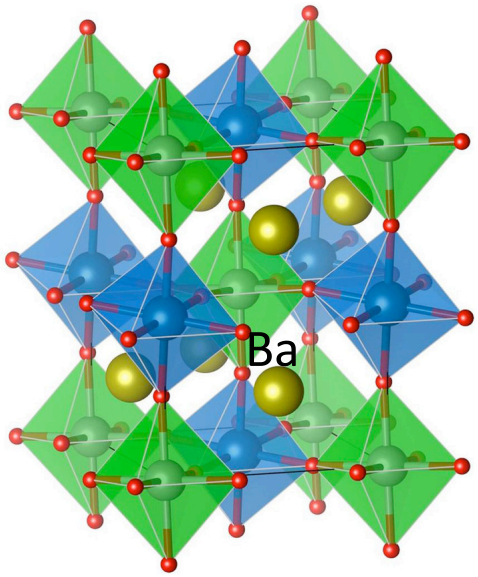
Right: Susceptibility has sharp peak near g_c:





Interplay of Spin-Orbit Coupling and Strong Correlation Effects: Three Osmate Double Perovskites Ba_2AOsO_6, A=Na,Ca,Y

S Gangopadhyay & W E Pickett, arXiv:1510.01719



AO_6

OsO_6

Why Osmium? Why not isovalent Fe?

- high formal valence: Os^{7+}, Os^{6+}, Os^{5+}

* high Z: large spin-orbit coupling

* BNOO has small total magnetic moment

* osmates are moderately strongly correlated

Why the double perovskite structure?

- simple, cubic structure, often undistorted

* large class with hundreds of members

* OsO_6 clusters are isolated; A is a vegatable

Some basic questions posed by presence of several competing energy scales

- Os $5d^1$ ion in BNOO is JT unstable, yet BNOO remains cubic. Why?

* BNOO is rare FM insulator; BCOO, BYOO are AFM insulators. Why?

* BNOO, BCOO are Dirac-Mott insulators: are large U + SOC necessary for gap?

* Pressure changes the energy scales, how will properties change?

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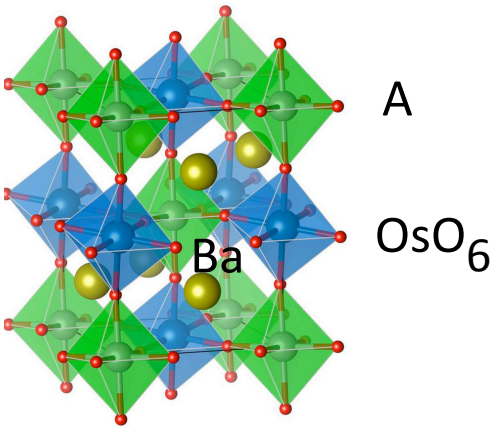

We propose that Ba_2NaOsO_6 is a canted AFM, not a true ferromagnetic insulator. This accounts for the reported small "FM" moment.

With strong SOC in which the ionic configuration has mixed orbital and mixed spin components, Interatomic exchange coupling $J_i * T_{i,j} * J_j$ is involved, tensor coupling $T_{i,j}$ instead of simple scalar exchange

Pi, Nanguneri, & Savrasov, PRL 2014,PRB 2014

Hence we do not study exchange coupling; compare these compounds only with FM alignment of spins.

