$BaV_{0.98}Ti_{0.02}S_3$

RIXS Observation of a Temperature Dependent Anti-Stokes-like Feature at the V L_3 Absorption Edge

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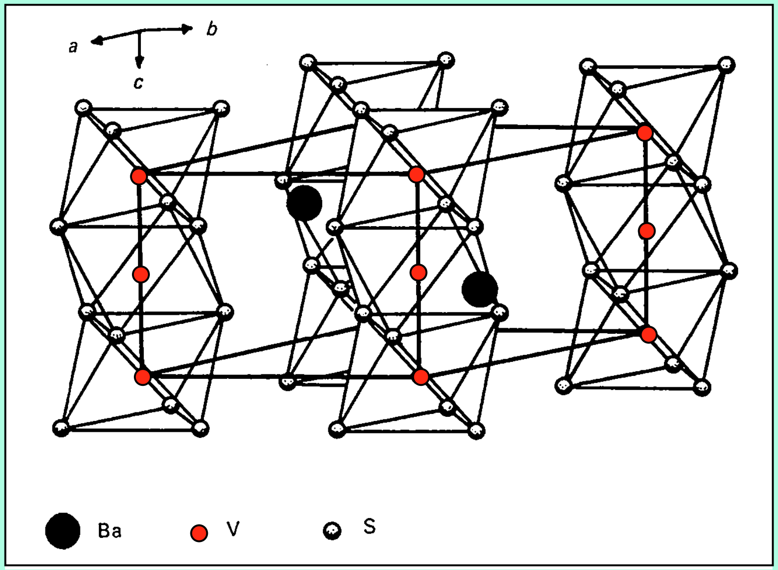
$BaVS_3$

- Quasi-one dimensional crystal structure
  - Resistivity is relatively isotropic
  - Bad metal
- Nominally V^{4+}, or *3d¹*
- Structure Phase Change at 240K
  - Hexagonal to Orthorhombic
  - Not much of an effect on physical properties
- Strong structural fluctuations observable below ~170K †
  - Short range Jahn-Teller instability ‡
  - Competes with lattice strain
- Metal-Insulator Transition at 70K
  - Appears to not exhibit Peierls distortion
  - Jahn-Teller driven ‡
  - Orbital Ordering
- Magnetic Transition at 30K
  - Spin ordering commensurate with room temperature lattice structure

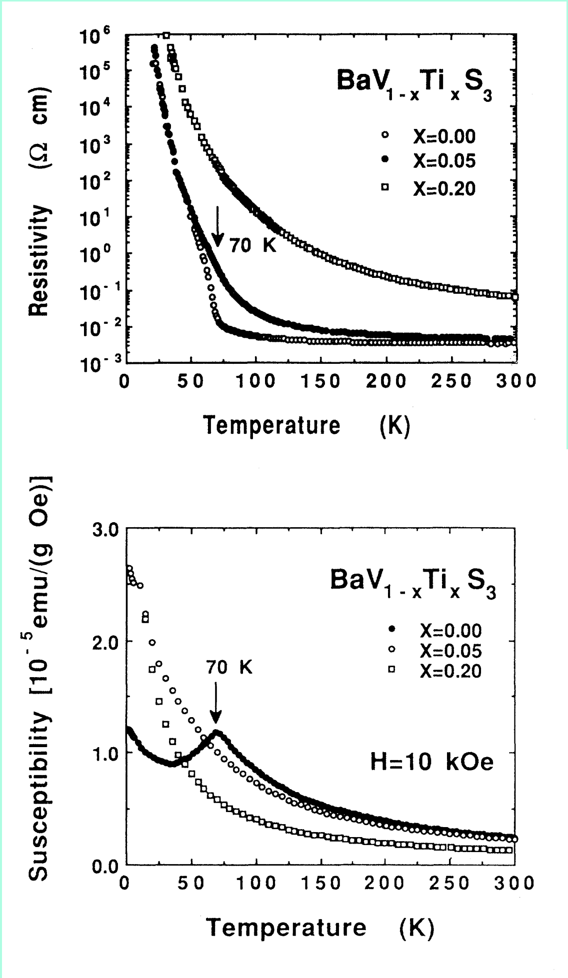


Gardner *et al*., Acta Cryst. **B25**, 781 (1969)

† Fagot *et al*., PRL **90**, 196401 (2003)   ‡ Whangbo *et al*., JSolStateChem **175**, 384 (2003)

