Role of sulfur in $BaVS_3$
Probed by S K edge absorption spectroscopy

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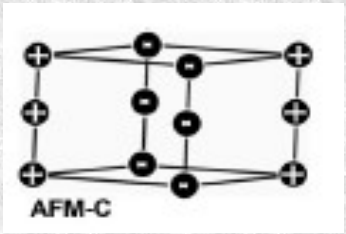
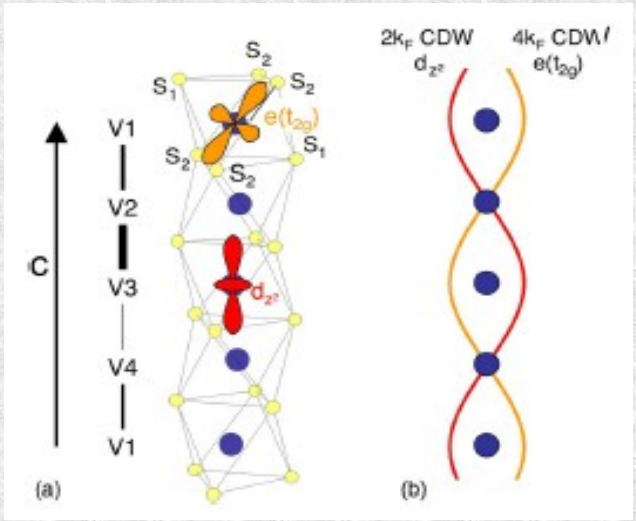
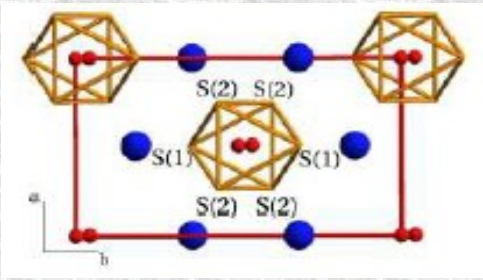
Outline

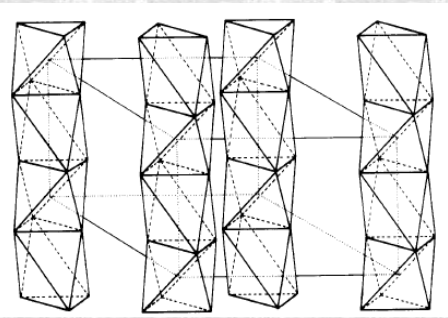
- Introduction to $BaVS_3$
- V L-edge measurements
- S K-edge XANES
- Summary and conclusion

Four phases of $BaVS_3$









(AFI) monoclinic (mPI) V zig-zag orthorhombic (oPM) hexagonal (hPM)

30K 69K 130K ρ_{min} 170K 240K T

Insulator
Incommensurate
AFM order

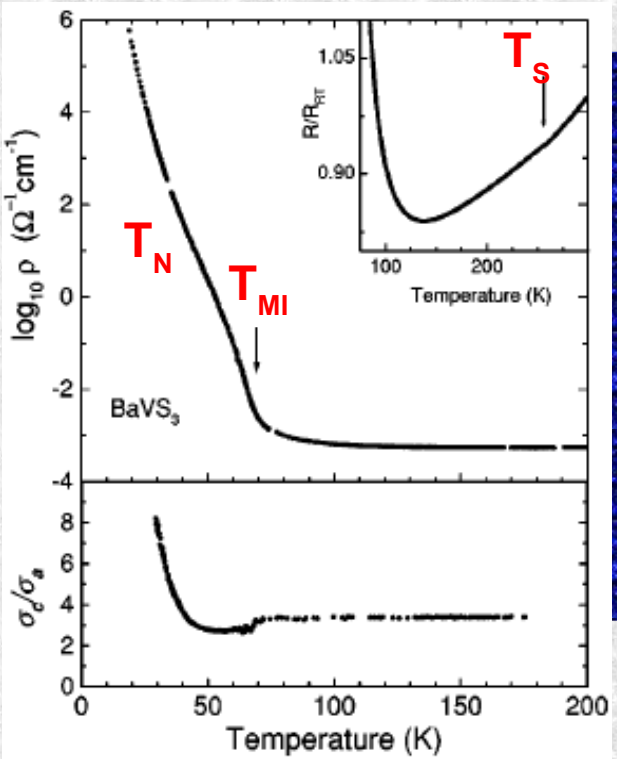
Insulator
Charge Density Waves
Orbital order ?

