Lecture Notes

Introduction to Strongly Correlated Electron Systems

WS 2014/ 2015

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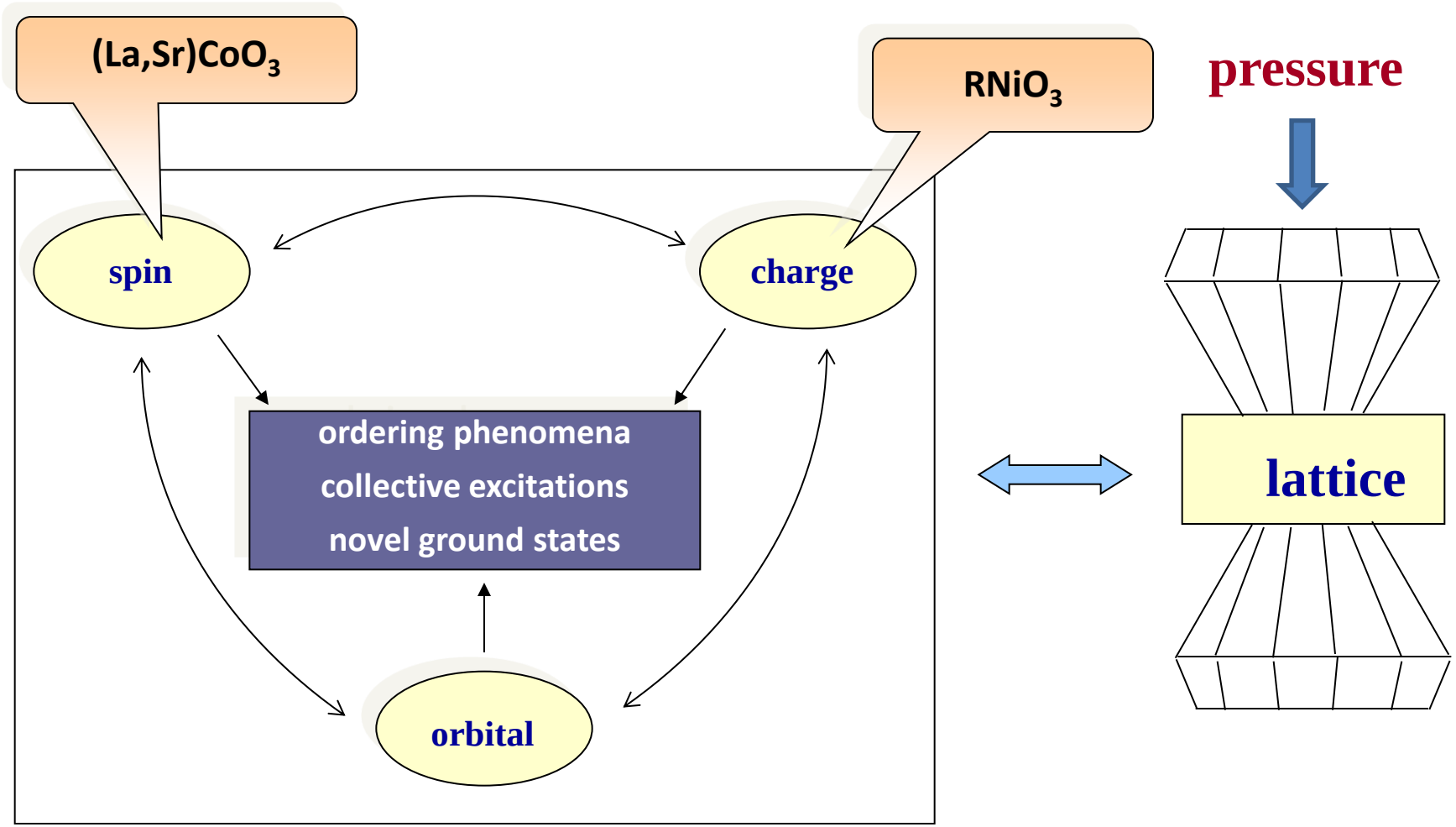
Selected correlated oxides



Investigation of the mechanism of the metal insulator transition!

Strongly correlated transition metal systems

Recent high pressure studies:

TiOCl: low dimensional spin 1/2 system (Ti^{3+}; $3d^1$) Mott insulator

Metal Cluster compounds: AM_4X_8 (A=Ga; M=Nb,Ta; X=S,Se)
a new class of Mott insulators

TiOCl

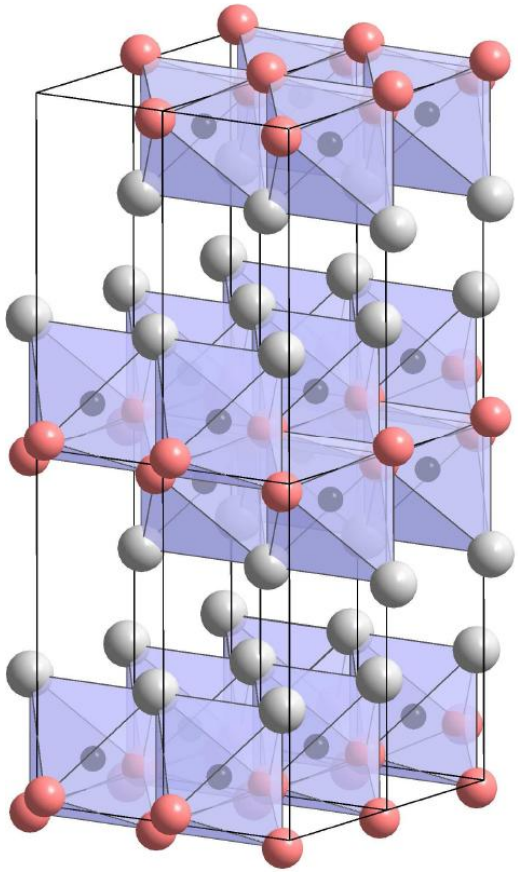
University of Cologne: structural and transport properties

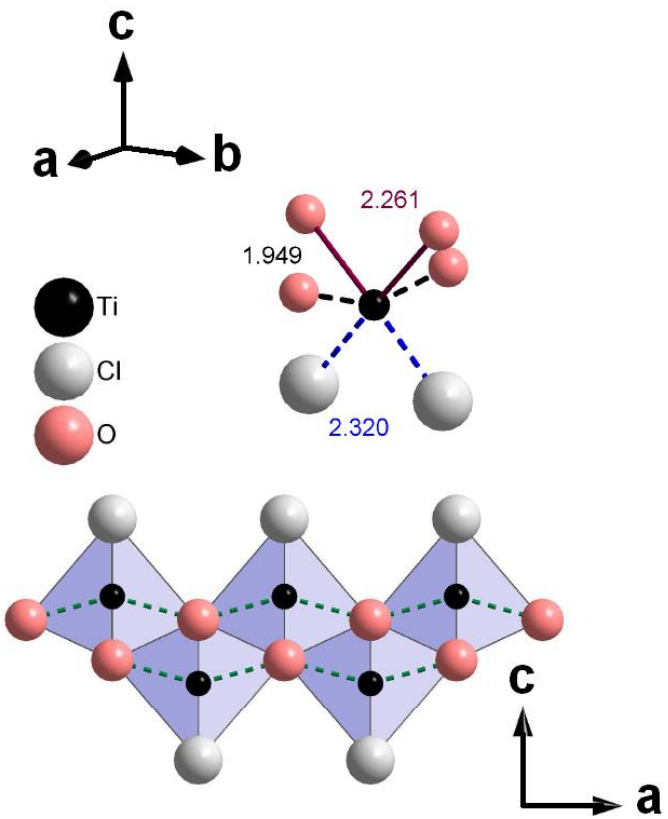
M. K. Forthaus, D. I. Khomskii, A. Möller, T. Taetz, MMA

Universidad de Santiago de Compostela: structural, magnetic properties, and theoretical description

S. Blanco-Canosa, **F. Rivadulla**, A. Piñeiro, **V. Pardo**, D. Baldomir, M. A. López-Quintela

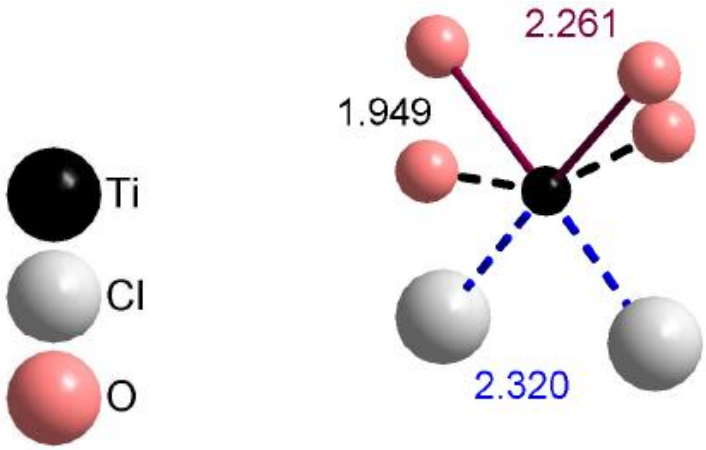
TiOCl – structural properties

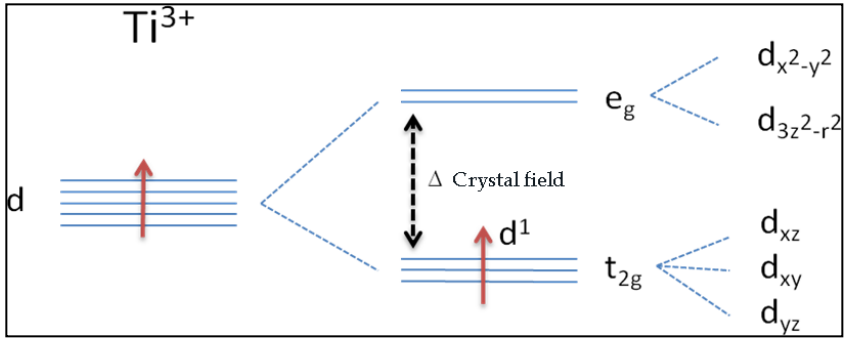


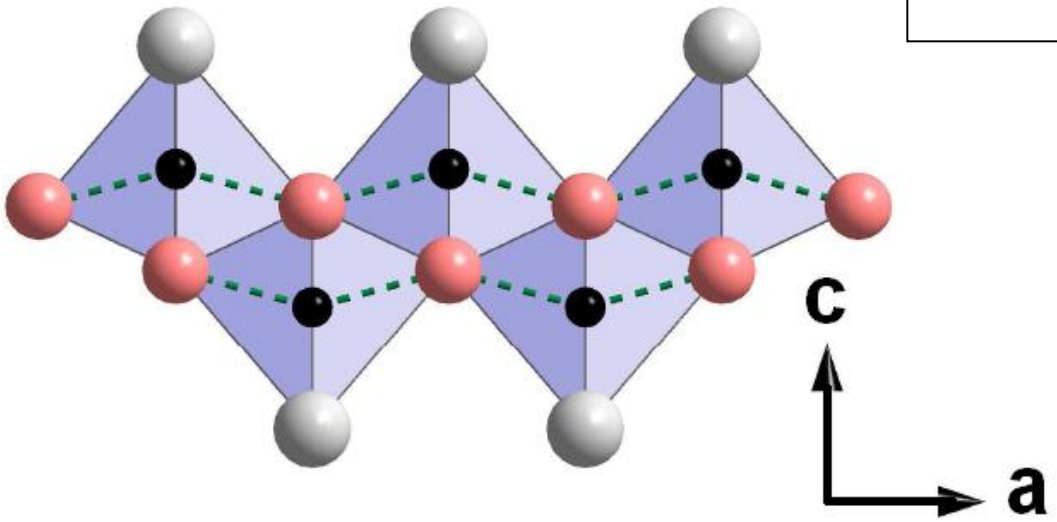


- orthorhombic FeOCl-structure (*Pmmn*)
- separated bilayers of TiO_4Cl_2-octahedra
- Formation of Ti^{3+}-chains along b-axis ($Ti^{3+} \Rightarrow 3d^1$)
- spin-1/2-chains weakly coupled by O^{2-}-chains

H. Schäfer et al., Z. Anorg. Allg. Chem. 295, 268 (1958)

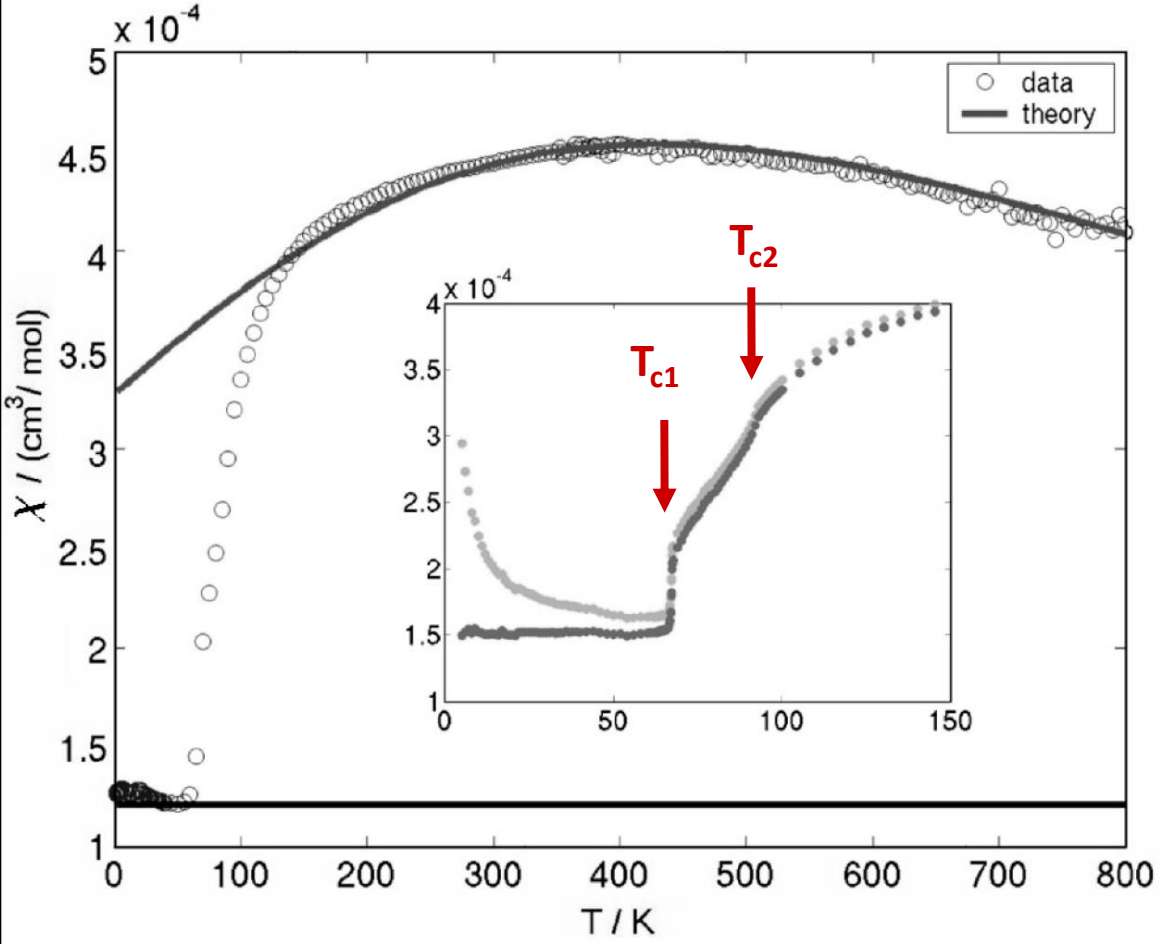

2.261
1.949
Ti
Cl
O
2.320


Ti3+
d
Δ Crystal field
d1
eg
dx2-y2
d3z2-r2
t2g
dxz
dxy
dyz


c
a

TiOCl – magnetic properties

- **high temperatures:**
  Heisenberg AF (J ~ 660K)
- **at T_{c2} = 92 K: phase transition (second order, Hemberger et al., PRB (2005))**
- **$T_{c1} < T < T_{c2}$: incommensurate phase due to interchain frustration (Rückamp et al., PRL (2005))**
- **at T_{c1} = 67 K: phase transition to nonmagnetic state (spin-Peierls transition)**
- **$T < T_{c1}$ dimerized commensurate phase**