$BaTi_xV_{1-x}S_3$

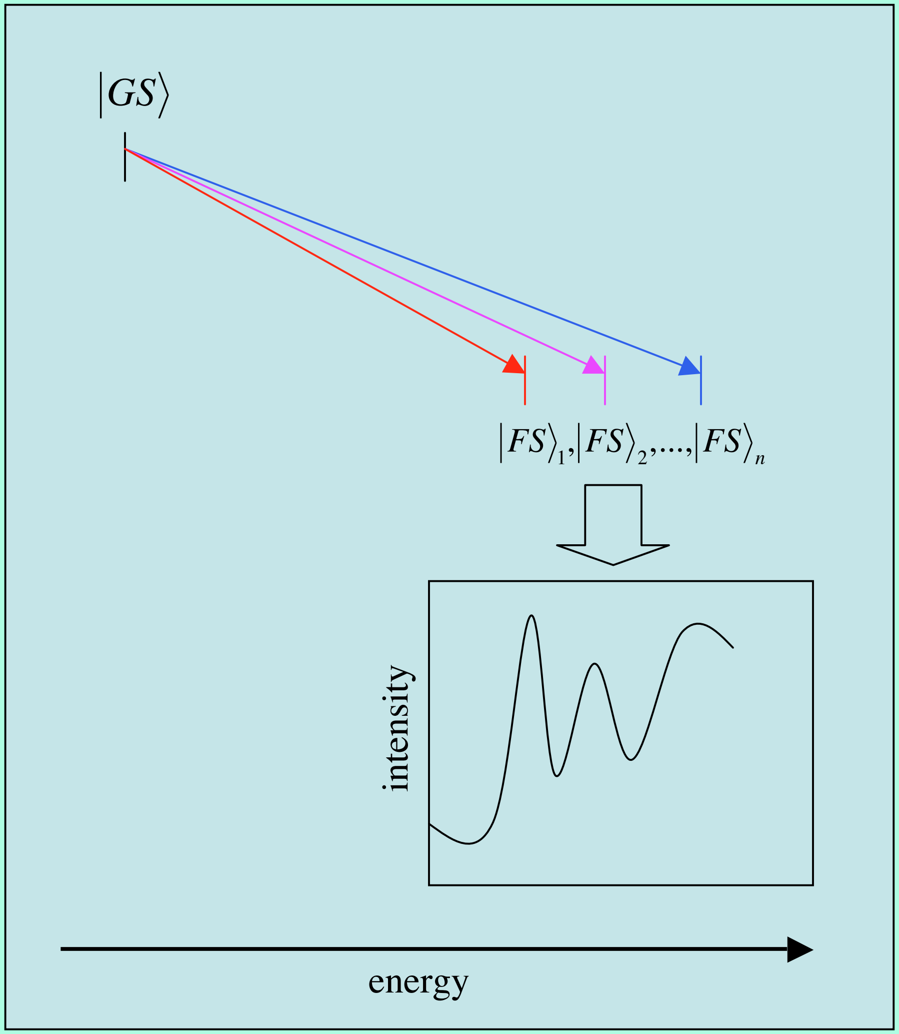
- Ti doping introduces *$3d^0$* sites on V-V chain
  - Now less than *$3d^1$*
  - At 2% doping, crystal structure likely similar
- Metal-Insulator Transition
  - Appears to be slower
  - Observed for any doping
  - Still Jahn-Teller active, even though V sites are less than *$3d^1$*
- Magnetic structure
  - Susceptibility cusp at MIT supressed at low doping
  - No longer able to form interchain spin singlets †



Matsuura et al., PRB **43**, 13118 (1991)

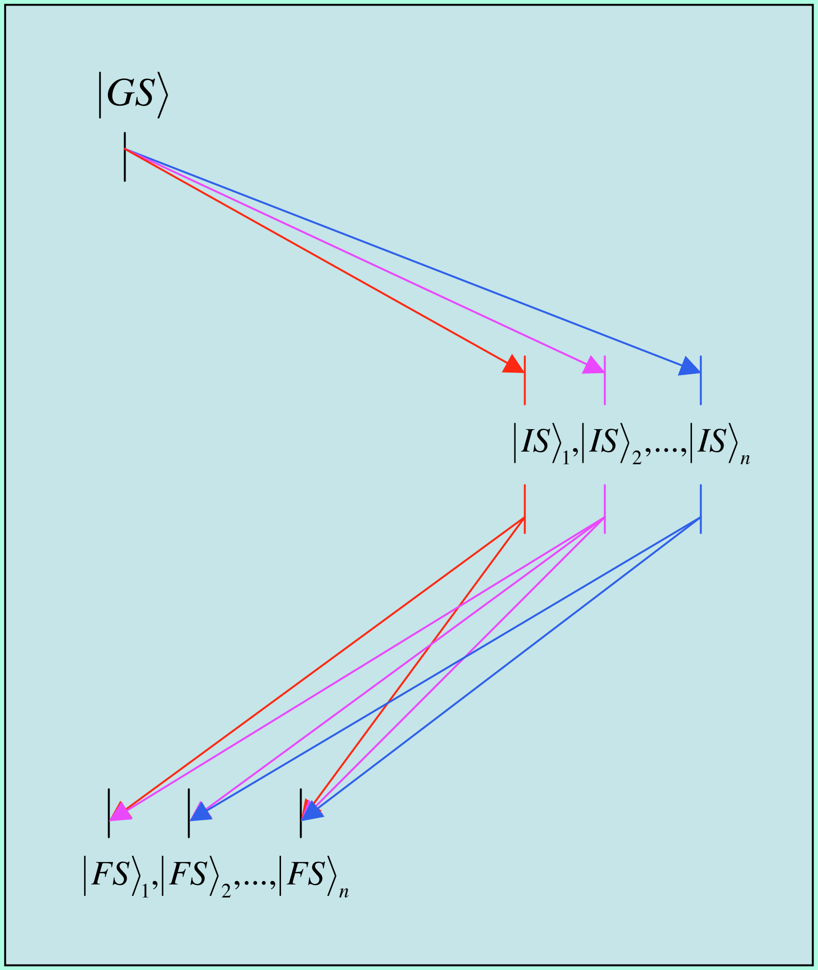
† Whangbo *et al*., JSolStateChem **175**, 384 (2003)