Metal
Localized Paramagnetism

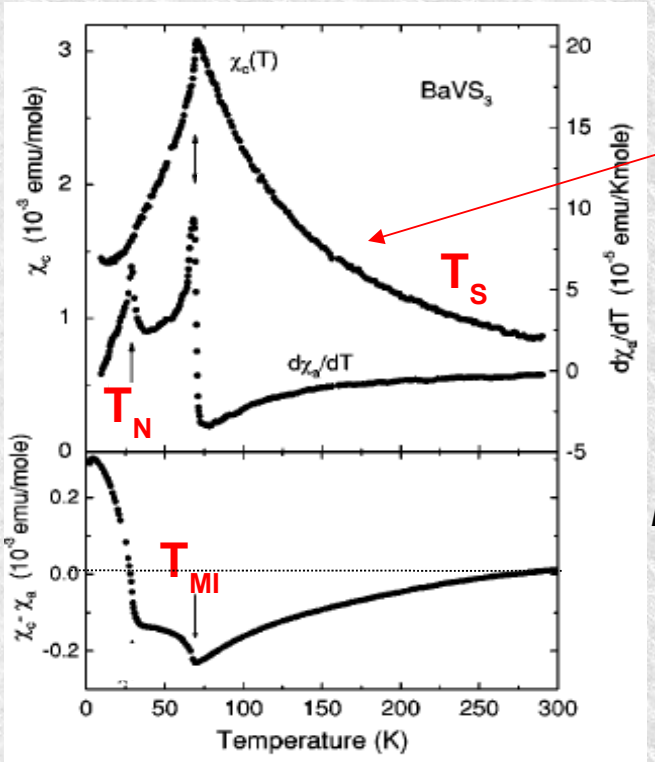
CDW fluctuations

A. Arakcheeva talk last weak BaS_3 layers (host) +
V-chain (guest) structure

Resistivity



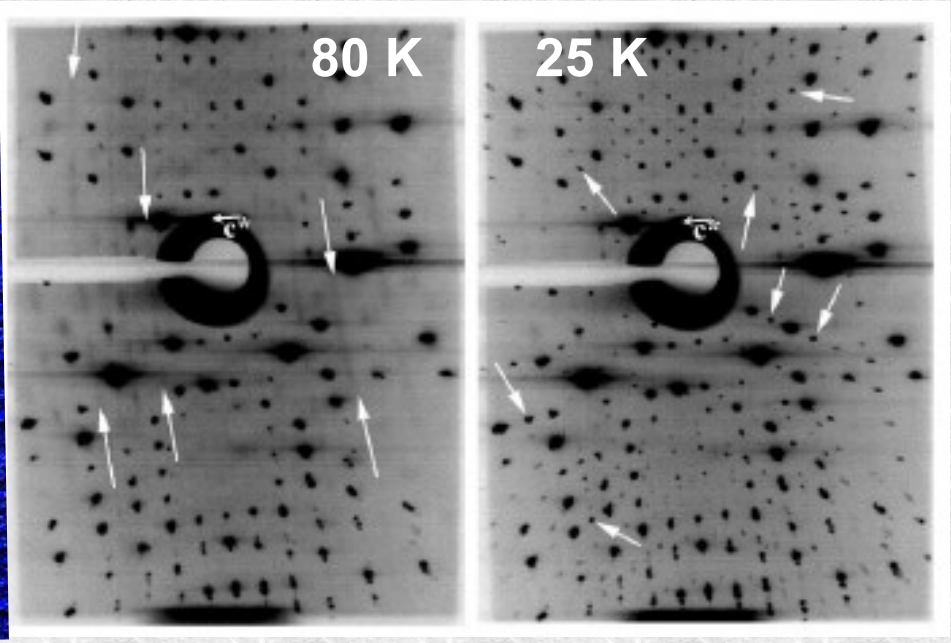
Susceptibility



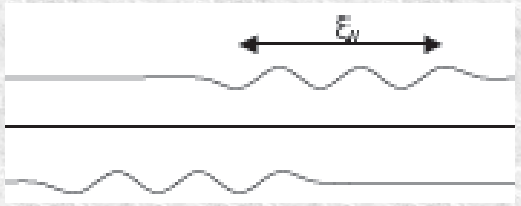
Curie-Weiss Paramagnet

Mihaly et al., PRB 2000

Diffuse Scattering



Charge Density Waves



$T > T_{MI}$

Diffuse Lines

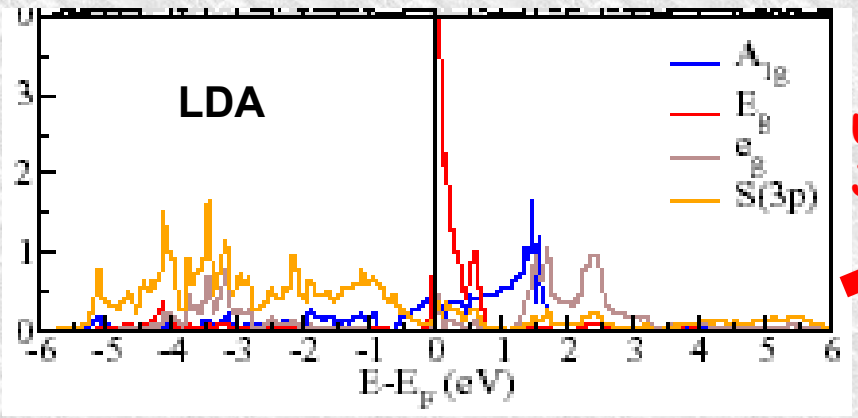
$T < T_{MI}$

Satellites

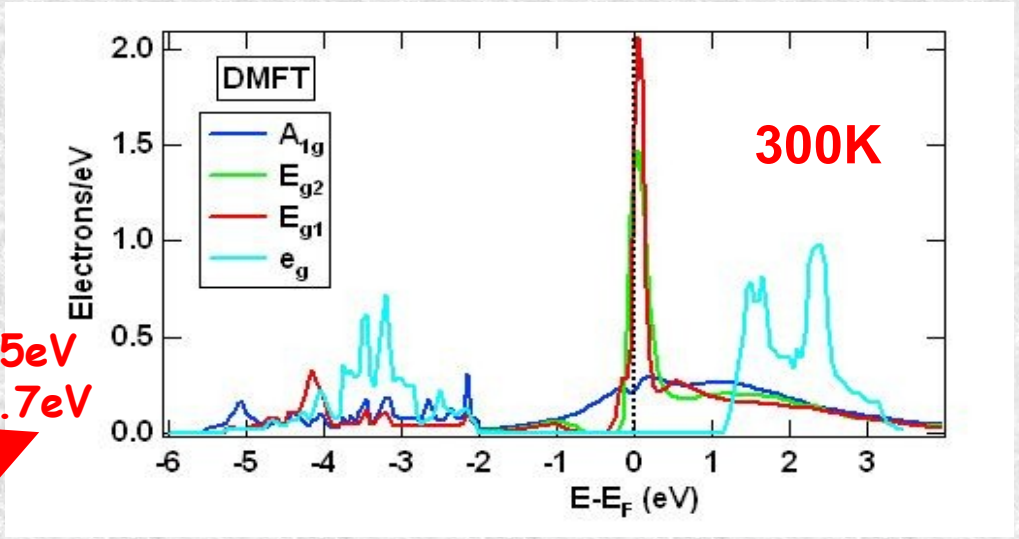
$2k_F = 0.5c^*$

Fagot et al., PRL 2003

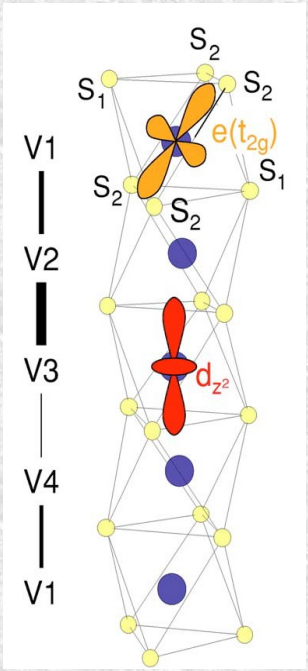
Electronic structure calculations