Some basic questions posed by presence of several competing energy scales

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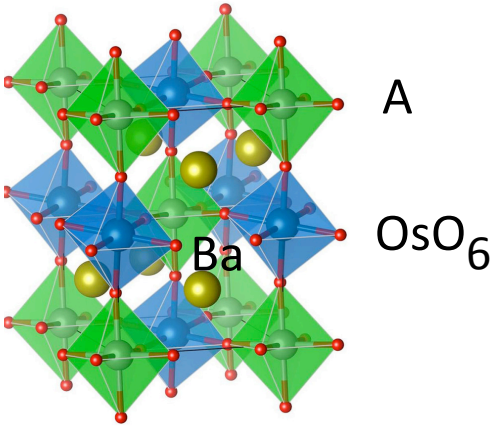
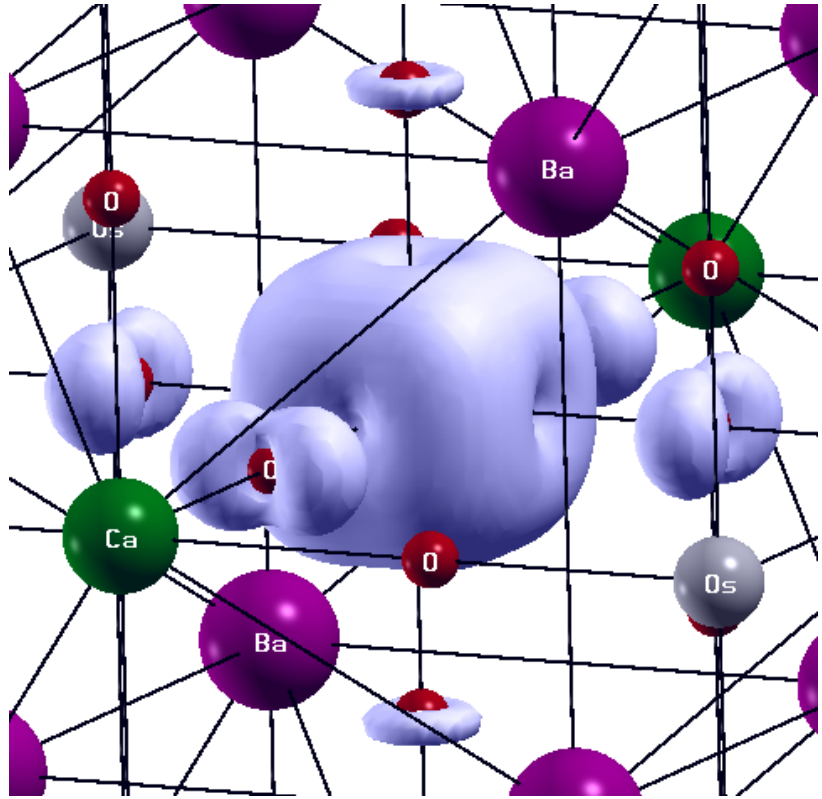
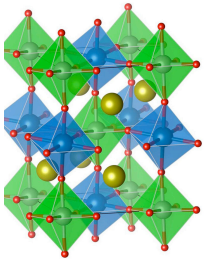


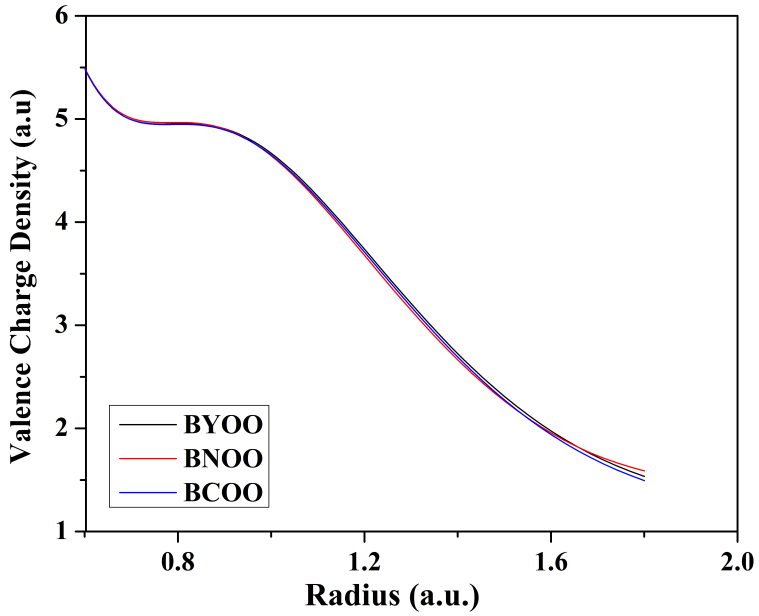


Spin density of the Os $5d^2$ ion in Ba_2CaOsO_6 ,(almost same as valence charge density), illustrating that the mixture of 5d orbitals (mixed with O 2p) is nearly cubic, destroying the tendency toward Jahn-Teller distortion hence remaining cubic. This is a consequence of strong spin-orbit coupling: mixing of orbitals by coupling to spin.