Soft X-ray Absorption



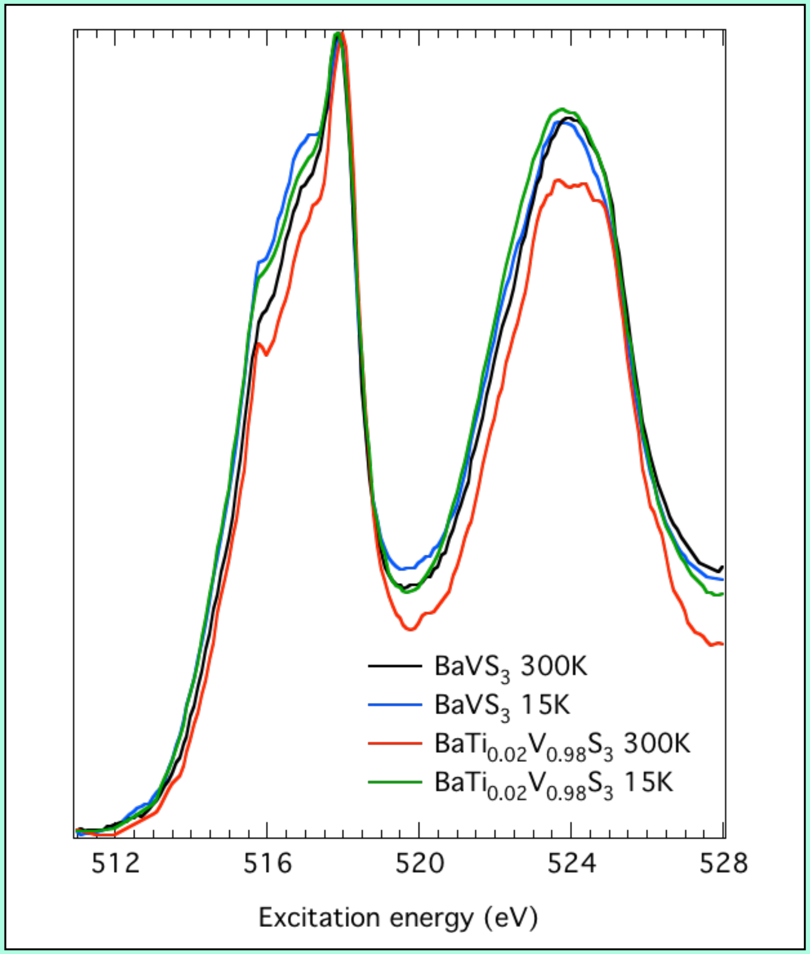
- Dipole selection rules
- Atomic site specific
- Each final state can be a combination of states
  - Better energy resolution helps
  - Even with infinite resolution, no guarantee of simple final state
- At L_3 edge, multiplets are important
  - Not a direct reflection of the partial density of states

Soft X-ray RIXS



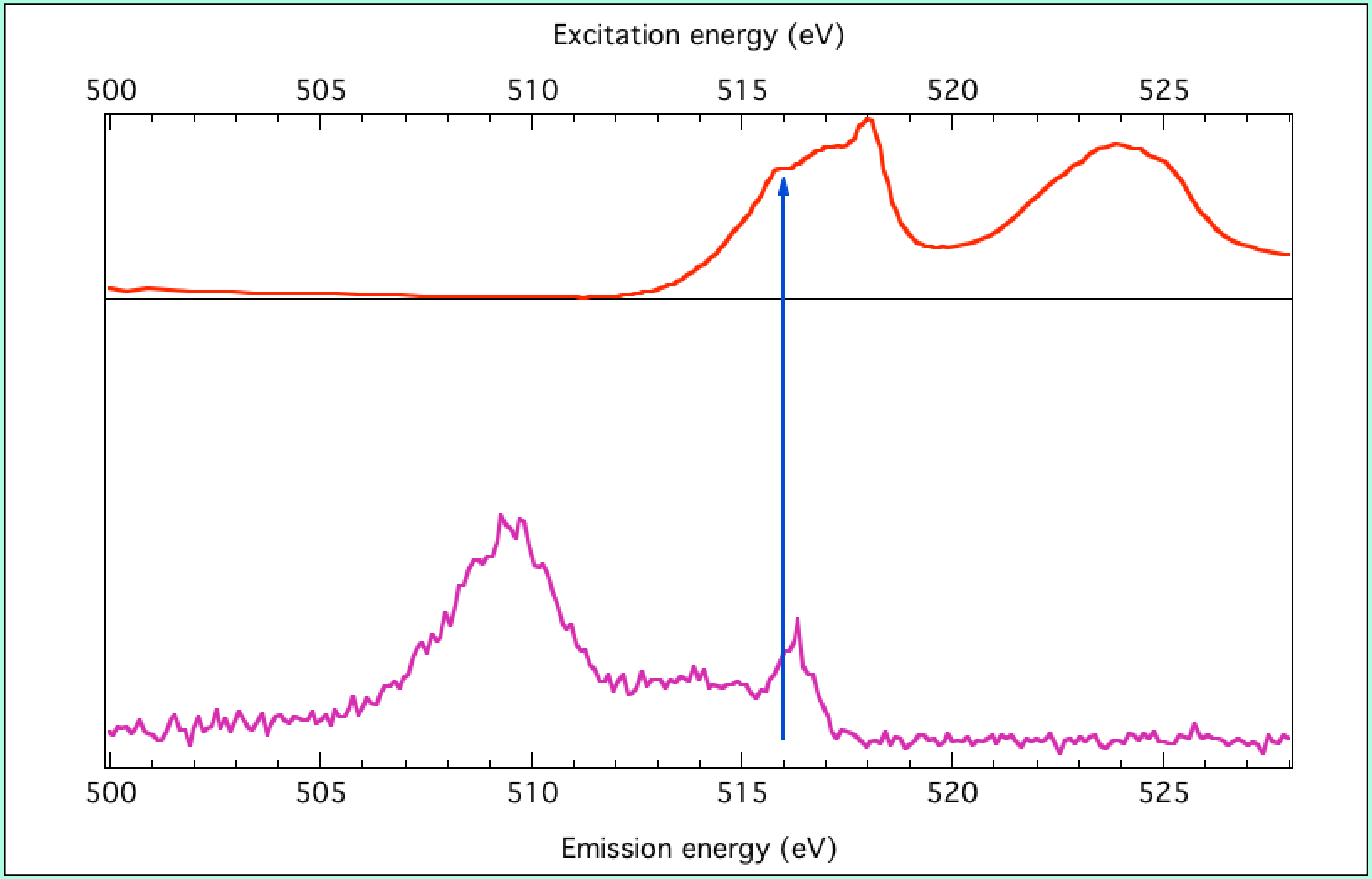
- Tune excitation energy to an intermediate state
  - Transitions from all accessible intermediate states to all final states are measured
- Localized intermediate states maximize resonance effect
  - Strong symmetry selection rules
  - Low energy excitations
- For light atom *L* edges, dominant core hole decay is Auger
  - Small emission cross-section
  - Experimentally challenging to resolve all possible intermediate and final states