A. Seidel et al., Phys. Rev. B 67, 020405(R) (2003)

What is **Spin-Peierls** transition?
See board!

First **Peierls** transition

Peierls transition

metal → insulator transition which occurs in 1-dimension metals with 1/2 filled band

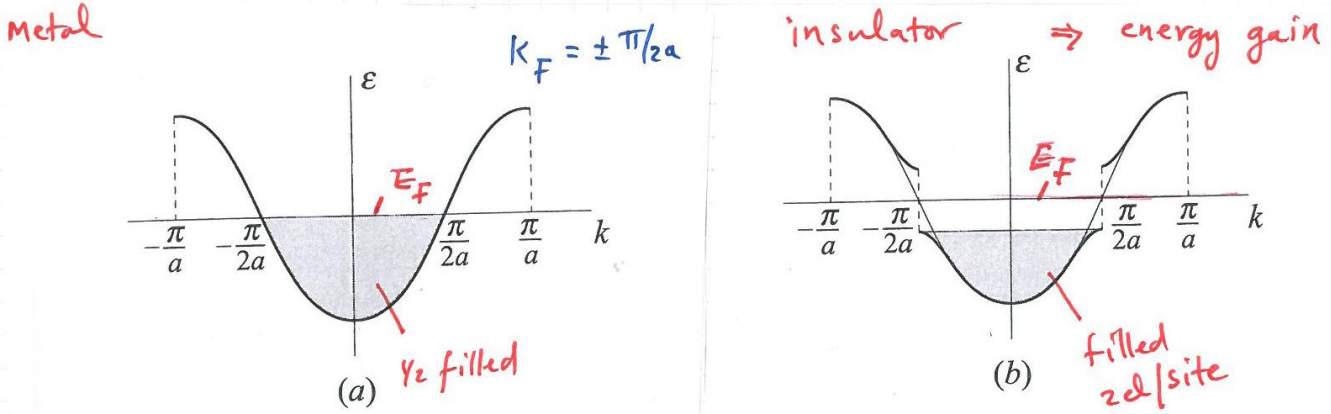
Origin: a structural transition (distortion) which leads to a doubling of the unit cell

⇒ dimerization !

- How lattice distortion leads to electron energy gain and gap ?

Consider 1-d chain with 1 electron / site and treat the electrons in th TB-approx.

⇒ Energy spectrum $\epsilon(k) = -2t \cos k a$ (t = electron-electron hopping, a lattice period)

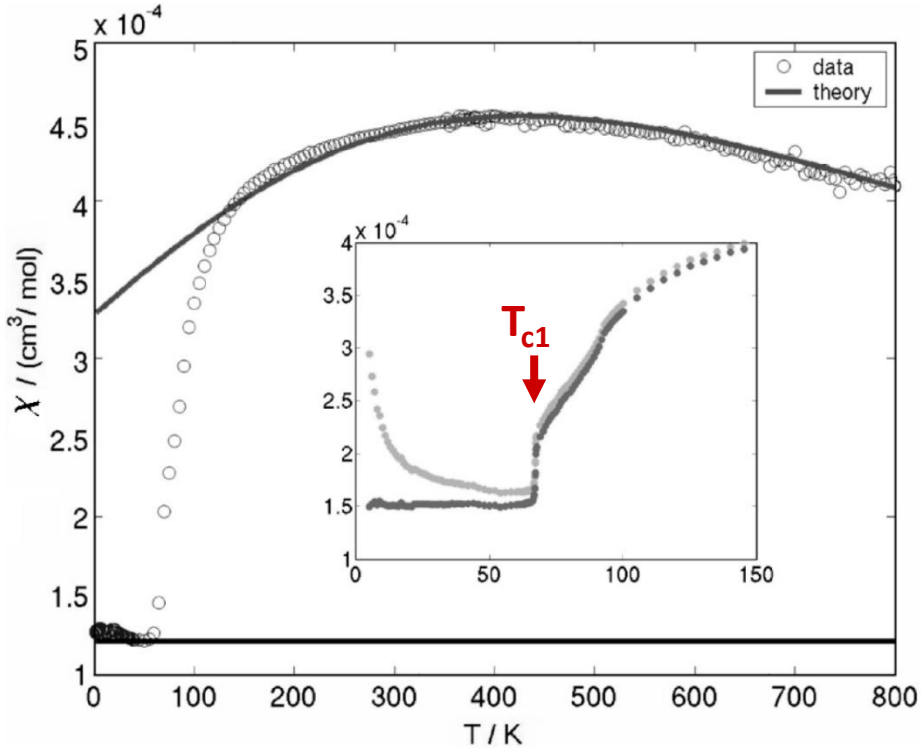


Electron energy gain, but we have to deform the lattice ⇒ elastic energy of a lattice distortion u is $\sim u^2$. However energy gain $\sim u^2 \ln u$

⇒ Electron energy gain always exceeds the elastic energy loss !

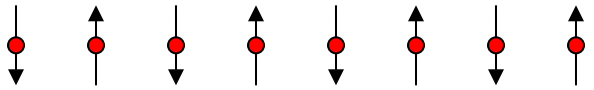
TiOCl: low-temperature phase

dimerization and magnetoelastic coupling → spin-Peierls instability !



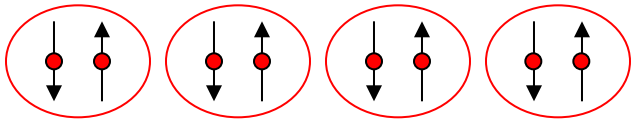
-at T_{c1} = 67 K: phase transition to nonmagnetic state (spin-Peierls transition)

- T < T_{c1} dimerized commensurate phase



S=1/2 antiferromagnetic chain

Spin-Peierls phase



formation of spin singlets S=0

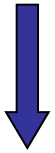
TiOCl – interesting aspects

- **low dimensional spin 1/2 system (Ti^{3+}; $3d^1$)**

  $\rightarrow$ S=1/2 layered Mott insulator

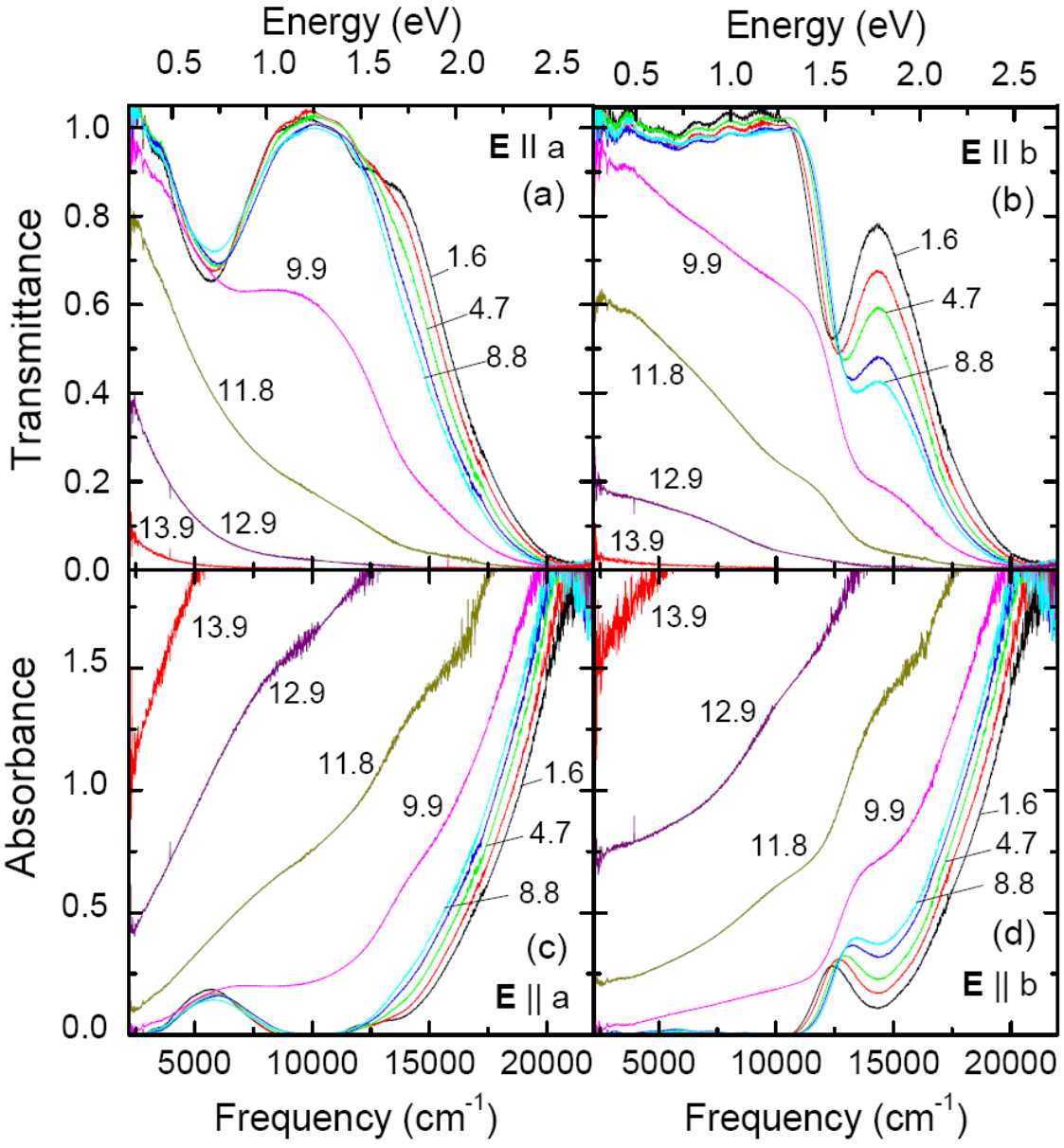
- **strong coupling of 1D antiferromagnetic chains to the lattice**

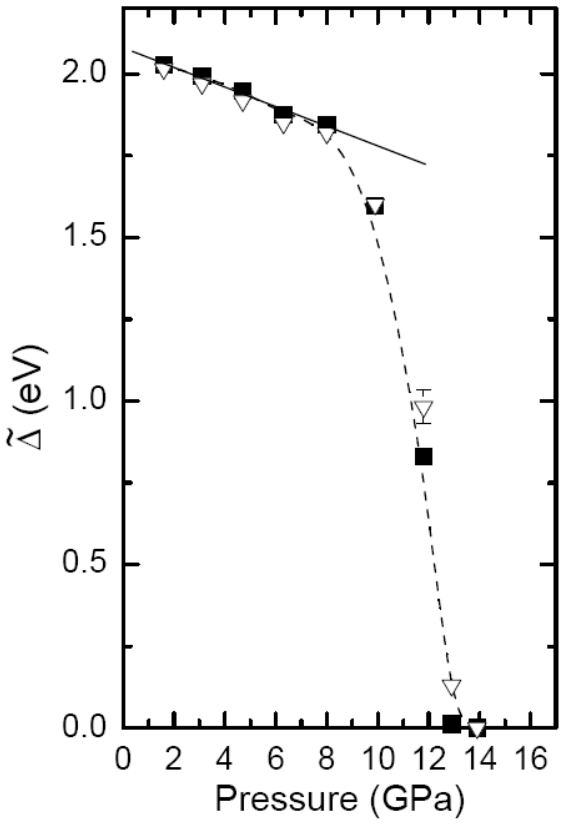
  $\rightarrow$ spin-Peierls transition and simultaneous lattice dimerization of Ti^{3+} ions



$\Rightarrow$ Promising system for the investigation of pressure-induced metal insulator transitions

effect of pressure on optical properties





Possible metal insulator transition at ~ 12 GPa !

C.A. Kuntscher et al. PRB (2008): connected to structural phase transition!