U = 3.5eV
J = 0.7eV



V K edge resonant diffraction

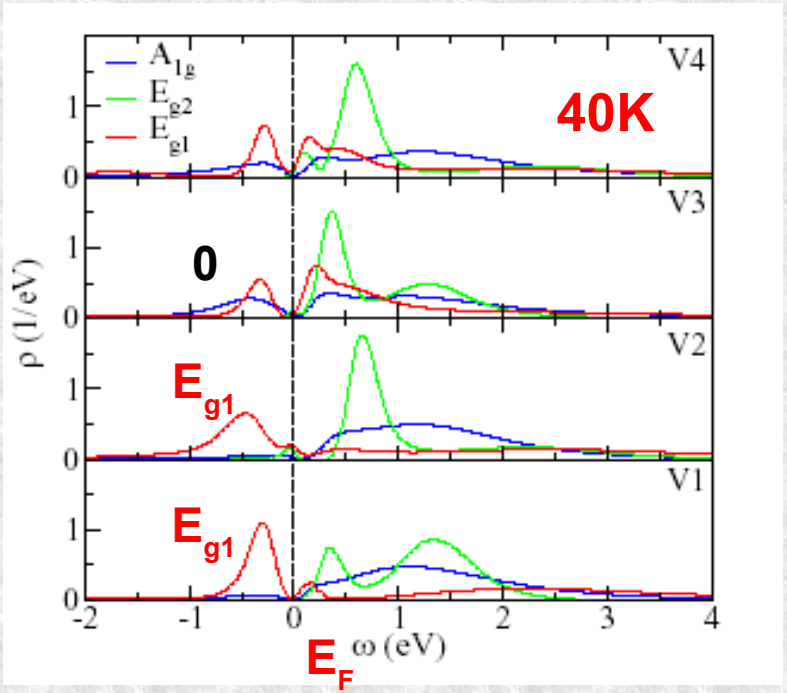


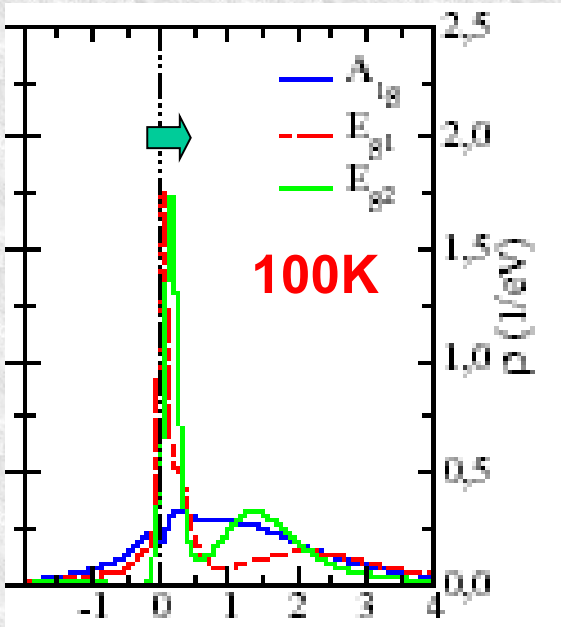
E_{g1}

0

A_{1g}

0





T < T_S: depleting of Eg_2

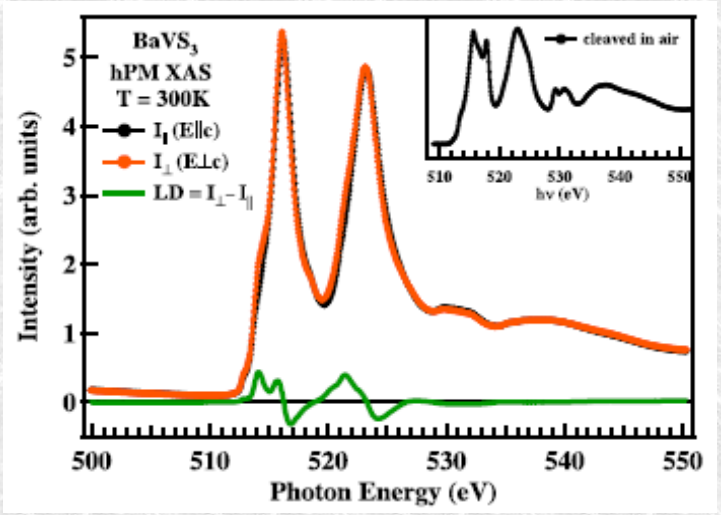
F. Lechermann et al., PRL 2005 PRB 2007

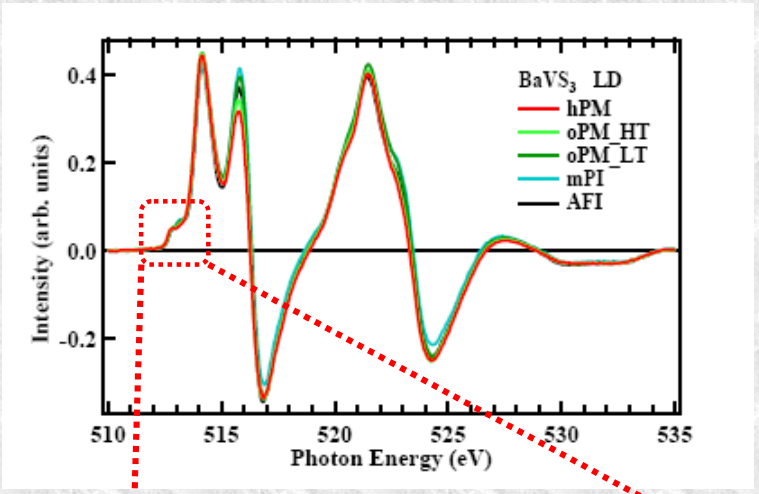
S. Fagot et al., PRB 2006

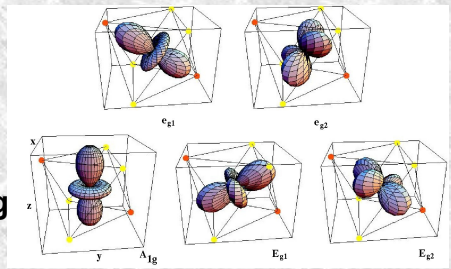
T < T_{MI}: 4 inequivalent V sites

V L edge X-ray absorption

ID08/ESRF





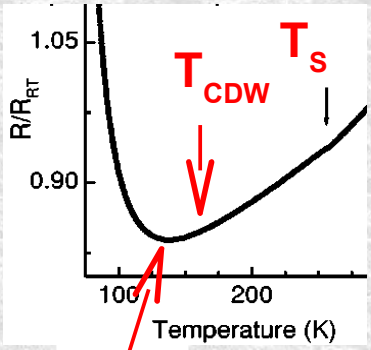


hν

V2p3/2

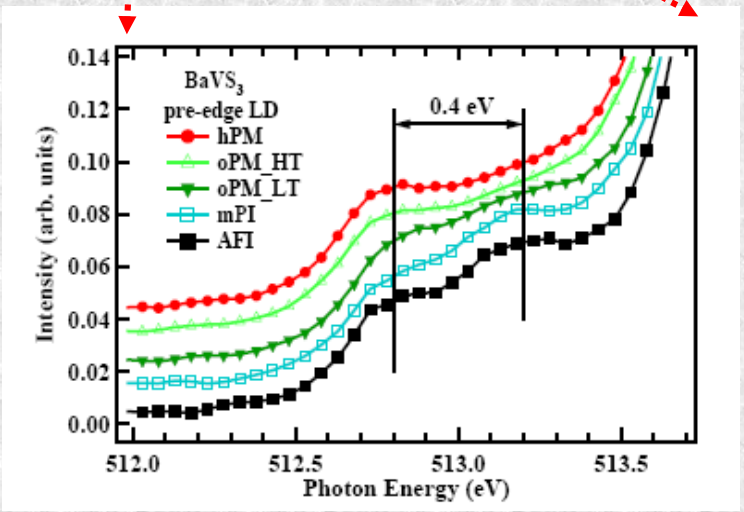
V2p1/2

hν ~ 520 eV



What happens at T_{min}?