X-ray Absorption Data

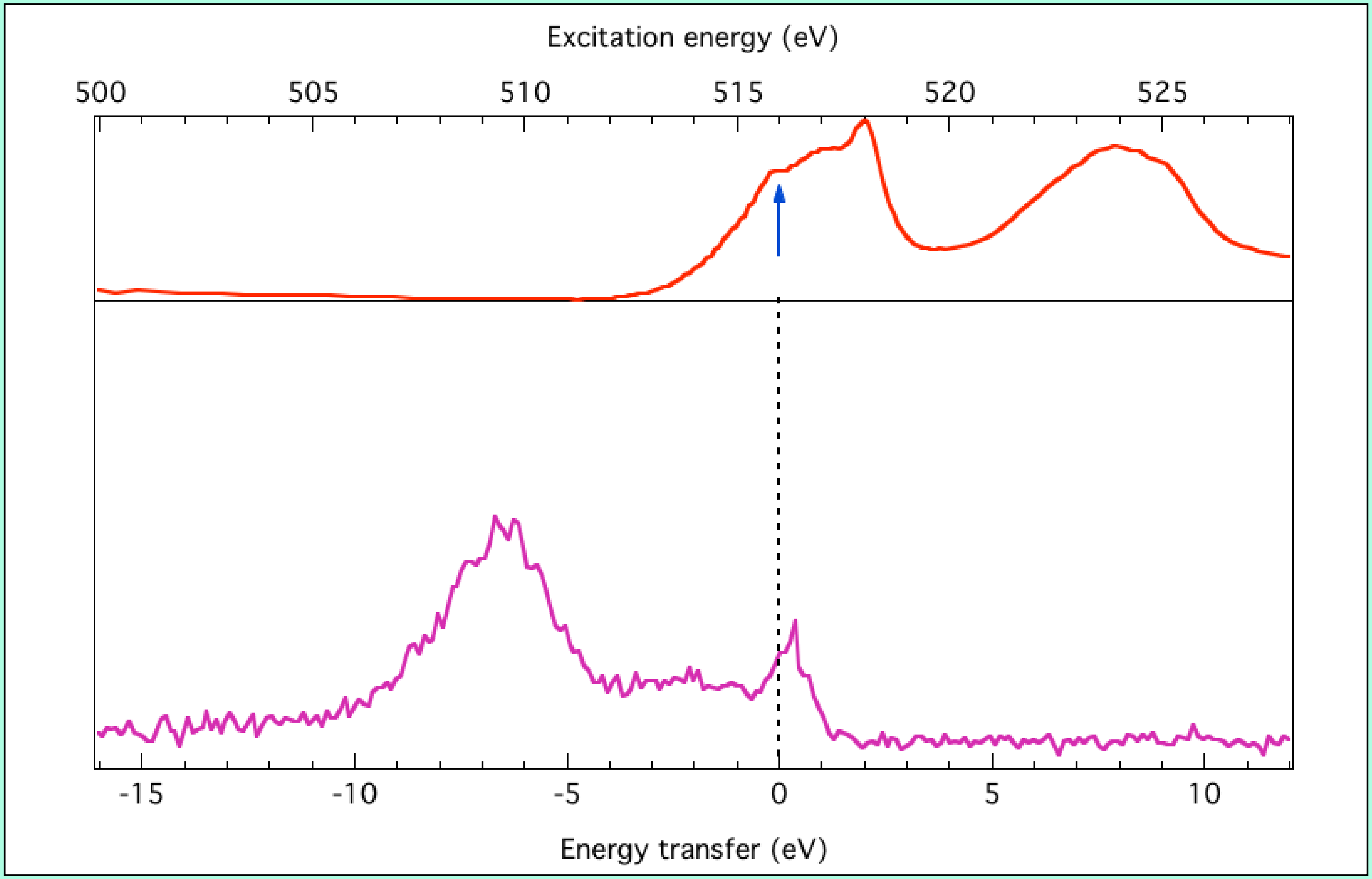


- Lowest energy peak related to lowest lying V *3d* t_{2g} states
- Both samples look similar
  - Overall shape
  - Sharpest peak does not move in energy