Interplay of Spin-Orbit Coupling and Strong Correlation Effects: Three Osmate Double Perovskites Ba_2AOsO_6, A=Na,Ca,Y



In several TM oxides we have found that ions with different formal valences have the same valence charge density. Then what does formal valence reflect?



Radial charge densities (outside the core) of the Os ion in the d^1, d^2, and d^3 configurations of Ba_2AOsO_6.
Note that they are indistinguishable.

Startling, but true. "Formal valence" is a property of an ion and its environment. Ionic sizes are a property of an ion and its environment, not of the ion alone.

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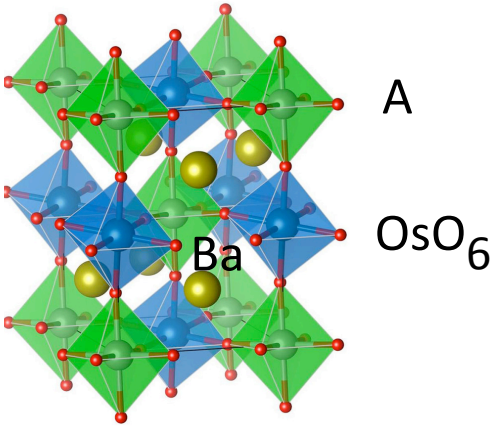
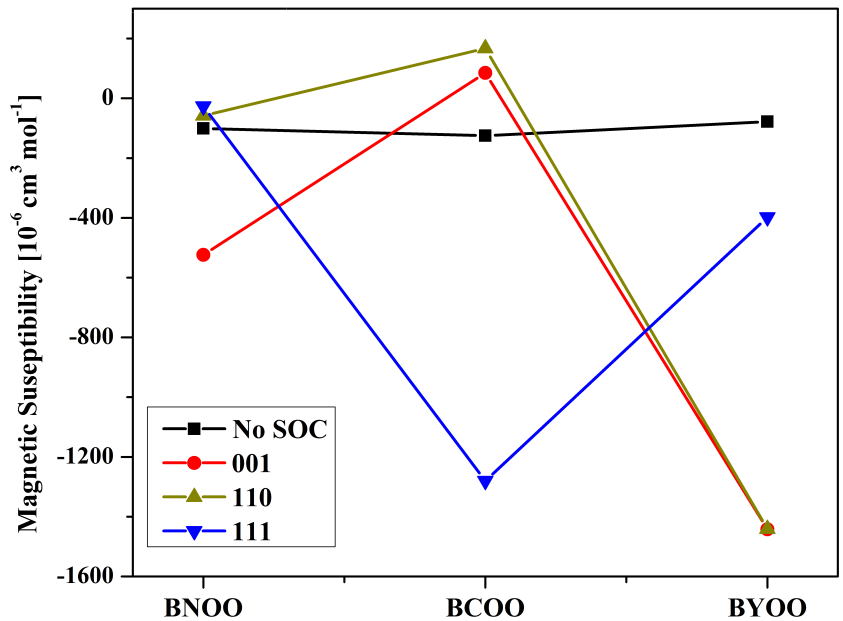


NMR-probed properties of Ba_2AOsO_6, predicted by DFT
With strong correlation included

Macroscopic magnetic susceptibility calculated for Ba_2AOsO_6



- strong effect of SOC (black line)
- strong variation with “band filling”
- experimental comparison is to follow

Interplay of Spin-Orbit Coupling and Strong Correlation Effects: Three Osmate Double Perovskites Ba_2AOsO_6, A=Na,Ca,Y

NMR-probed properties of Ba_2AOsO_6 , predicted by DFT
With strong correlation included

Isotropic shielding fraction σ (in ppm) calculated from density functional perturbation theory, for Ba_2AOsO_6, A=Na, Ca, Y. Top: neglecting spin-orbit coupling. Following panels for magnetization along the three symmetry axes.