C. A. Kuntscher et al., Phys. Rev. B 74, 184402 (2006)

aim of this work

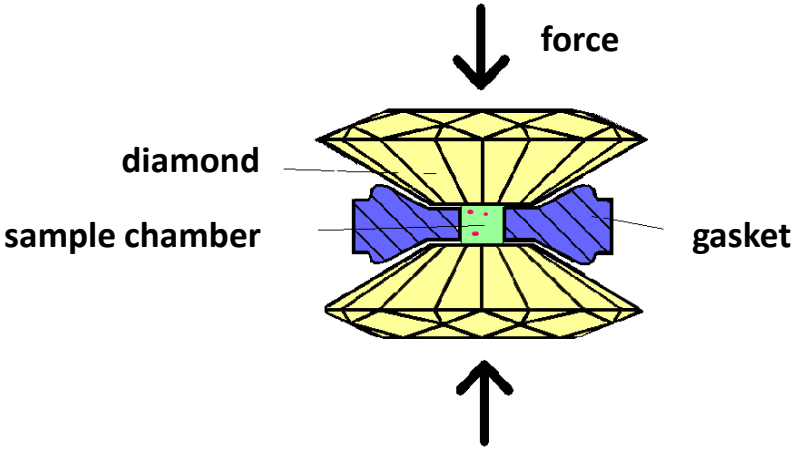
Effect of pressure on the electrical transport and structural properties of TiOCl

Experimental techniques:

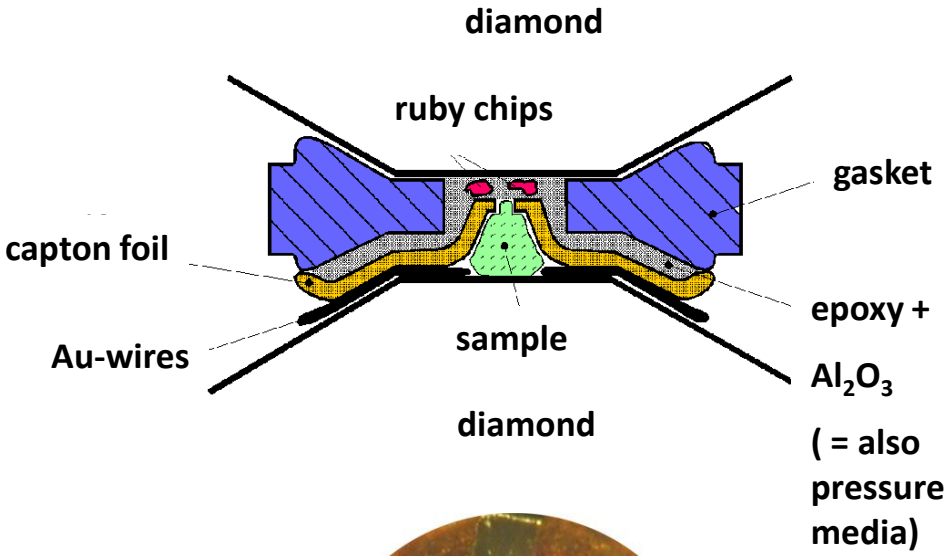
- electrical resistivity up to ~ 25 GPa
- x-ray diffraction:
  - energy dispersive XRD up to ~ 8 GPa (MAX 80) / ~ 17 GPa
  - **angle dispersive XRD up to ~ 15 GPa**
- EXAFS (Ti K edge) up to ~ 20 GPa
- **magnetic susceptibility up to 1 GPa (teflon cell in SQUID)**

Experimental setup: Diamond Anvil Cell

x-ray diffraction



resistivity measurements

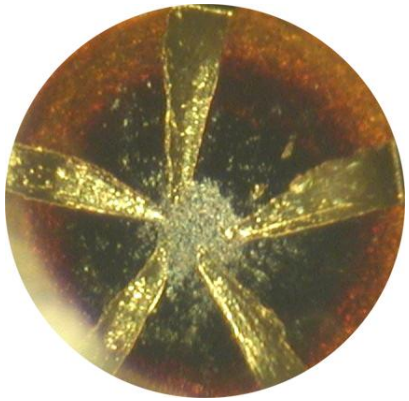


sample chamber Ø = 100 - 300µm;

height: 25-50 µm

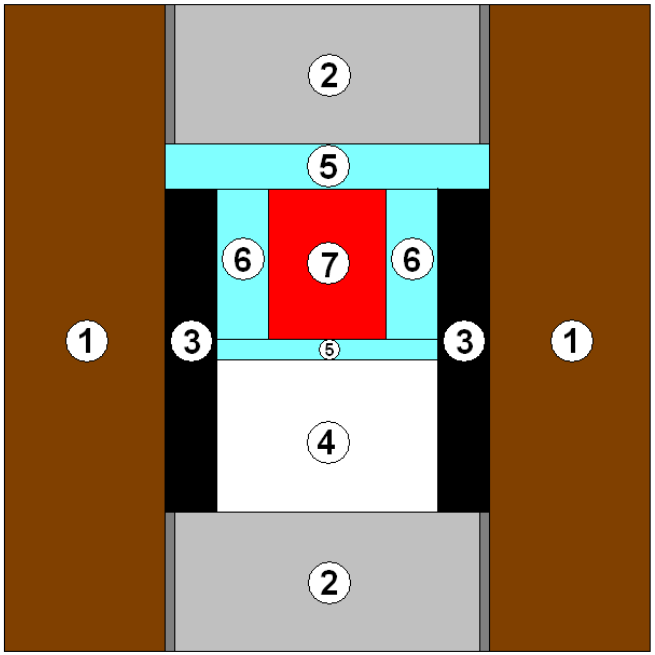
$p_{max} \approx 100$ GPa (= 1 Mbar)

Pressure media: e.g. **Methanol:Ethanol 4:1**, liquid Nitrogen, liquid Argon, liq. Helium, Oil, Epoxy, etc.



sample chamber Ø ≈ 100 µm

Experimental setup: MAX 80 at F2.1, HASYLAB



1) Boron-Epoxy cube

2) steel-ring with pyrophilite

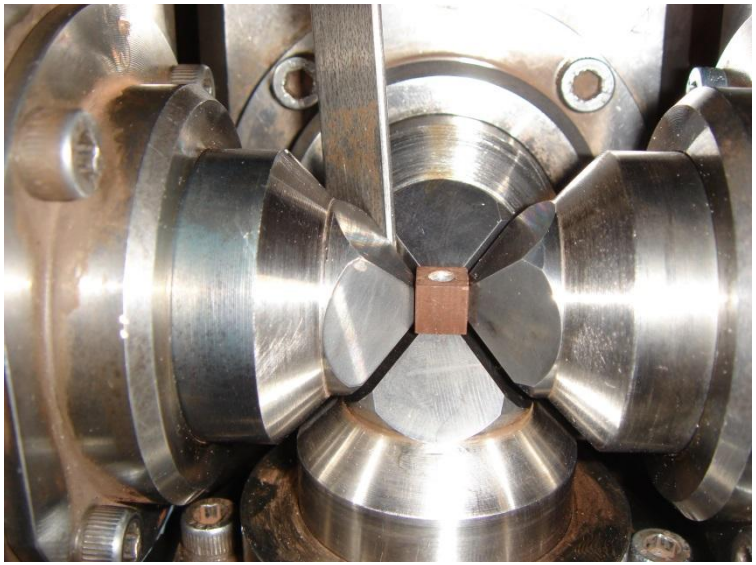
3) graphite cylinder

4) NaCl

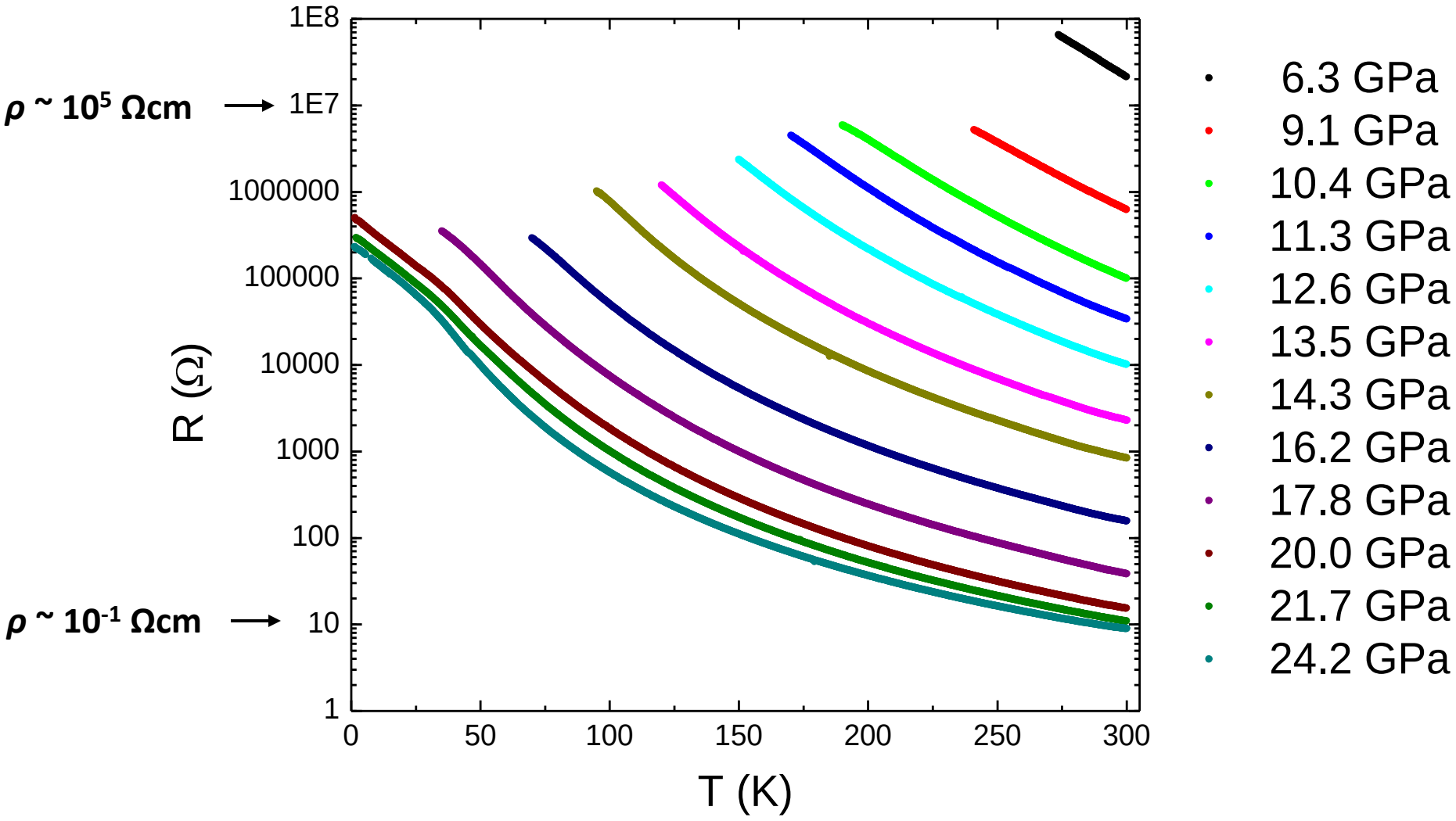
5) BN powder

6) BN cylinder

7) SAMPLE

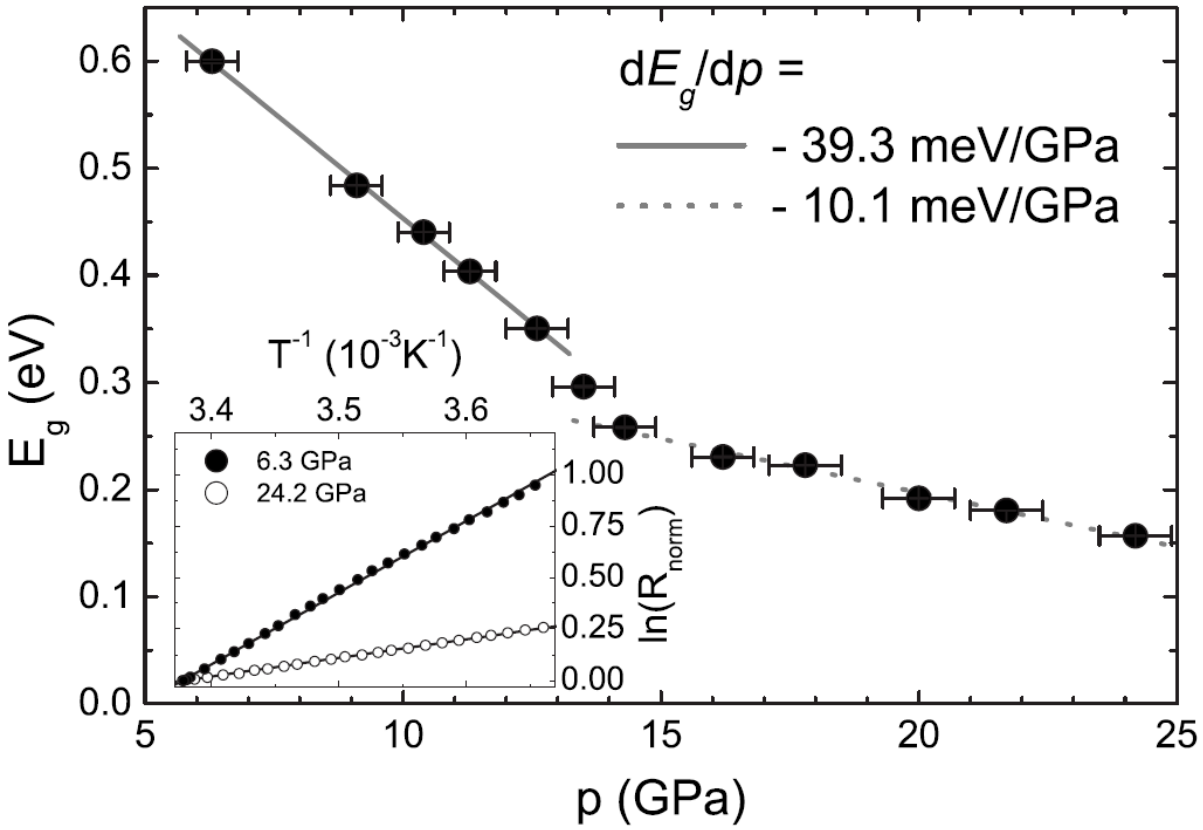


electrical transport under pressure

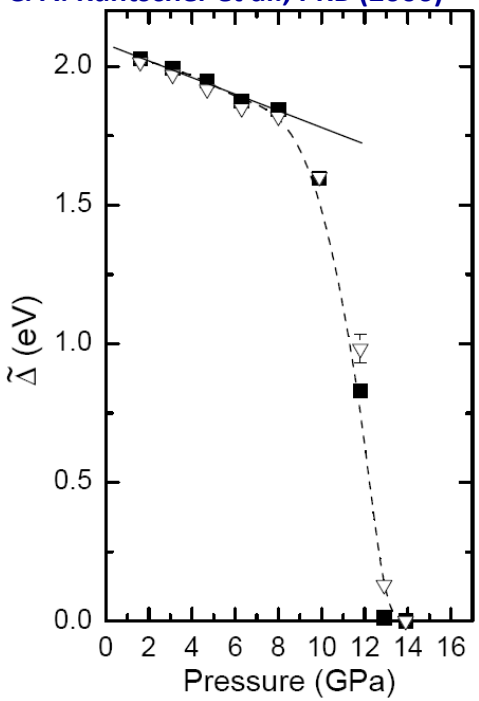


- **dramatic reduction of R_{294K} with pressure - more than 6 orders of magnitude**
- **Temperature dependence: no metallic behaviour up to 24.2 GPa**

energy gap $E_g(p)$ at room temperature



C. A. Kuntscher et al., PRB (2006)



abrupt change of pressure dependence of $E_g(p)$ at ~ 12 GPa:
Slope of $E_g(p)$ decreases by a factor of 4!