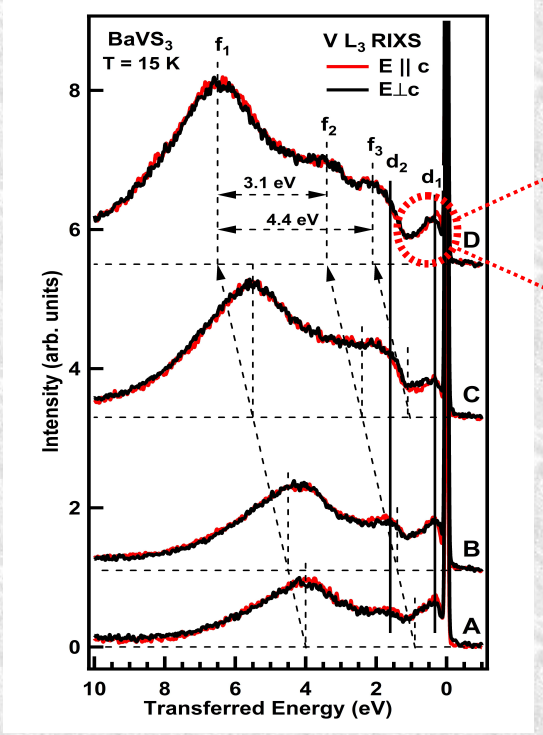
A. Arakcheeva talk : Structural change !