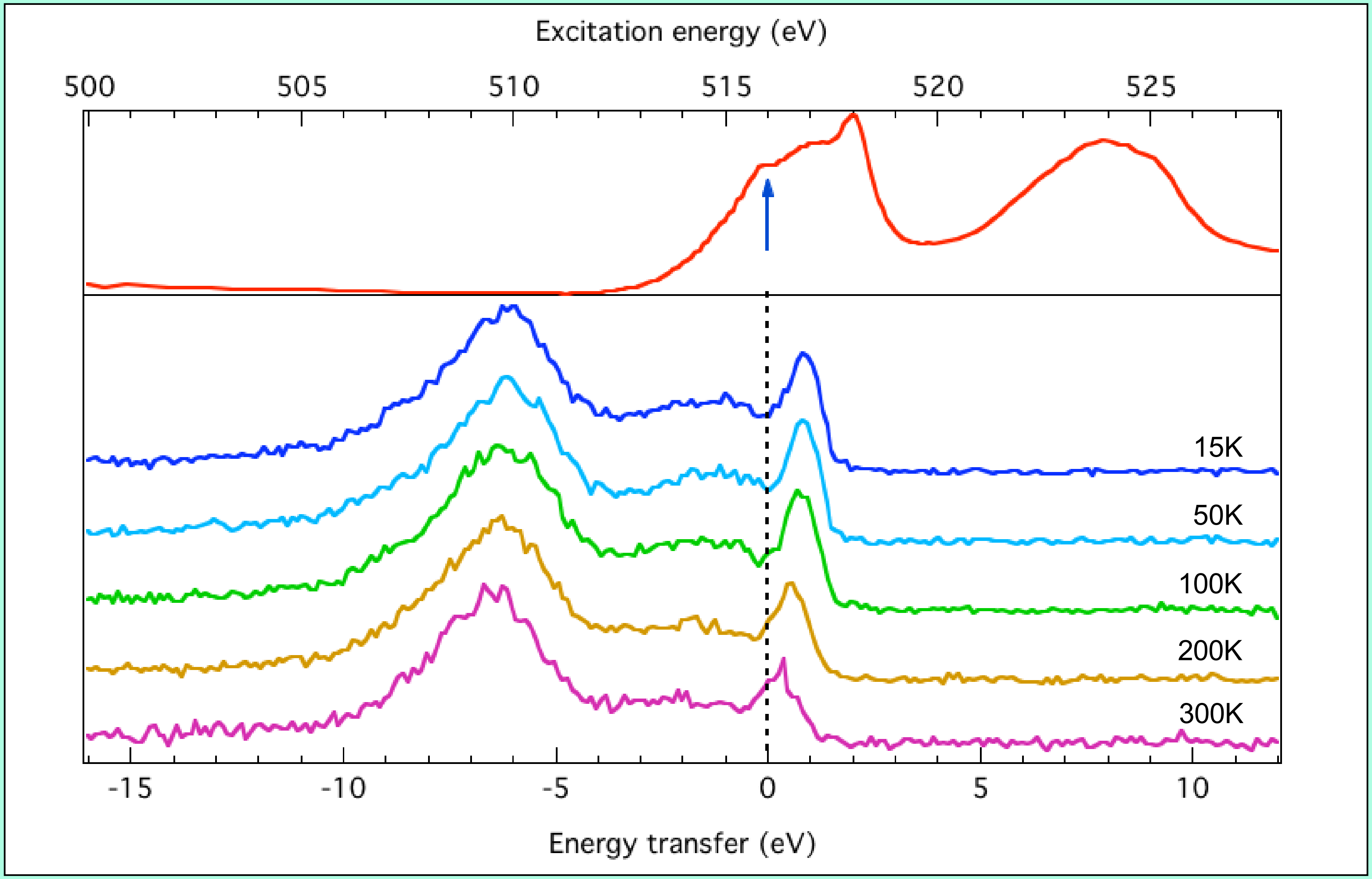
$BaV_{0.98}Ti_{0.02}S_3$ X-ray Emission



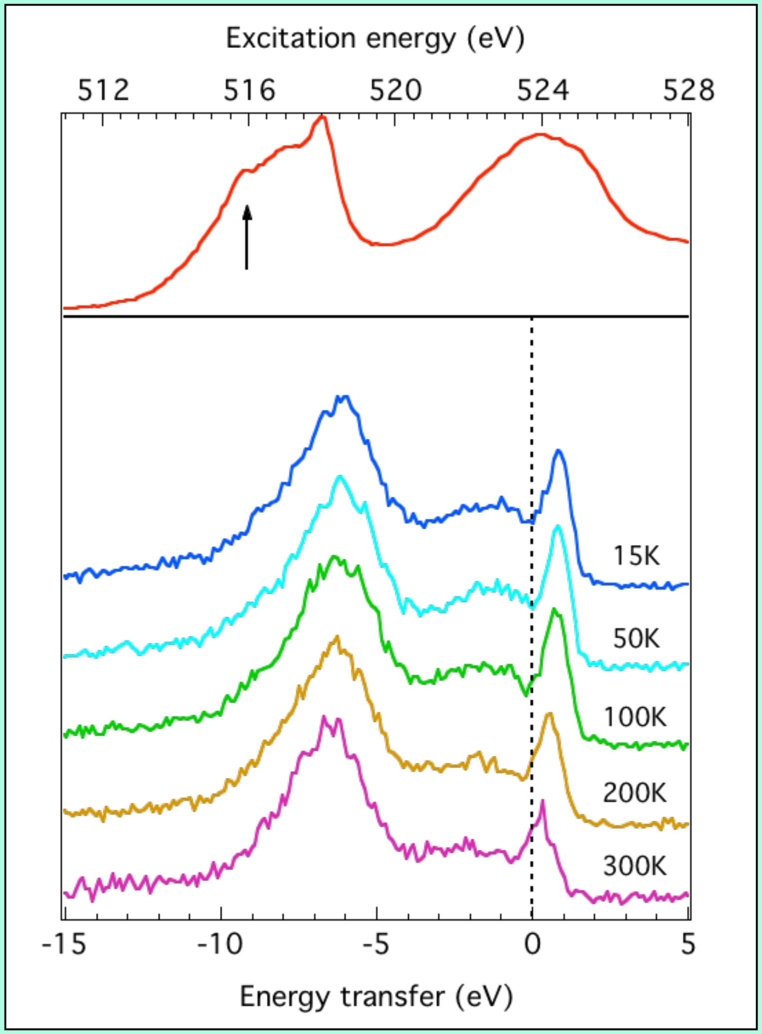
$BaV_{0.98}Ti_{0.02}S_3$ X-ray Energy Loss