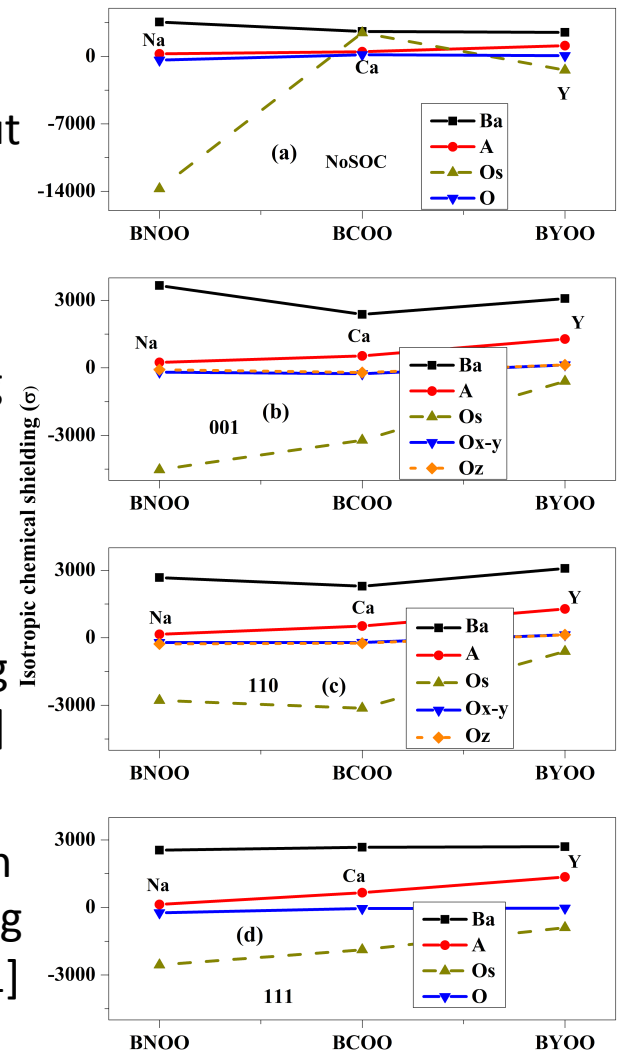
- strong SOC effect for osmium
- weak dependence on spin direction
- physical interpretation is difficult

Without SOC

Spin along [001]

Spin along [100]

Spin along [111]



4. Resonant Inelastic Xray Scattering: Ce → Pr

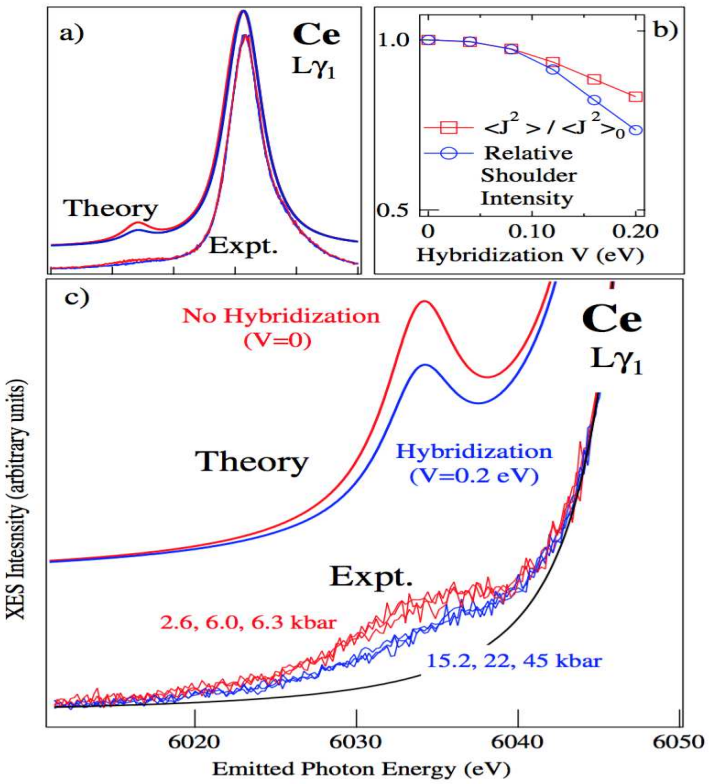
Reproduced prior results for Ce RIXS.

Disappearance of shoulder with increasing pressure (hybridization V): loss of moment.