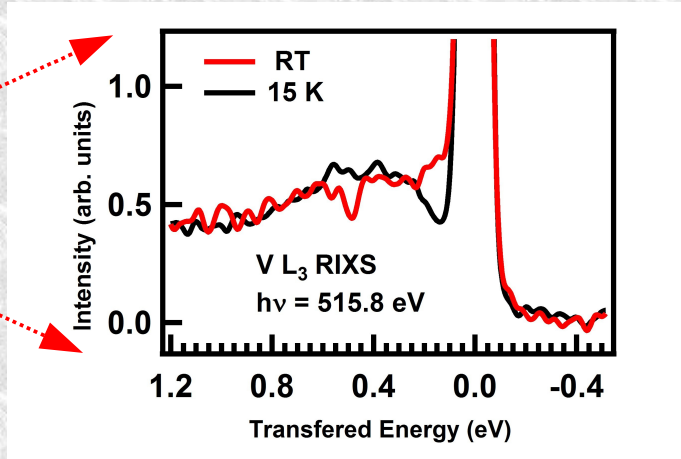


Ilakovac at al., JPCM 2012

V L edge Resonant Inelastic X-ray Scattering

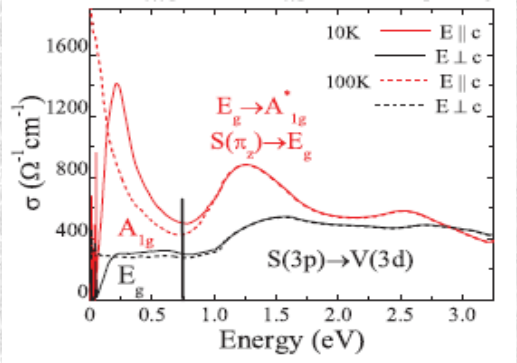
SAXES / SLS



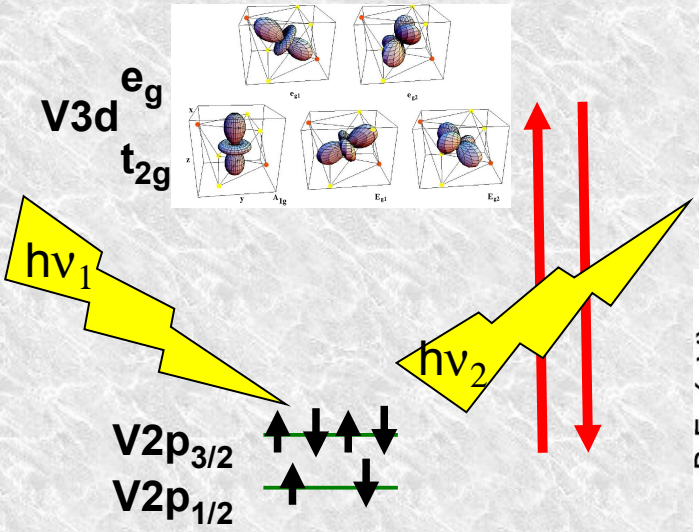


Peierls gap
Δ_{ch} < 70 meV
V 3d states
Ilakovac et al.,
JPCM 2012

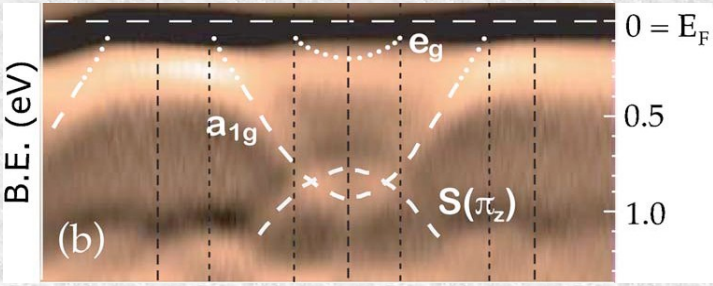
Optical conductivity:
Δ_{ch} ~ 40 meV



Kezsmarki et al., PRL 2006



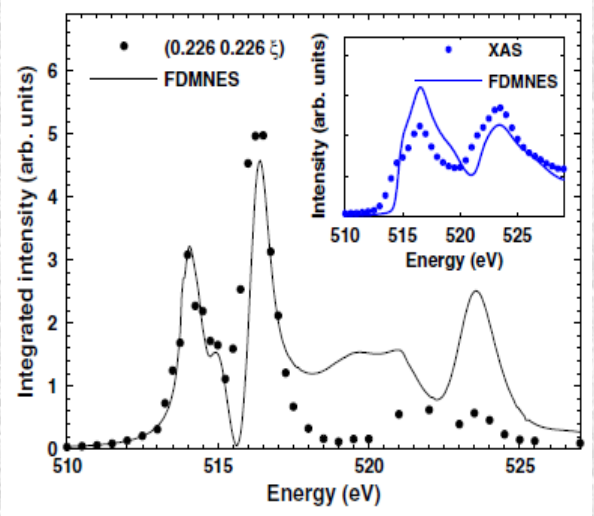
ARPES:
Δ_{ch} ~ 60-70 meV

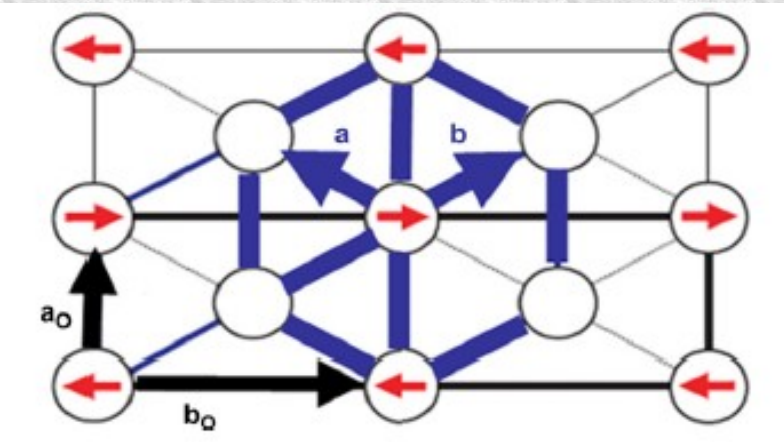


Mitrovic et al., PRB 2007

V L edge Resonant X-ray diffraction / Single crystal

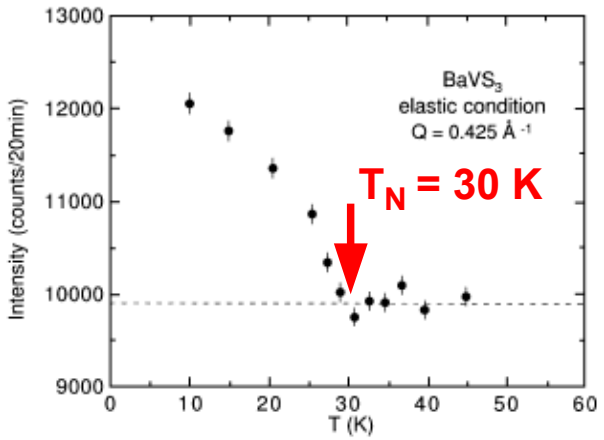
BESSY II
UE46-PGM1





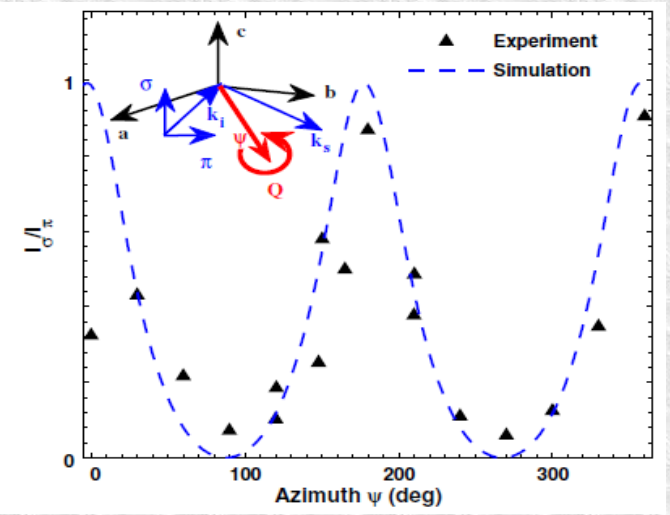
Reflections of magnetic origin at q = (0.226 0.226 0.016)$_H$

Powder neutron diffr.



q = (0.226 0.226 0)$_H$
Nakamura et al., JPSJ 2000

Triply incommensurate AF spins lie in the (a,b) plane



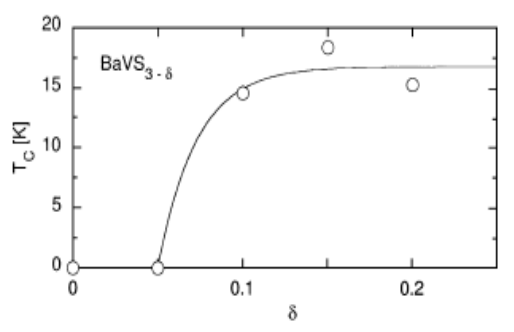
Leininger et al, PRL 2011
R. A. de Souza, et al., PRB 2011

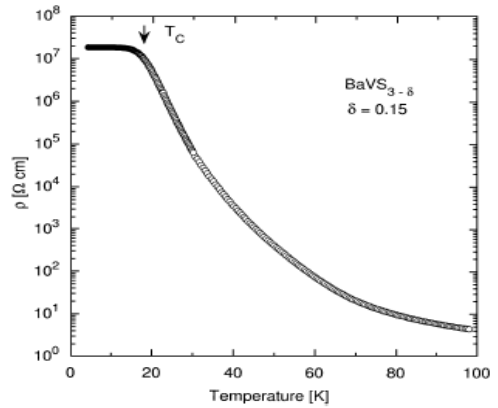
Why are we interested in the $BaVS_3$ S K edge ?

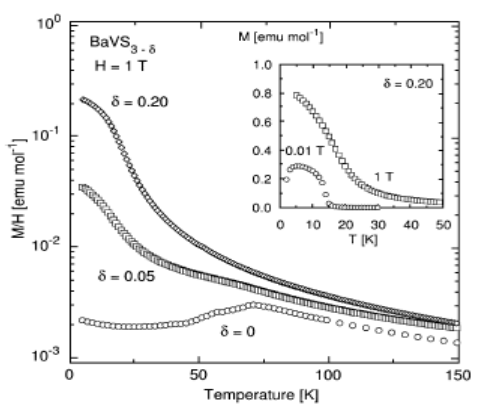
Sulfur deficiency is extremely destabilizing for $BaVS_{3-\delta}$.

Already for $\delta > 0.1$, $BaVS_{3-\delta}$ is a :

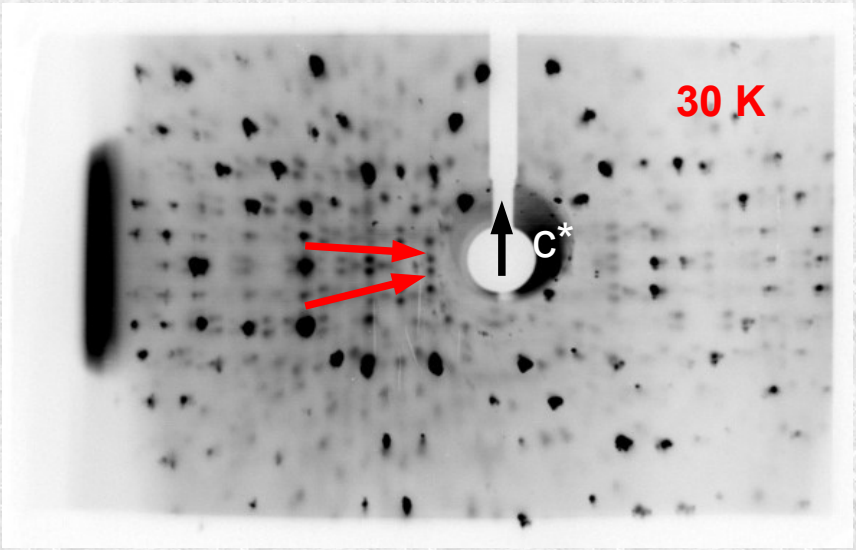
- Semiconductor at 300 K,
- Para → ferromagnetic transition below T_C = 16 K,
- No CDW transition (Peierls instability),
- Charge ordering at T_{CO} = 110-220 K,
- $q_{CO} = (2/3, 0, \approx 0.2)_O$,
- 3D CO pretransitional fluctuations already at 300 K.