$BaV_{0.98}Ti_{0.02}S_3$ Temperature Dependent RIXS

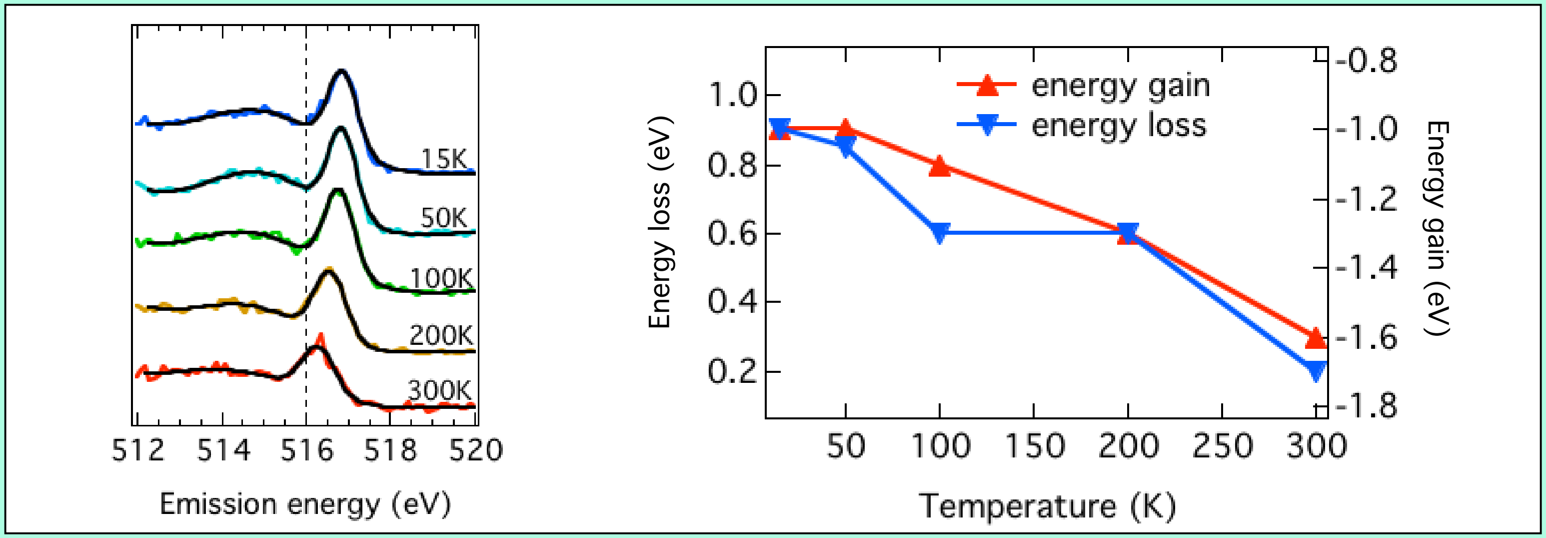


$BaV_{0.98}Ti_{0.02}S_3$ RIXS Features



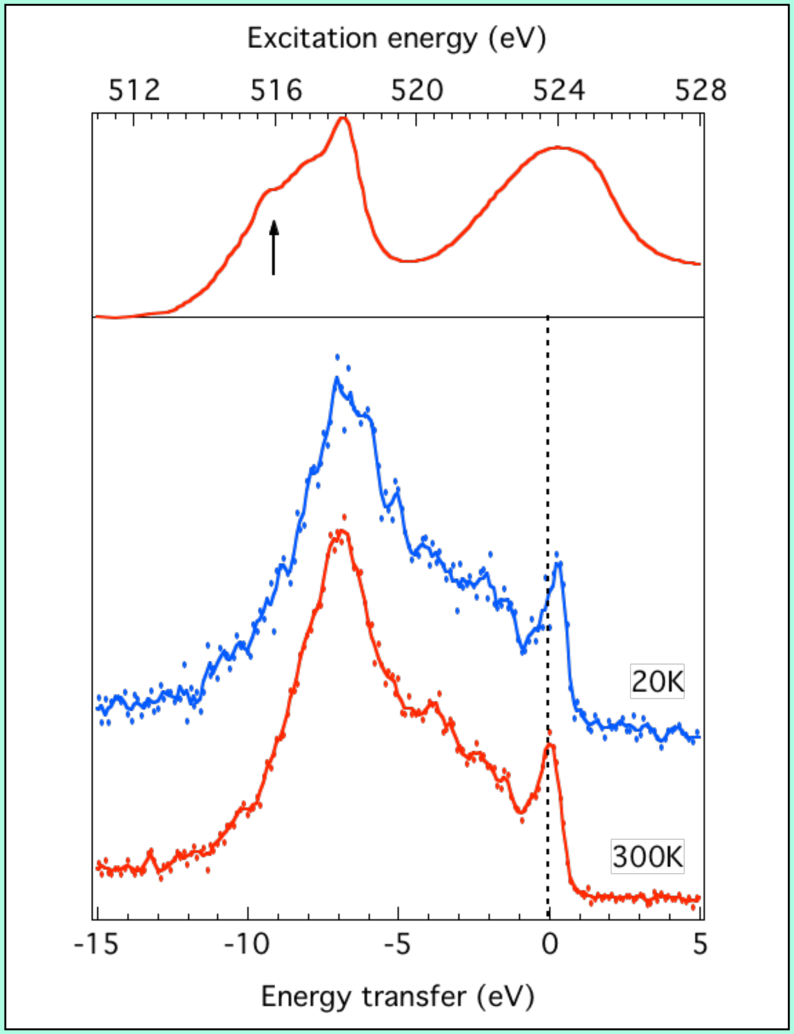
- Energy gain feature
  - Saturates between 100K and 200K
  - Not saturated at 300K
- Emergence of energy loss feature
  - Broad
  - Background looks excitonic
- Energies carefully calibrated

Temperature Dependence of Energy Loss and Gain Features



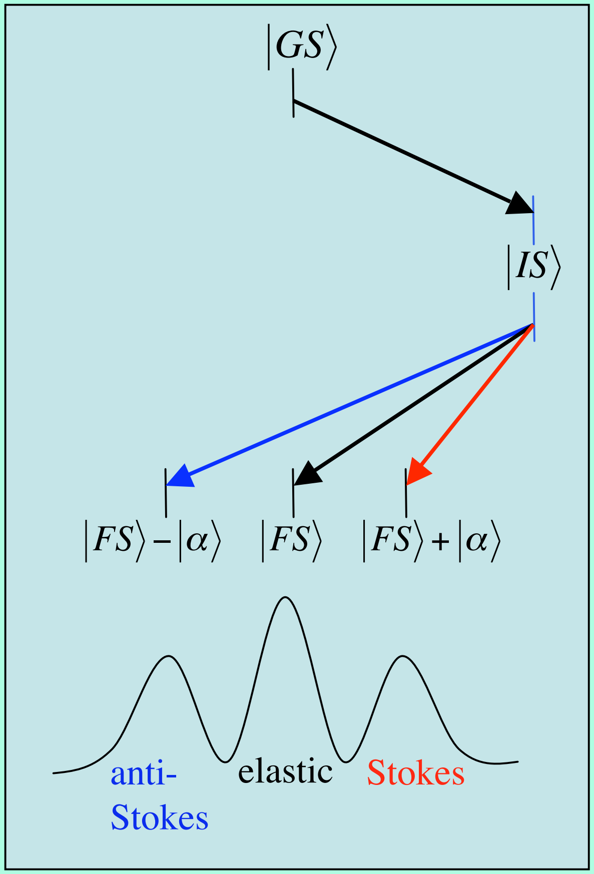
- Both peaks move in a similar way
  - Approximately 2 eV between them
  - Energy shifts appear to saturate between 100K and 200K
  - Large error bars on broad peak position
- Could both of these features be connected to the lattice fluctuations along the V-V chains?
  - 170K temperature
  - Ti doping should shift the balance between Jahn-Teller and lattice distortions

$BaVS_3$ RIXS Data



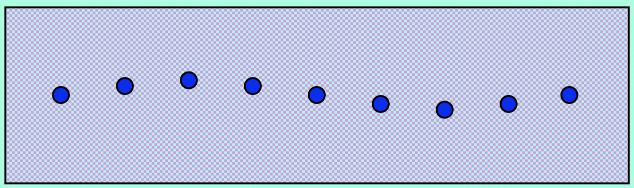
- No large energy gain feature
- Small shift?
  - At resolution threshold (~0.2 eV)
- Broad loss feature
  - Still large background between PDOS peak and energy gain peak
  - Too weak and noisy
- Fundamental difference in RIXS between $BaVS_3$ and $BaTi_xV_{1-x}S_3$ at this excitation energy is evidence of orbital ordering along the V-V chains

Anti-Stokes?