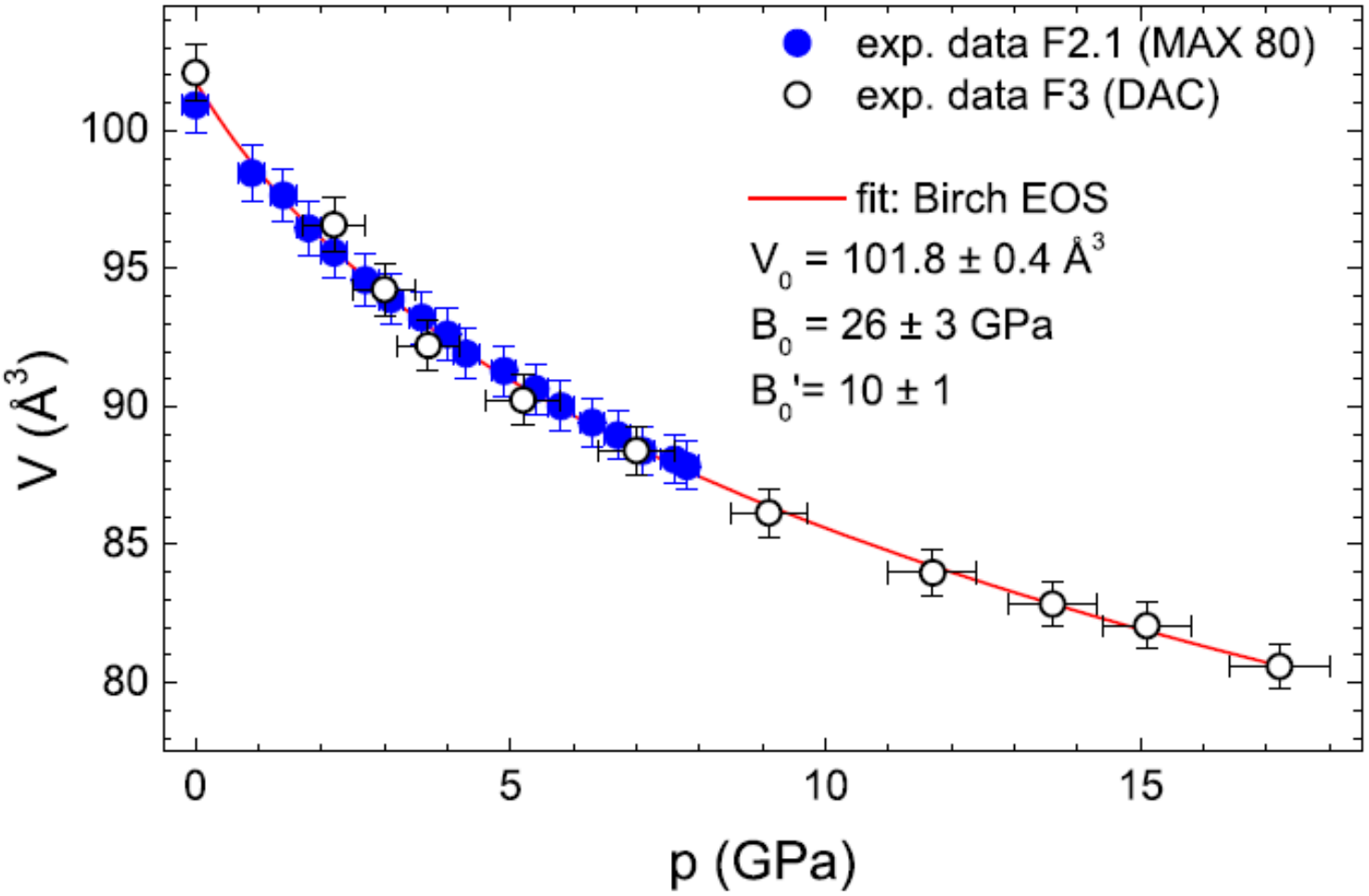
- **drastic change of the electronic properties above 12 GPa !**
- **but no metallic state up to ~ 24 GPa !**

What drives the pressure-induced electronic phase transition ?

Structural instability due to layered structure under pressure?

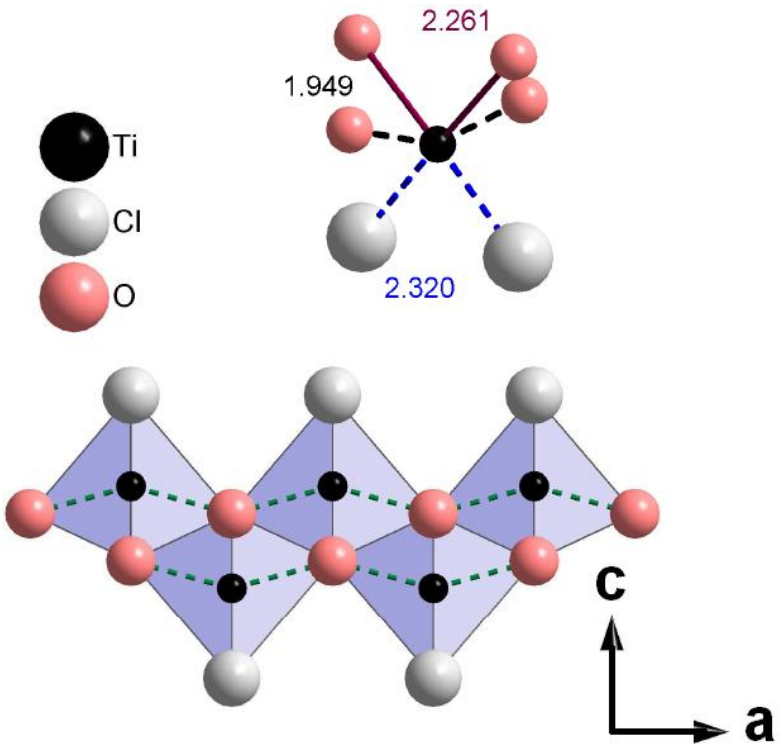
pressure dependence of the volume at room temperature

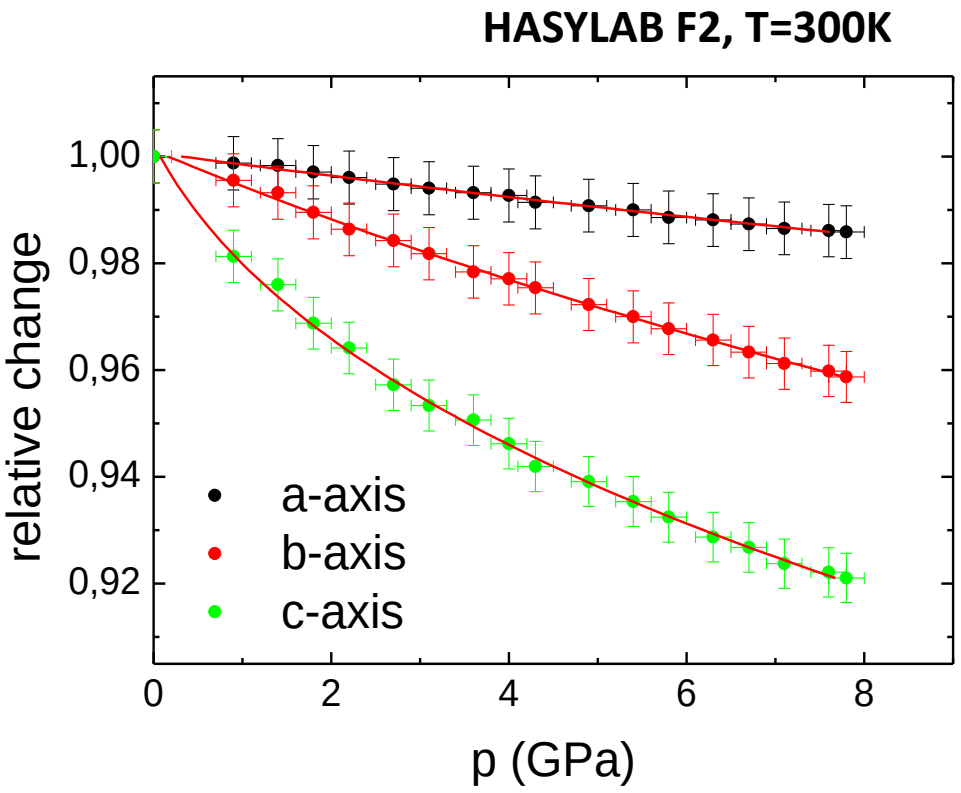
HASYLAB F2.1 (MAX 80) and F3 (DAC), T=300K, EDXRD



small Bulk modulus
no indication of a structural phase transition up to ~ 17 GPa within the experimental resolution

pressure dependence of a-, b- and c-axis at room temperature



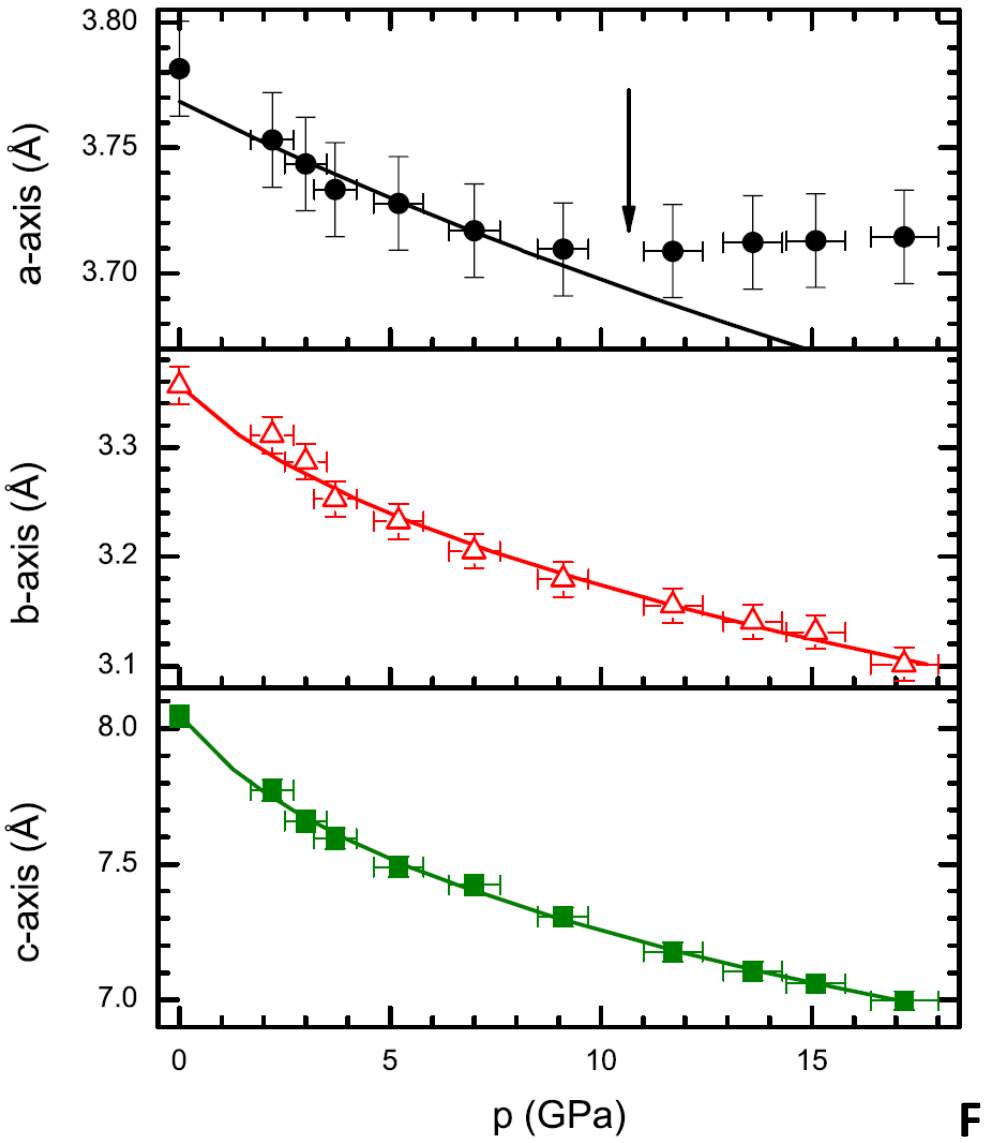


$B_a/B_c \approx 15 \Rightarrow$ extreme large anisotropy

structural instability - consequence:
Possibility of structural phase transition at higher pressure?
$\Rightarrow$ driving mechanism of electronic phase transition above 13 GPa?

pressure dependence of the lattice parameters at room temperature

connection between structure and electrical transport:



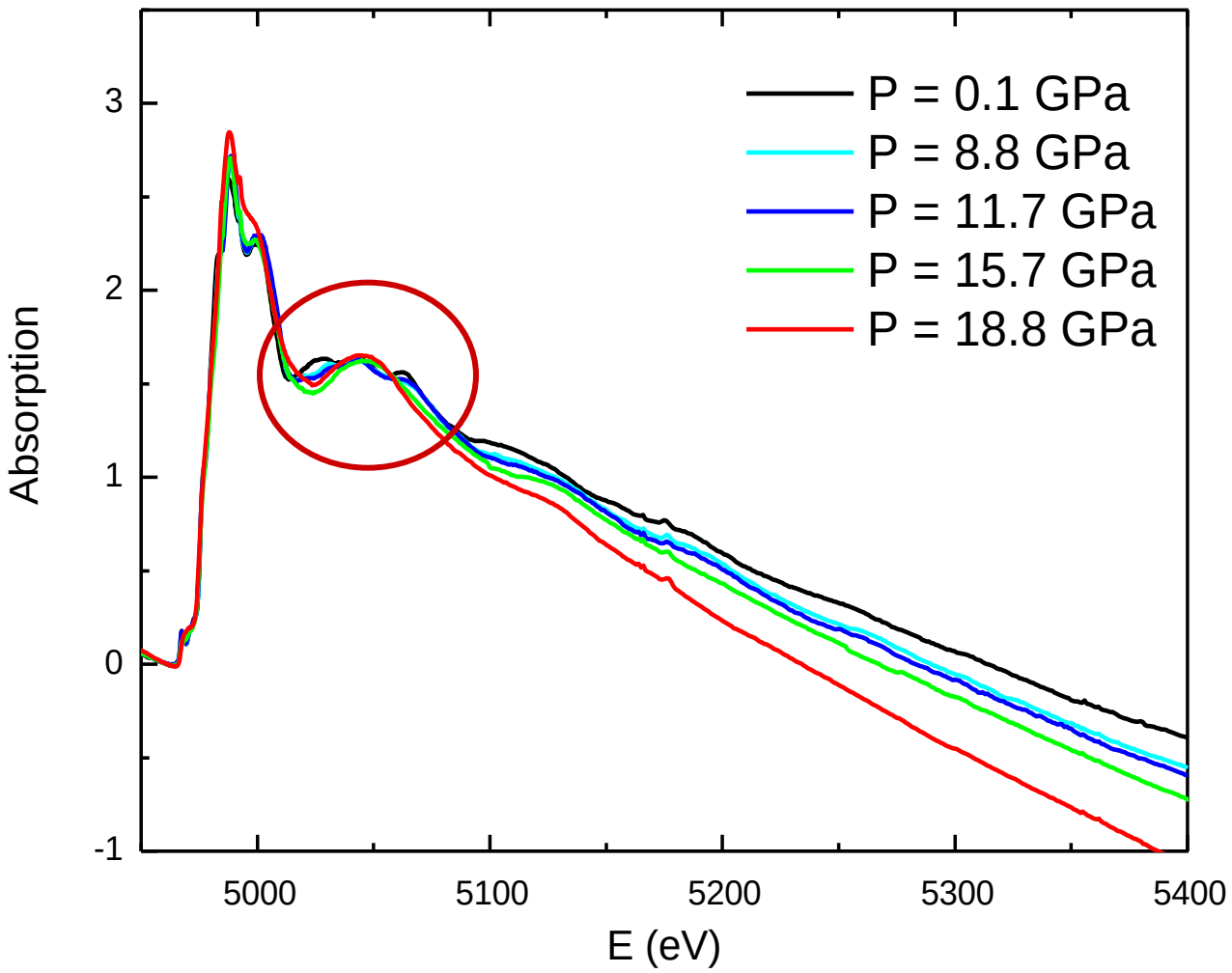
simple picture:
direct hopping (Ti-Ti) along *b*
indirect hopping (Ti-O-Ti) along *a*

anomaly of the *a*-axis above 10 GPa strongly affects the indirect hopping (Ti-O-Ti) and transport along *a*
⇒ **anomaly in $E_g(p)$!**

Further structural studies required!

Extended X-ray Absorption Fine Structure (EXAFS)

EXAFS
→ informations about:
- **numbers and distances of next neighbors of Ti**
- **Ti-Ti distances**

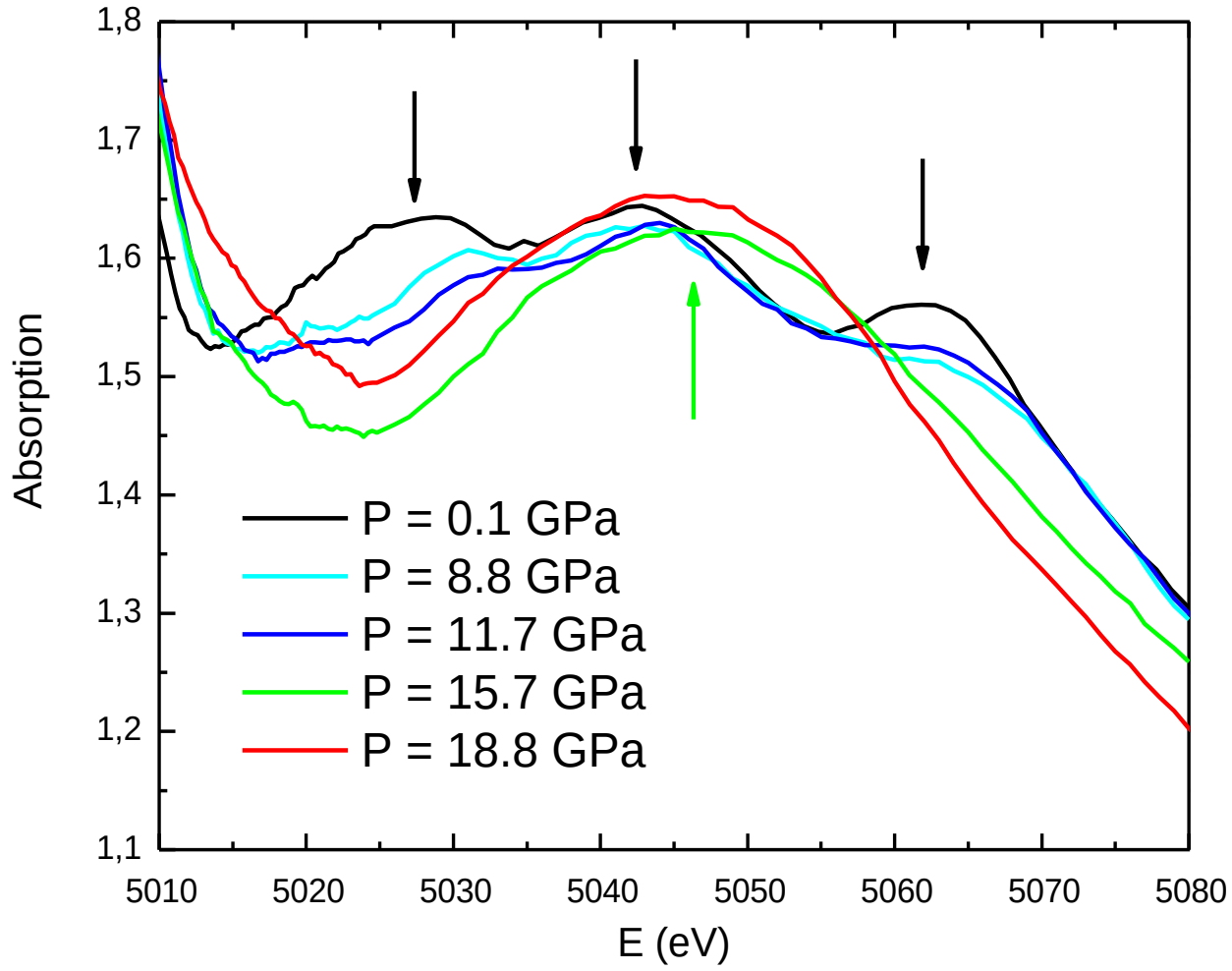


local structure under pressure probed by EXAFS (Ti K-Edge)

J.-P. Itié and A. Polian (2007)

SLS, LUCIA Beamline, T = 300K

Extended X-ray Absorption Fine Structure (EXAFS)



GOOD NEWS!

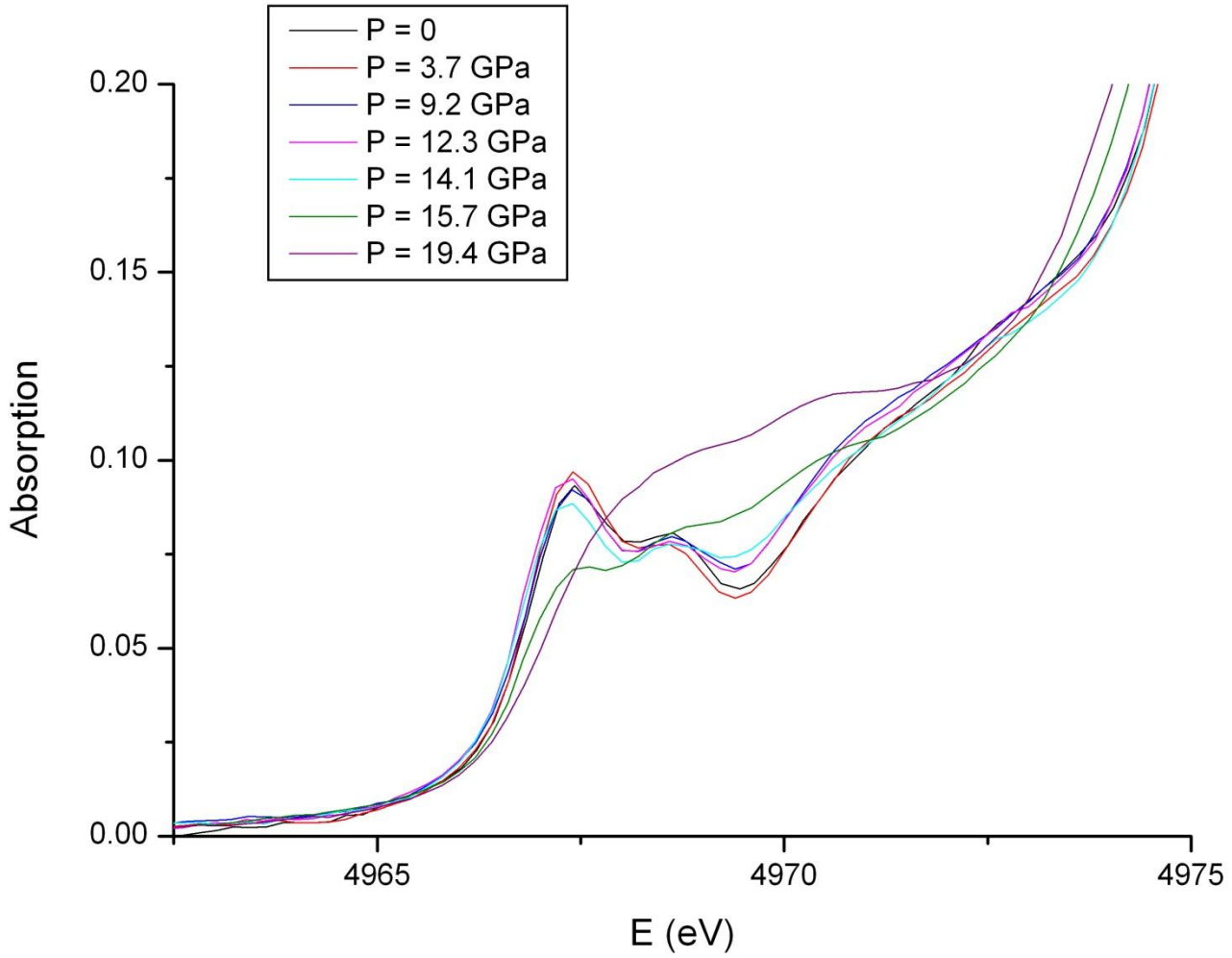
Significant modification of EXAFS signal

$\Rightarrow$ change in local structure around Ti atoms above 12 GPa!

J.-P. Itié and A. Polian (2007)

SLS, LUCIA Beamline, T = 300K

pre-edge (EXAFS)



GOOD NEWS!

Significant modification of the pre-edge part of EXAFS
$\Rightarrow$ change of electronic structure above 12 GPa!

J.-P. Itié and A. Polian (2007)

SLS, LUCIA Beamline, T = 300K

Extended X-Ray Absorption Fine Structure (EXAFS)

bad news:

no quantitative analysis possible!

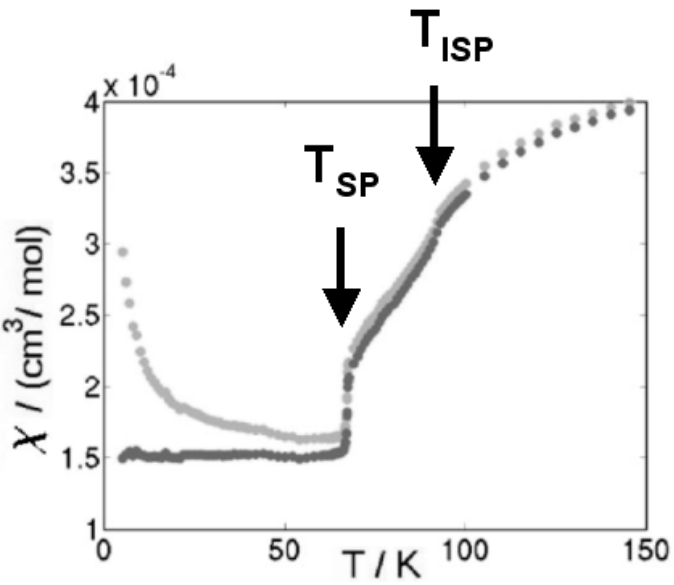
EXAFS signals: main problem → positional beam instability