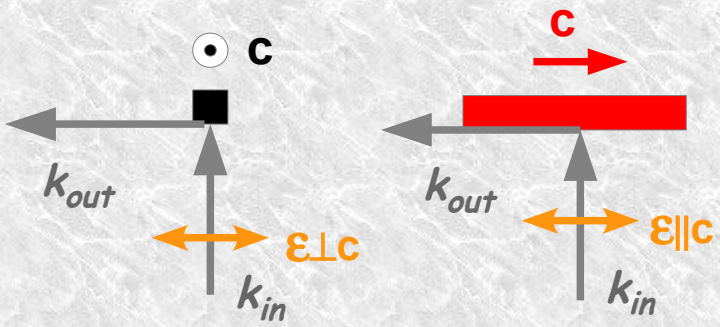


Massenet et al., MRB 1978
Yamasaki et al., JPSJ 2000

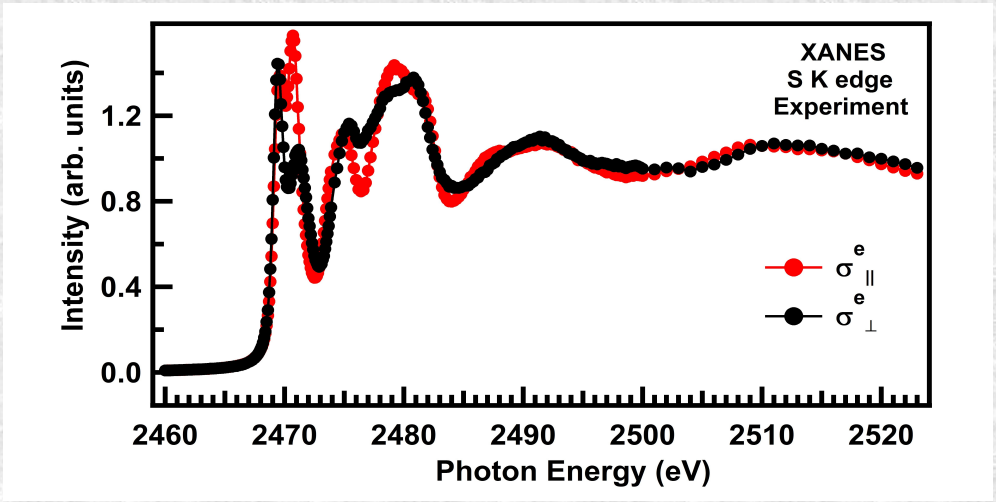


Bernu et al., EPL 2010

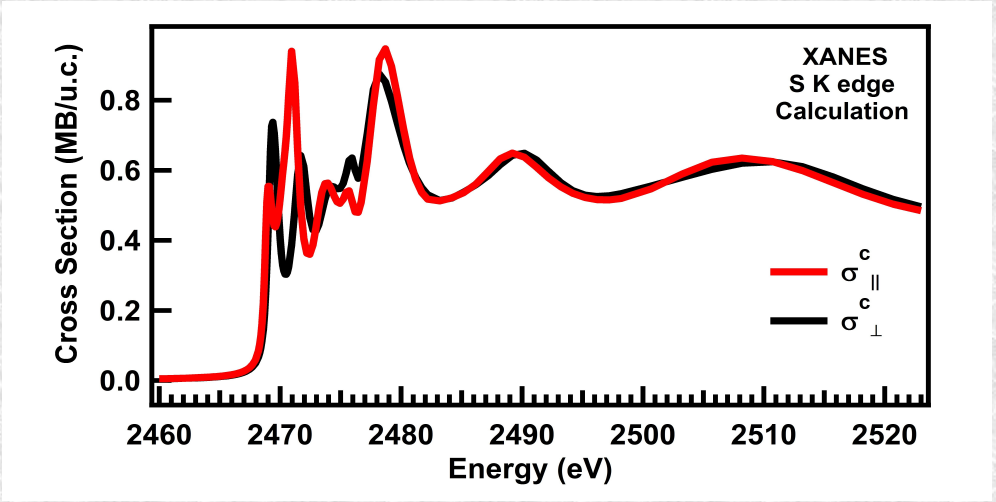
$BaVS_3$ S K-edge LUCIA/SOLEIL

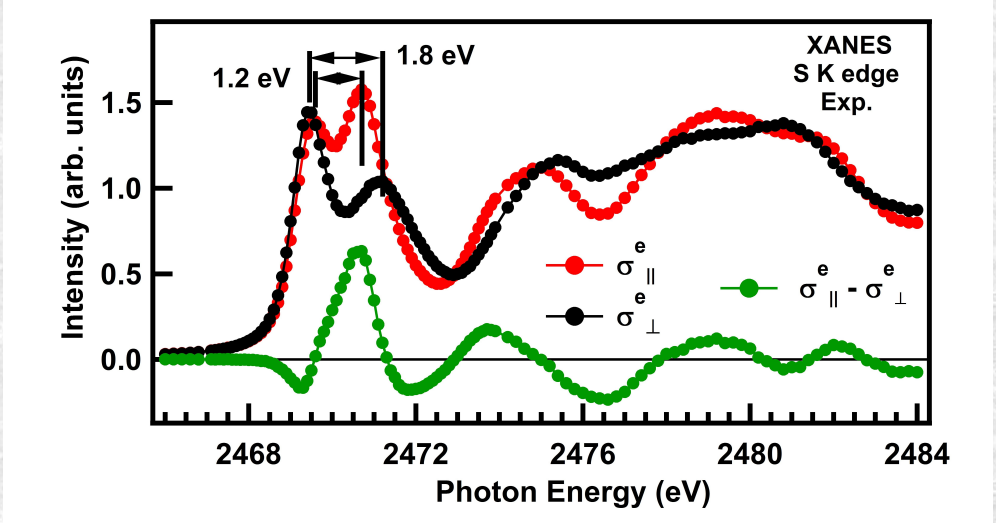


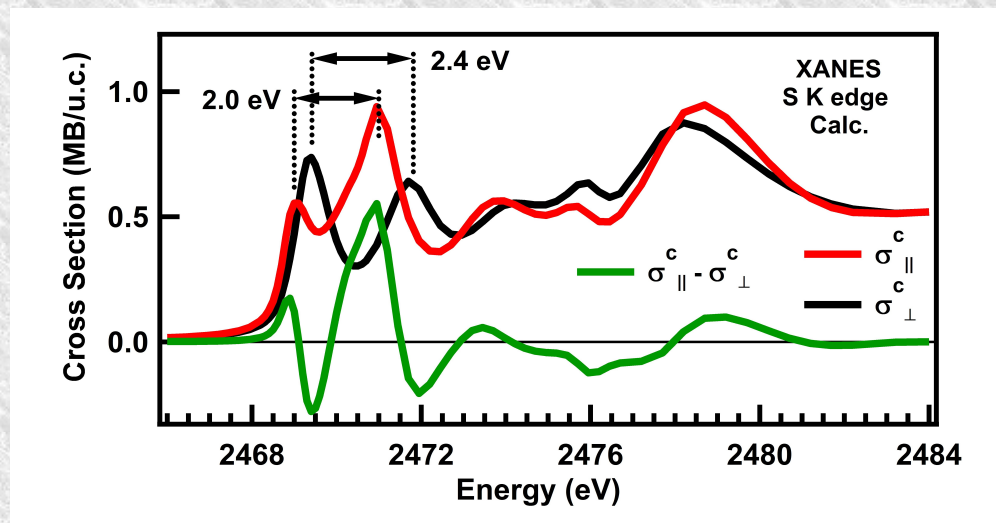
EXPERIMENT