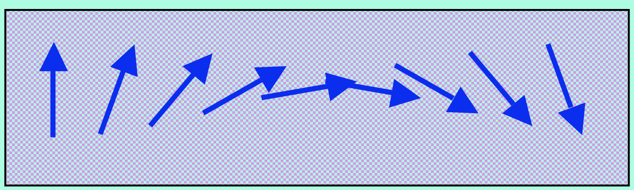


- Stokes and anti-Stokes peaks correspond to emission and absorption of an excitation by the outgoing photon
  - If there is an anti-Stokes peak at energy E_{Stokes}, there should also be a corresponding Stokes peak at energy $-E_{Stokes}$
  - Both peaks need not have the same intensity
- Our data does not clearly show a Stokes peak
  - There may also be a Stokes peak buried in the spectral weight between the anti-Stokes peak and the PDOS emission peak
  - As the anti-Stokes peak increases in energy, the broad energy loss peak decreases in energy loss
- There are two separate things going on here.

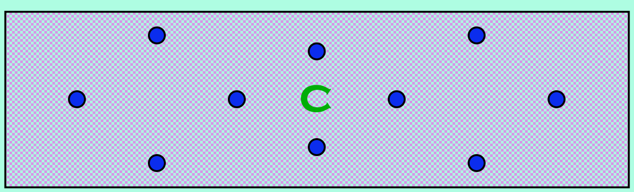
Excitations



- Phonons
  - Order of magnitude too low energy
  - Appealing since they are known to cause anti-Stokes shift at optical photon energies

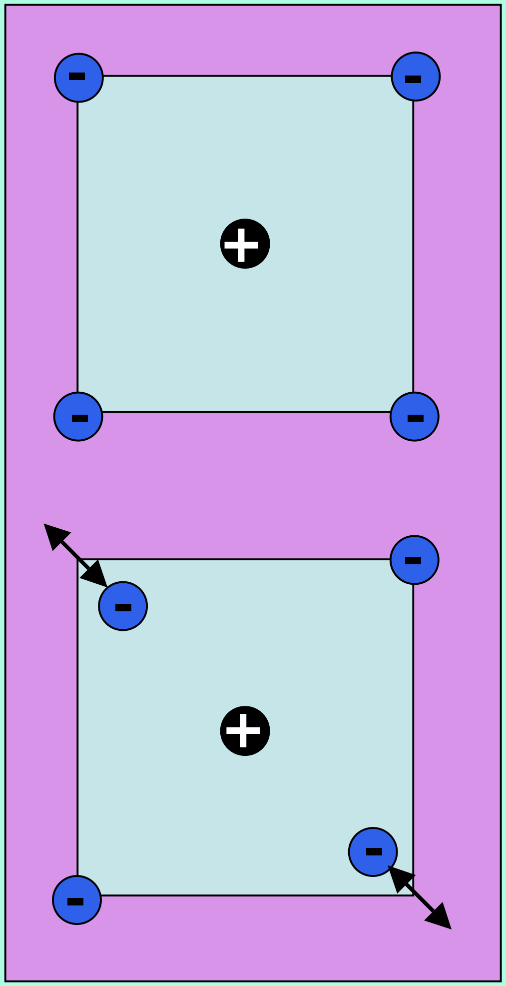


- Magnons
  - Also known to cause anti-Stokes shift at optical photon energies
  - Not clear they exist in $BaTi_xV_{1-x}S_3$



- Polarons
  - Jahn-Teller instability
  - Almost certainly exist in $BaTi_xV_{1-x}S_3$
  - Unknown coupling mechanism for anti-Stokes feature

Polarons



- Charge coupled with local lattice distortion
- V atoms in $BaVS_3$ exist inside S_6 octahedra
  - A charge in the center (addition or omission of e^-) can drive a distortion of the octahedron
  - This can be a Jahn-Teller distortion
- May broaden *d-d* excitations or cause separate energy loss mechanism
  - Obscure Stokes and elastic peaks
- How does this couple to photons?
  - Presumably not directly, as polarons contain charge
  - How long does the intermediate RIXS state live?

Conclusions

- Large anti-Stokes-like feature at low temperature
  - Uncertain origin
  - Phonons, magnons lower in energy
- Emergence of broad loss feature
- Polarons?
- Unexplained spectral weight between anti-Stokes and PDOS peak
  - Excitonic sideband
  - Sum of Stokes, *d-d*, elastic peaks
- Doping dependence is evidence of orbital ordering amongst low lying V *3d* states
- Different levels of Ti doping are worth examining

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