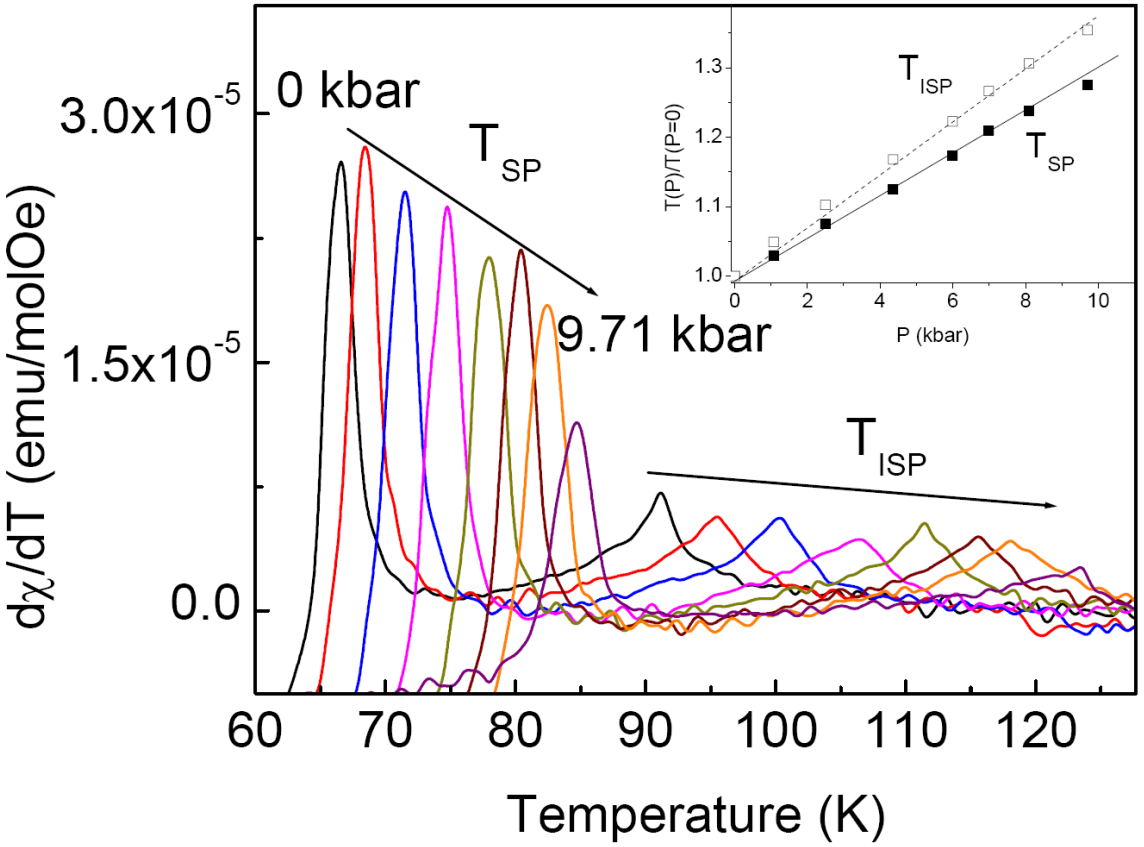
⇒ different amplitudes of EXAFS wiggles

⇒ inaccurate analysis

pre-edge structure: **analysis requires solid work on ab-initio calculations**

pressure dependence of spin-Peierls transition T_{SP}





TiOCl: $\partial \ln T_{SP}/\partial p = 2.88 \cdot 10^{-1} GPa^{-1}$, $\partial \ln T_{ISP}/\partial p = 3.64 \cdot 10^{-1} GPa^{-1}$
(TiOBr: $\partial \ln T_{SP}/\partial p = 3.4 \cdot 10^{-1} GPa^{-1}$, Fausti et al., PRB (2007))

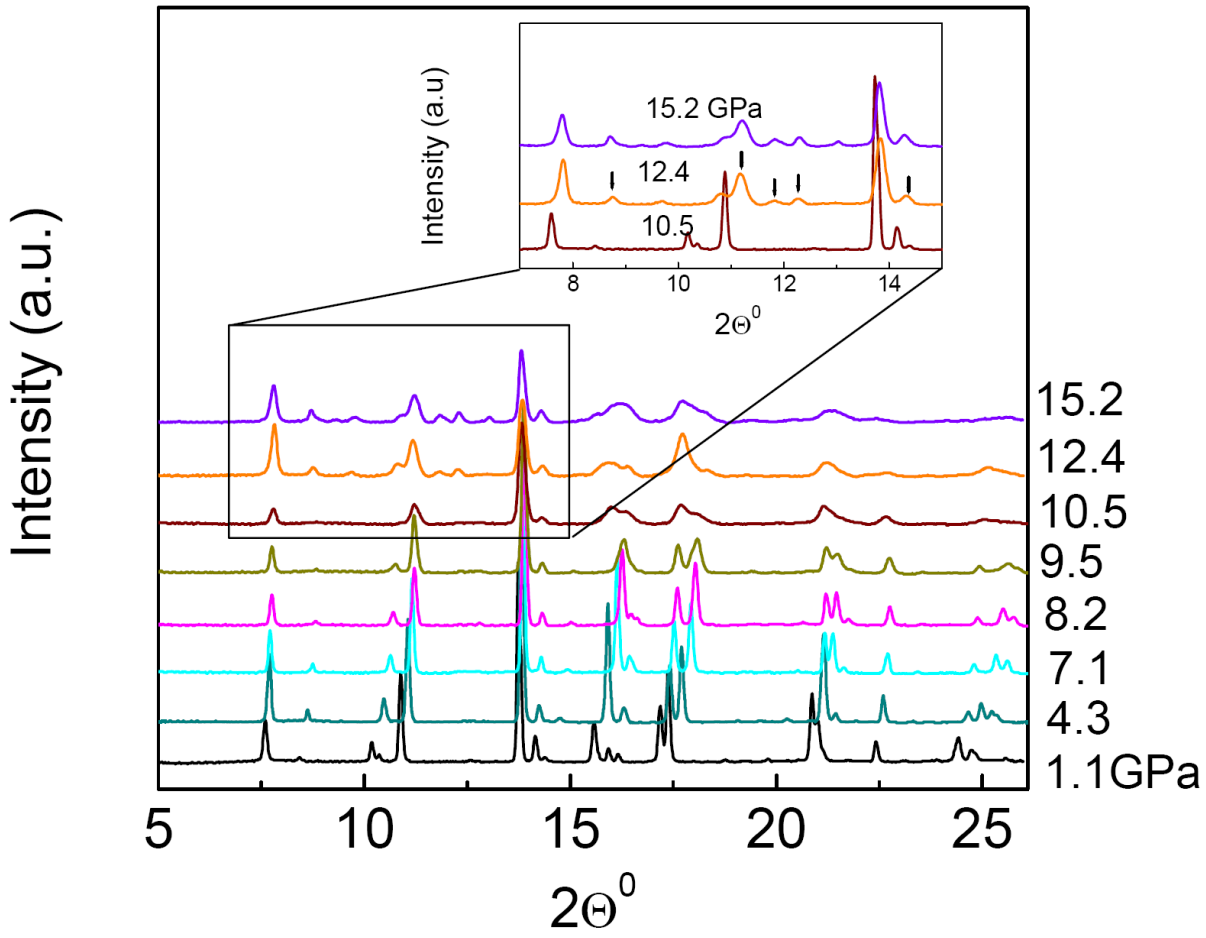
T_{SP} strongly increases with pressure

$\Rightarrow$ consistent with enhanced dimerization at 300 K!

S. Blanco-Canosa et al., arXiv/cond-mat 0806.0230 (2008); PRL (2009)

angle dispersive x-ray diffraction

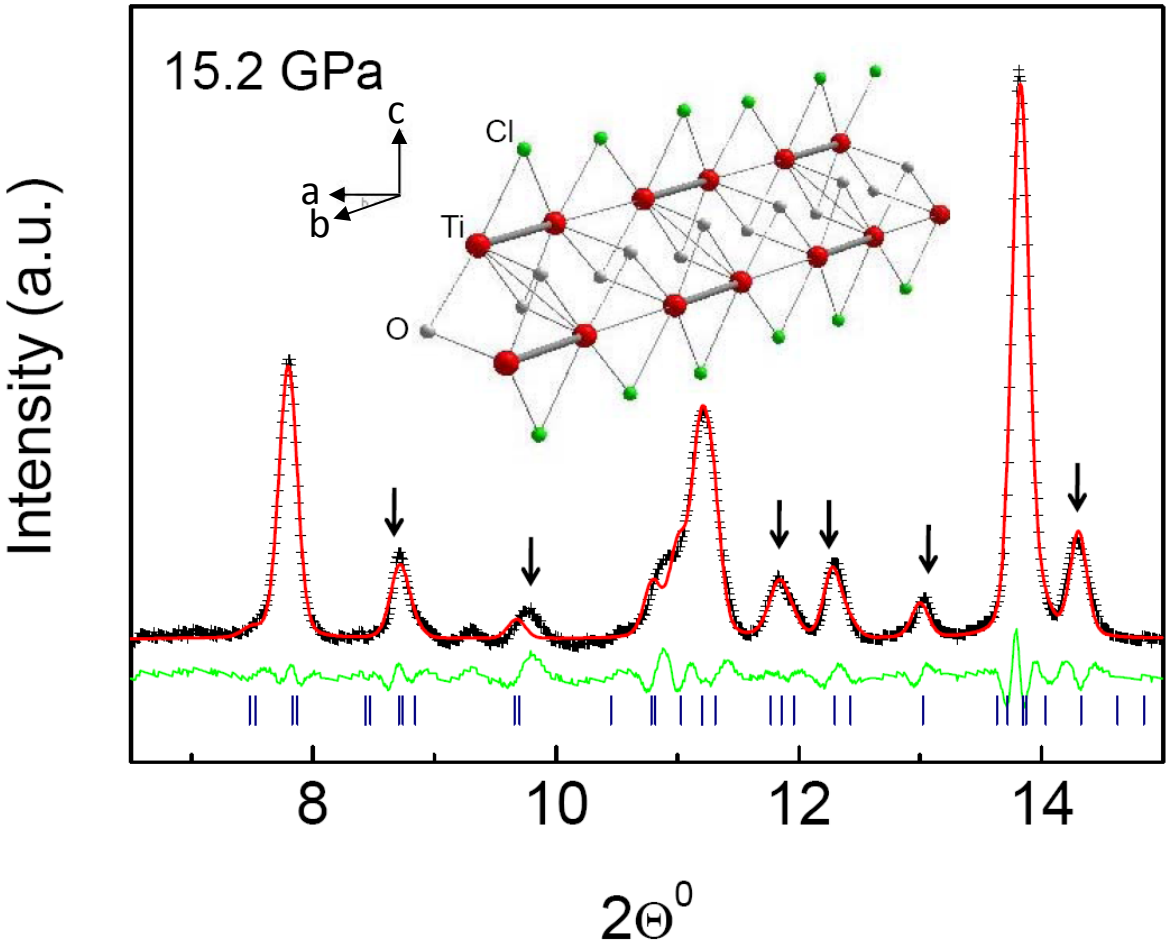
Daresbury Synchrotron Radiation Source (Warrington, UK)



pressure-induced structural phase transition above 11 GPa!

S. Blanco-Canosa et al., arXiv/cond-mat 0806.0230 (2008); PRL (2009)

Rietveld refinement: structural phase transition (orthorhombic *Pmmn* → monoclinic $P2_1/m$)



Two inequivalent Ti^{3+} sites along the *b* direction in monoclinic $P2_1/m$:
Ti-Ti (short): 2.95 Å
Ti-Ti (long): 3.69 Å
→ Δd ~ 20 %

(ambient pressure: Δd ~ 5 % at low T)

⇒ enhanced dimerization under pressure at 300 K!

Theoretical description of structural and electronic proerties of TiOCl under high pressure

Victor Pardo

Ab initio studies at high pressure on TiOCl: electronic structure of the orthorhombic and monoclinic phases

Gap evolution

Value near experiment

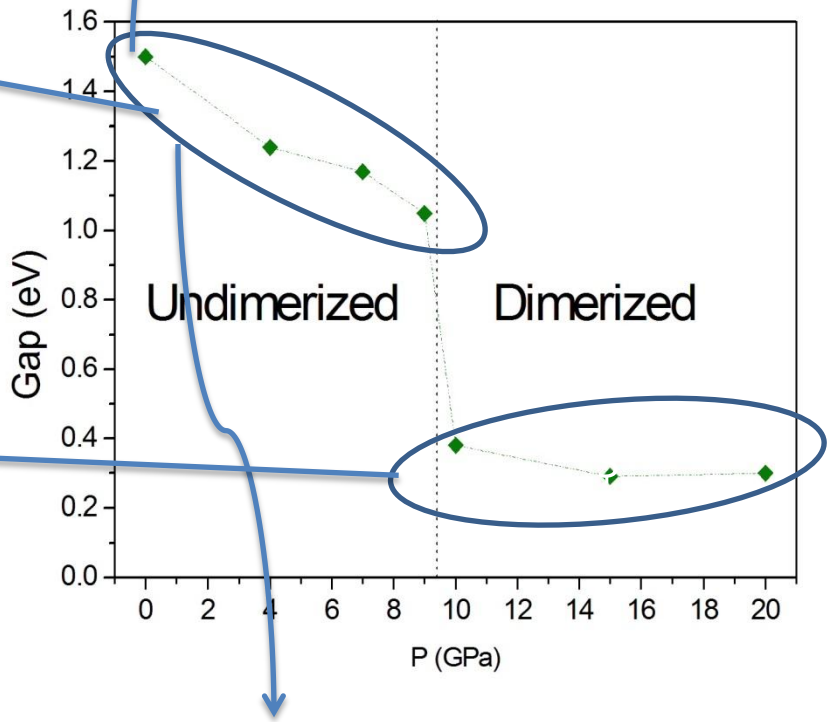
Decrease of the gap ~ 30%
In orthorhombic structure

In concordance with experimental data (resistivity measurements):

M.K. Forthaus et al., Phys. Rev. B 77, 165121 (2008)

Drastic reduction of the gap:
Structural transition

In concordance with experiment



We would need more than 30 GPa to get an insulator-to-metal transition in orthorhombic structure!!