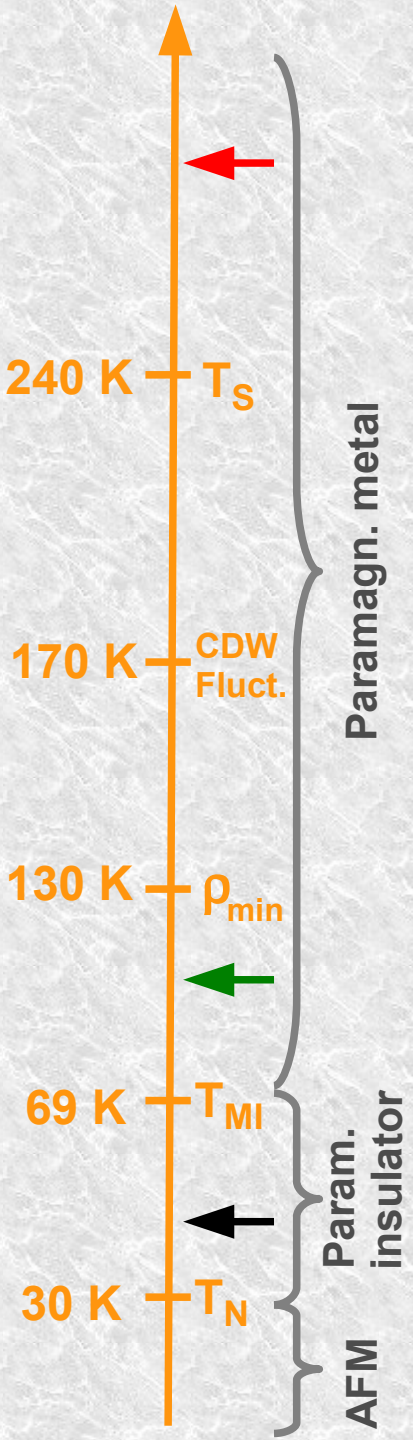


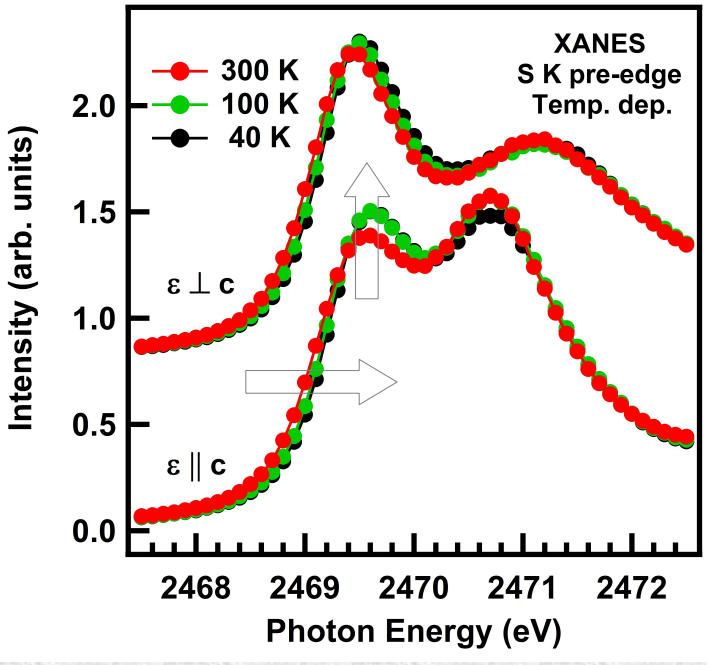
FDMNES calculation



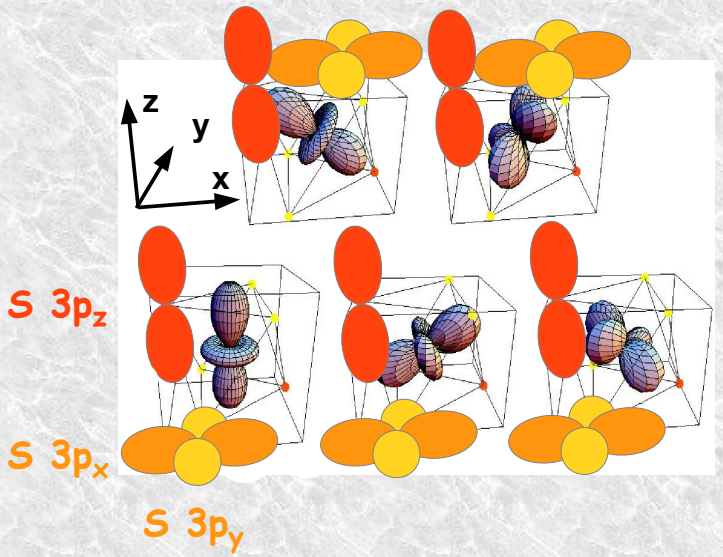


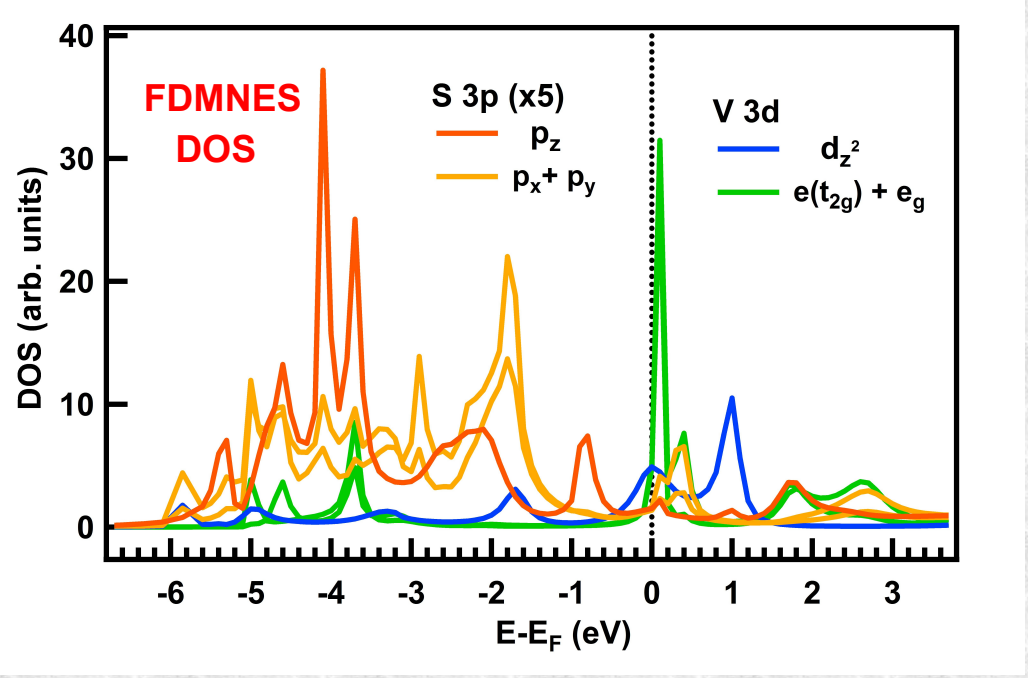






Temperature dependence, pre-edge
80 meV shift + increase for E || c





Structural « zig-zag » deformation induce depleting of active states at T > T_{MI} !