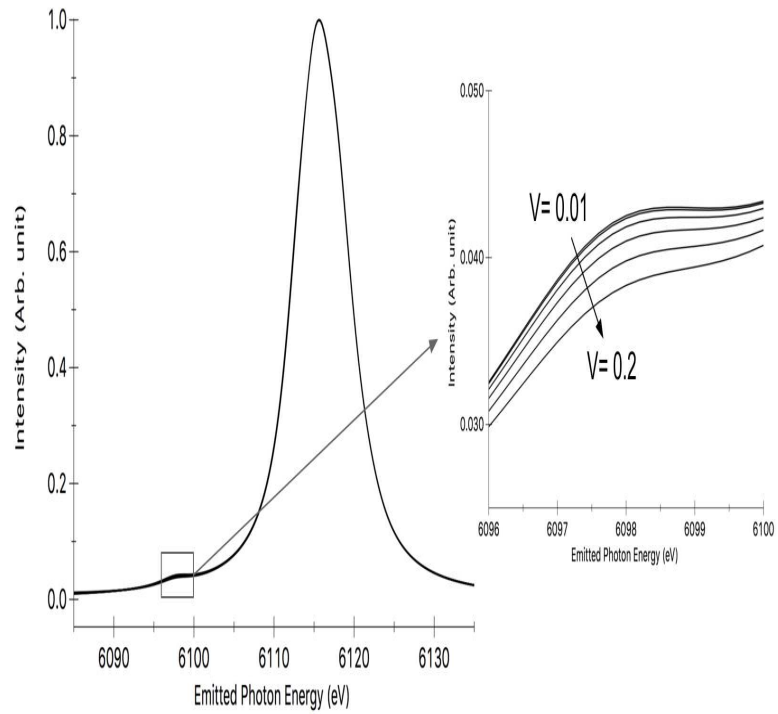
New method which reduces Hilbert space time.

Makes investigation of $4f^n$ with $n > 1$ feasible.

Previous results (Sorini, Lipp etal.)



New Results

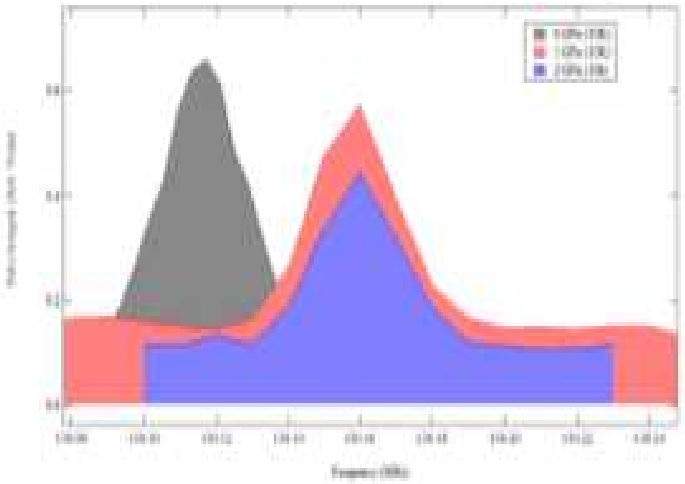


5. Al-27 NMR in a Diamond Anvil Cell

Composite Gasket DAC for NMR

Intact microcoil after the pressure cell was opened

Resulting Spectra at 10K



NMR spectra of ^{27}Al in Ruby at 1 and 2 GPa, as well as ambient pressure

Summary and Near-Term Planned Work

NMR Experiment

- Al-27 NMR in Diamond Anvil Cell
- Cu NMR on La_2CuO_4 to 5 GPa in recently developed DAC.

Electronic Structure Calculations

- NMR-probed properties of Ba_2AOsO_6 (A=Na,Ca,Y) predicted by DFT with strong correlation included.
- Magnetic coupling of high-Z materials at high pressure

Quantum simulations:

- Computed NMR relaxation rate in uniform system
- Extracted AF impurity susceptibility
- Distribution of NMR relaxation rates around impurity
- Other inhomogeneities which locally change g (Cd doping for In).

RIXS

- Reproduced results for Ce with improved method.
- Computations for $4f^n$ with $n > 1$.

Thanks to SSAA Program!

- Fantastic experience for our UC Davis graduate students.
- Adam Dioguardi now Postdoctoral Fellow at LANL.