Ab initio studies at high pressure on TiOCl: electronic structure of the orthorhombic and monoclinic phases

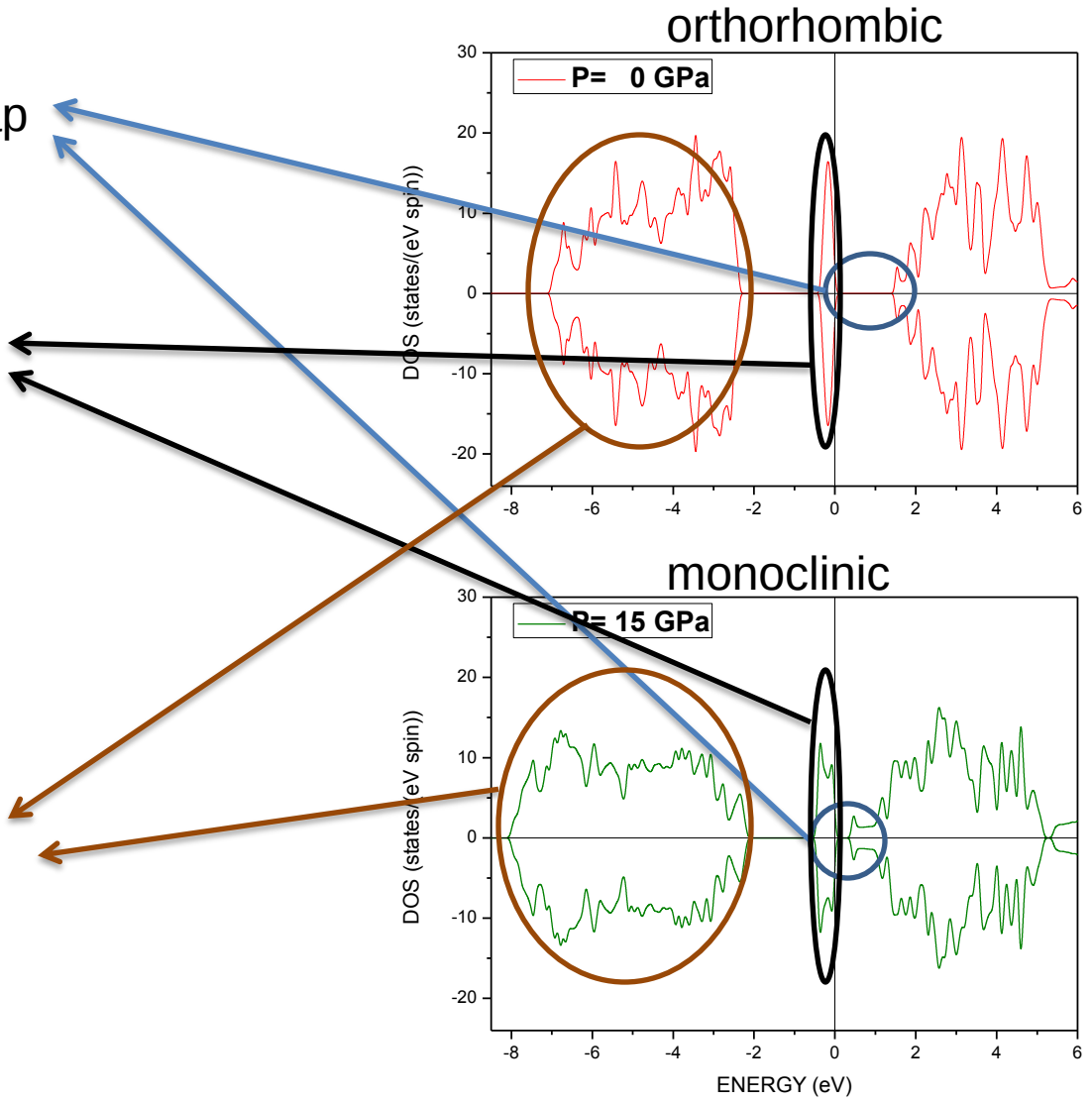
Drastic reduction of the gap (from 1.5 eV to 0.3 eV)

States of d^1 electron of Ti are good localized in a ~ 1 eV band near Fermi energy

Mot-Hubbard type gap (d-d gap)

Increase ~20% of the bandwith

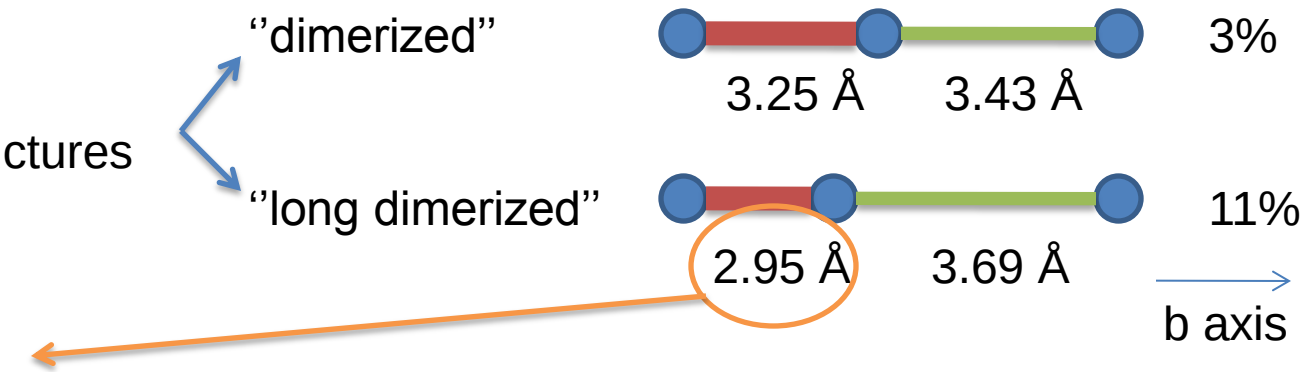
Oxygen bands are in energies down than -2 eV



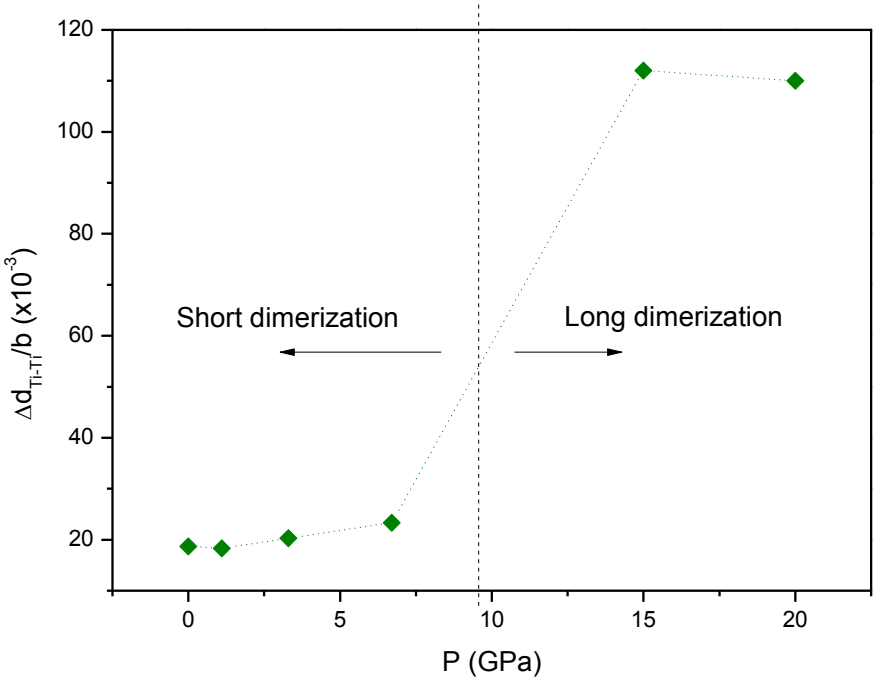
Ab initio studies at high pressure on TiOCl: electronic structure of the orthorhombic and monoclinic phases

Monoclinic space group:
2 types of dimerized structures

Ti atom



Close to metal Ti bond length!!!
Limit for electron-itinerancy
Spin-Peierls distortion is expected to be supported by a conventional Peierls distortion of the 1D chain



Strongly correlated transition metal systems

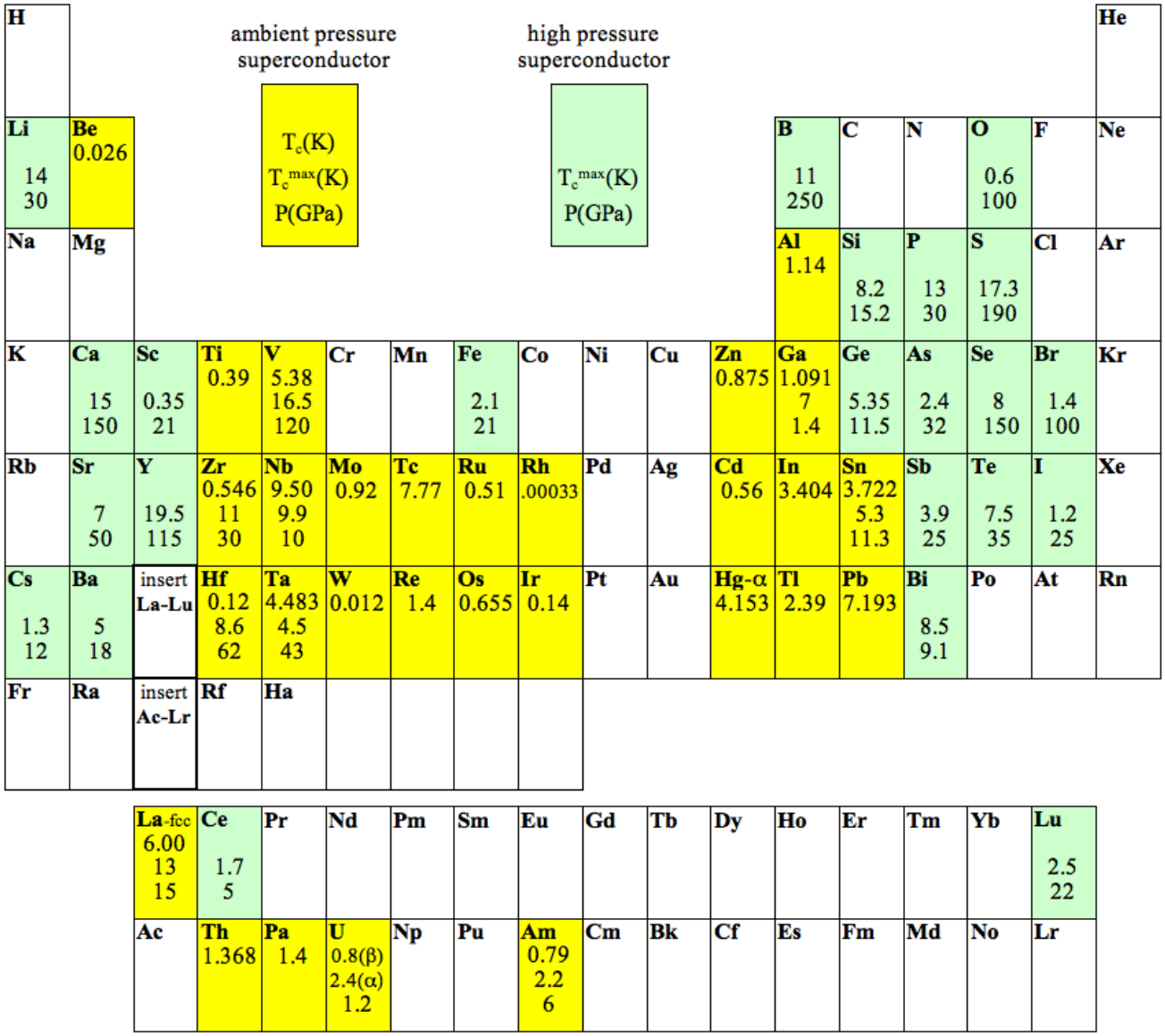
Recent high pressure studies:

TiOCl: low dimensional spin 1/2 system (Ti^{3+}; $3d^1$) Mott insulator

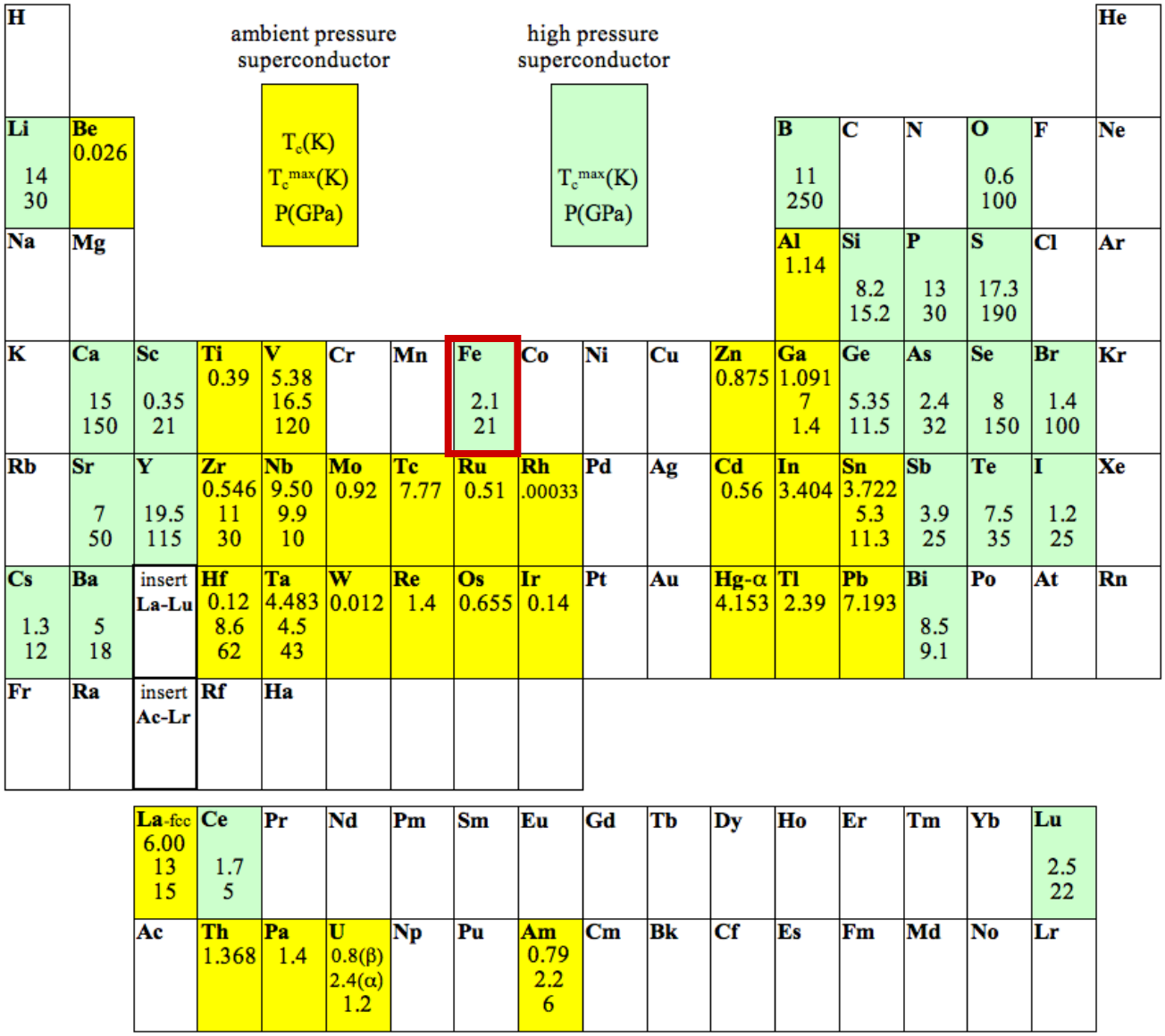
Metal Cluster compounds: AM_4X_8 (A=Ga; M=Nb,Ta; X=S,Se)
a new class of Mott insulators

superconductivity close to a Mott transition

conventional superconductivity



conventional superconductivity ?