Paricularly for states Extended in z-direction

Summary and Conclusion

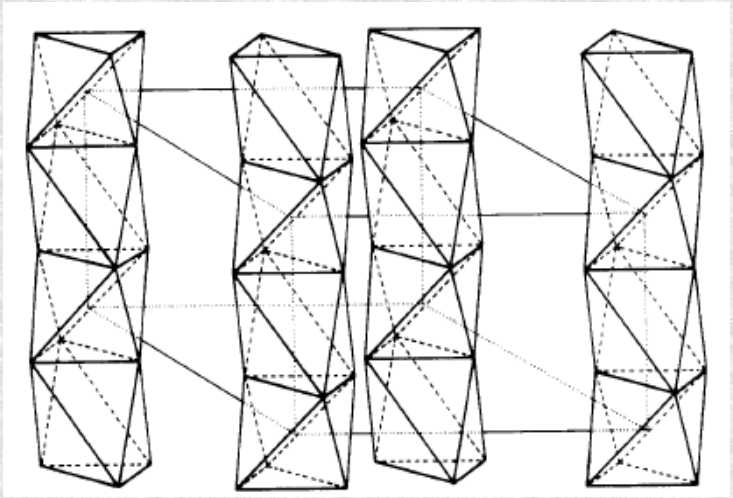
- S K edge of $BaVS_3$ is more polarization dependent compared to V L edge
→ sulfur is important actor for the quasi-1D behavior

- two pre-edge structures are identified as related to 3*d* t_{2g} and e_g states of *vanadium*

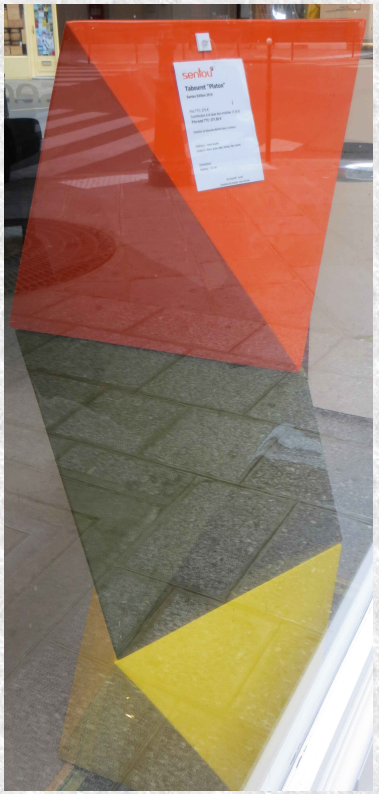
- first peak shifts to 80 meV higher energy when the temperature is lowered from 300 K to 40 K → sulfur states related to t_{2g} are modified by structural changes

- its intensity decreases for $\boldsymbol{\varepsilon \| c}$ polarization → orbitals extended in the c direction are more affected by temperature changes

$BaVS_3$ V-S octahedra chains



Stool chair
« Platon » stack

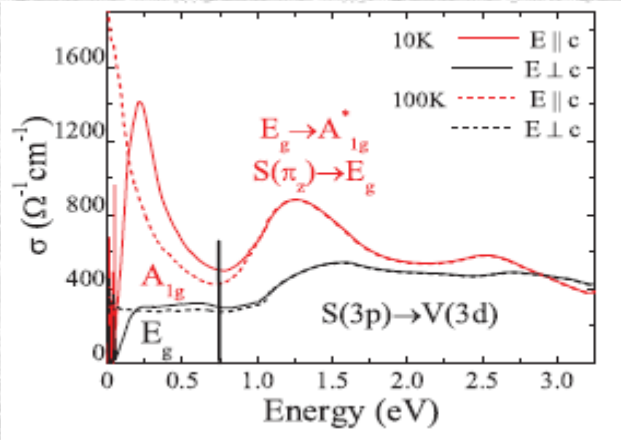


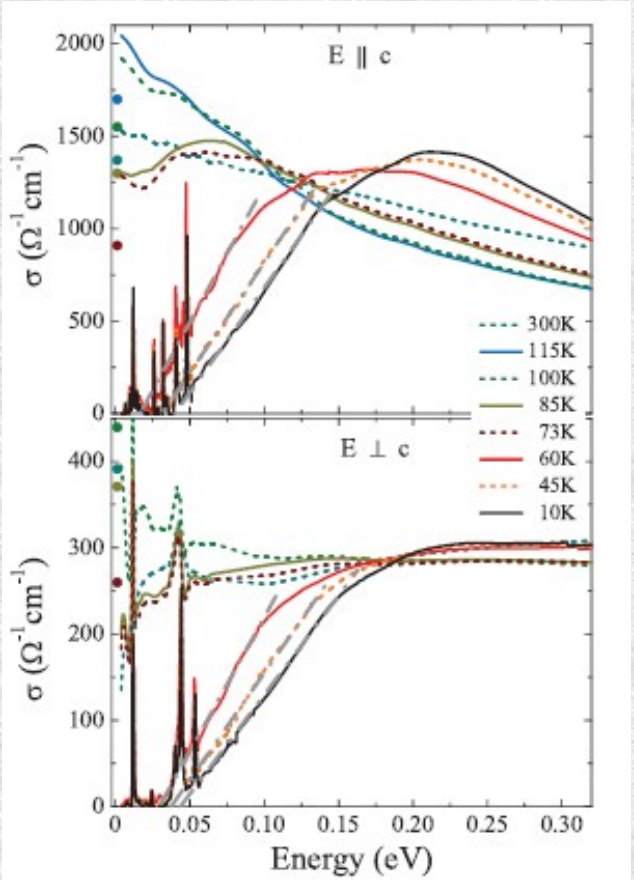
Thank you for your attention !

Optical conductivity

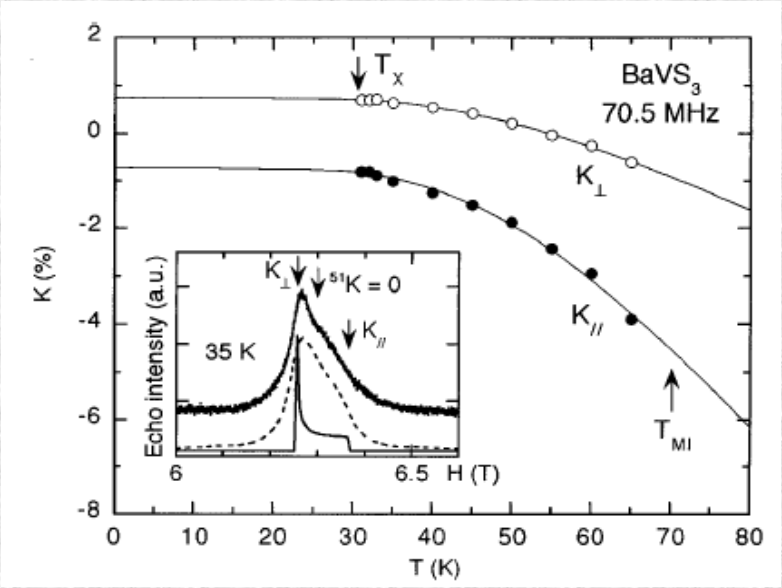
Charge gap ~ 42 meV

Kezsmarki et al., PRL 2006





^{51}V NMR and Neutrons



Spin gap ~ 10-22 meV

Nakamura et al., PRL 1997, JPCS 1999