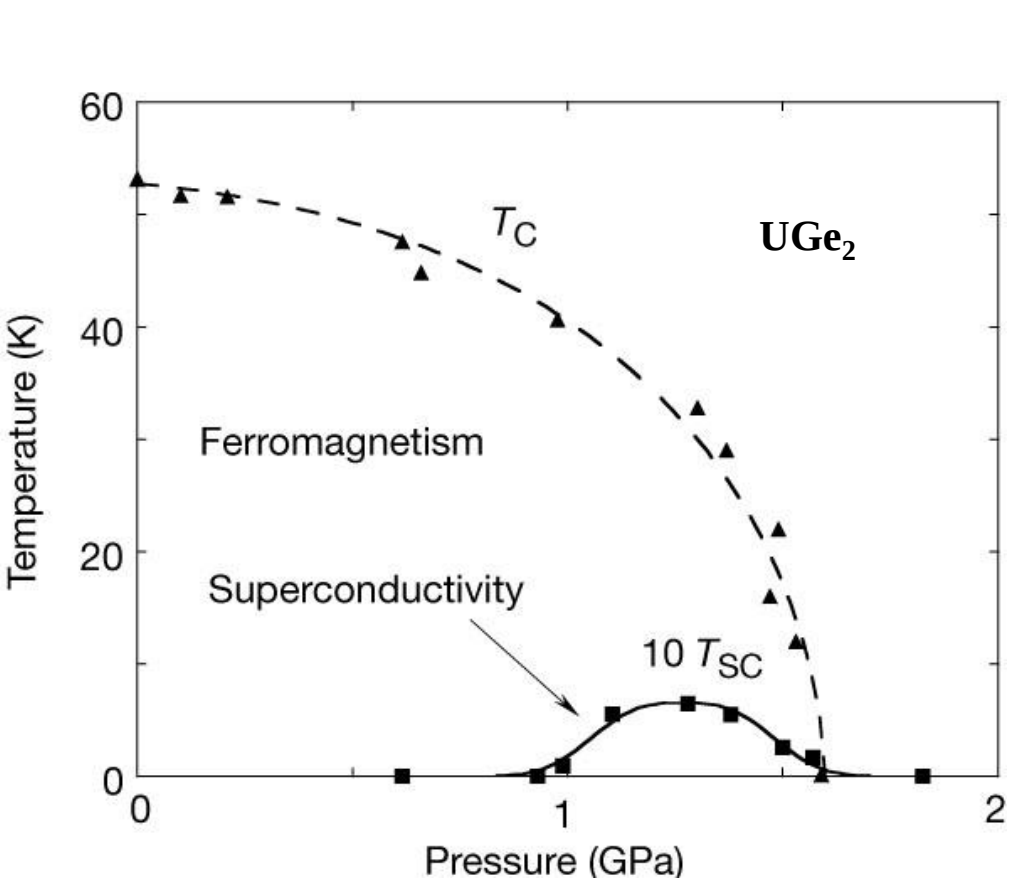
Motivation:

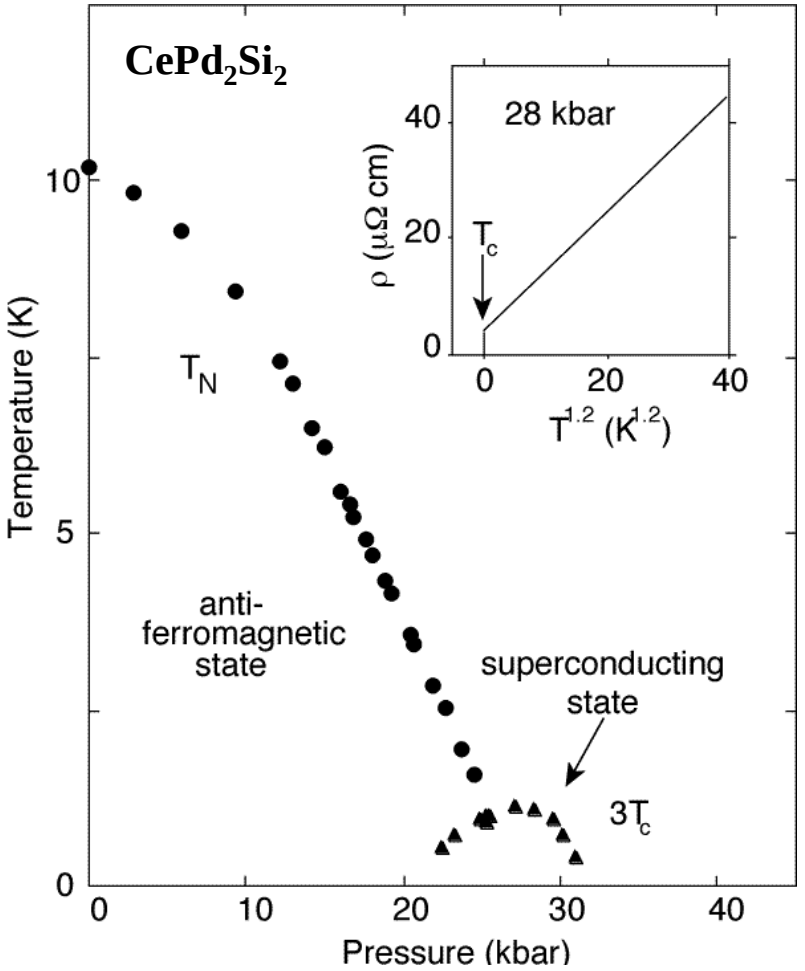
Search for superconductivity in the presence of strong electron correlations.

different concepts!

a) Metallic systems on the border of intinerant electron magnetism

Heavy fermion systems

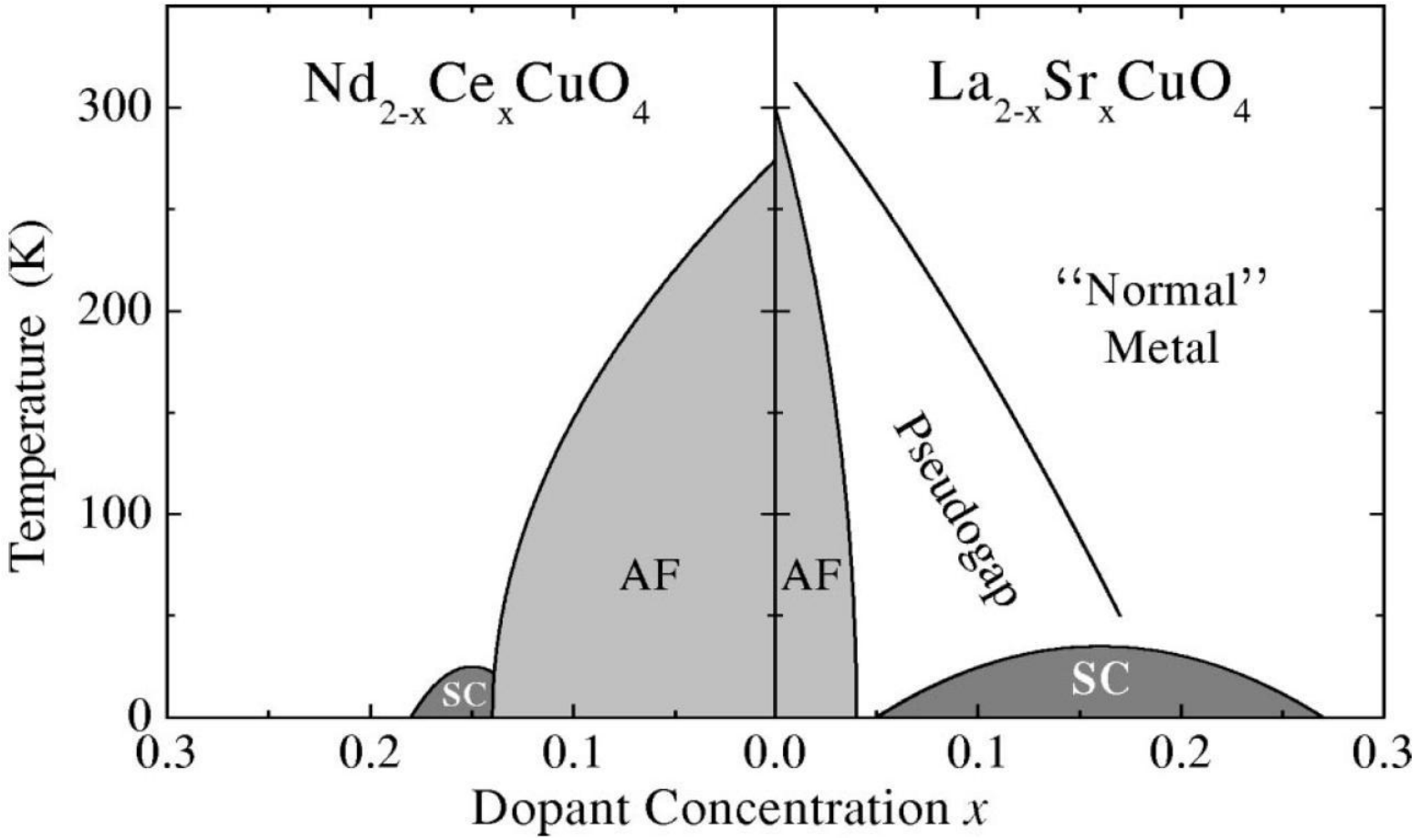




S. S. Saxena et al., Nature 406, 587 (2000) N. D. Mathur et al., Nature 394, 39 (1998)

b) doped Mott-Insulators

HTC-Superconductors



A. Damascelli, Z. Hussain, Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003)

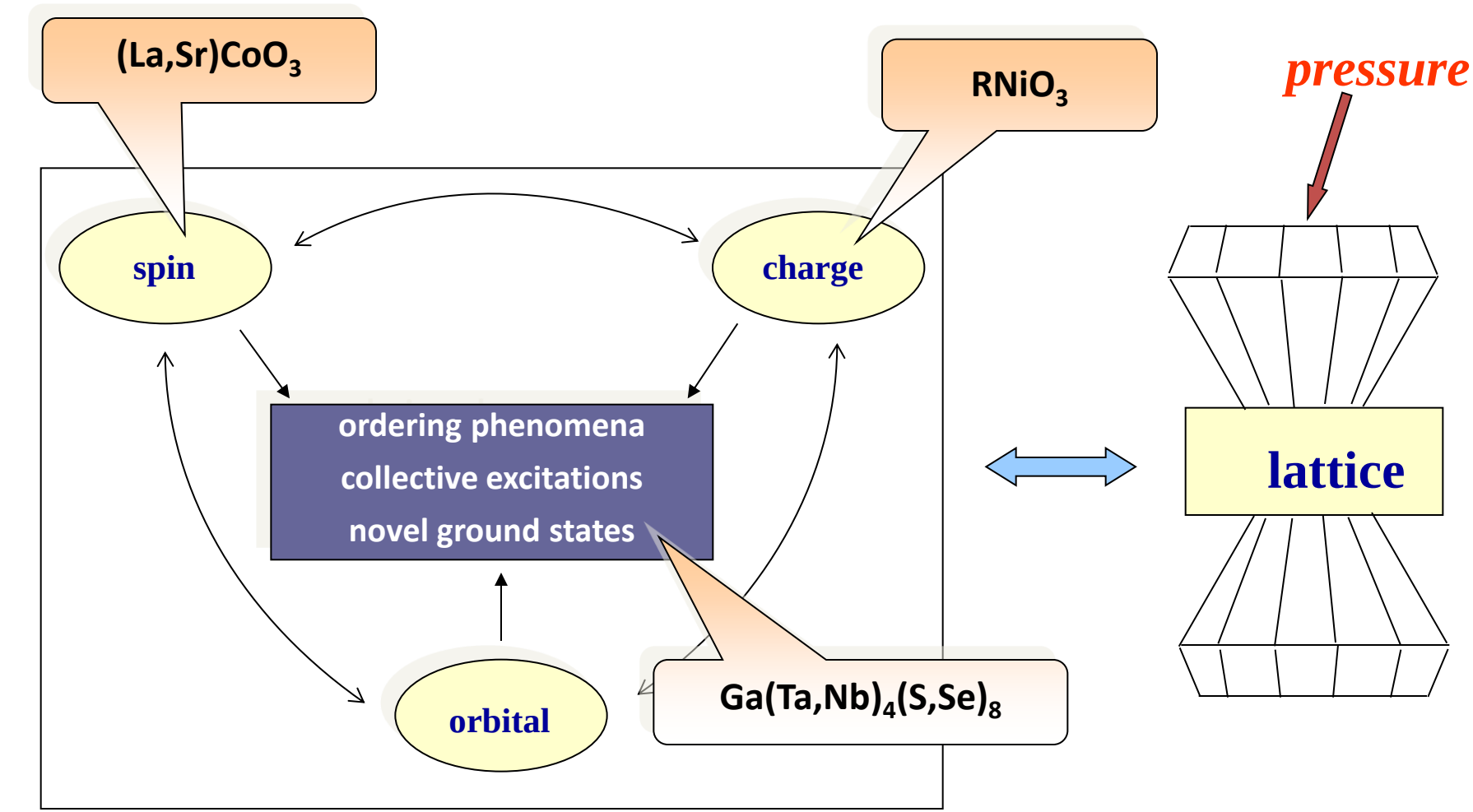
c) stoichiometric Mott-Insulators

Another option

inducing superconductivity by pressure in stoichiometric systems in the proximity to a Mott transition

Advantage → Absence of disorder!

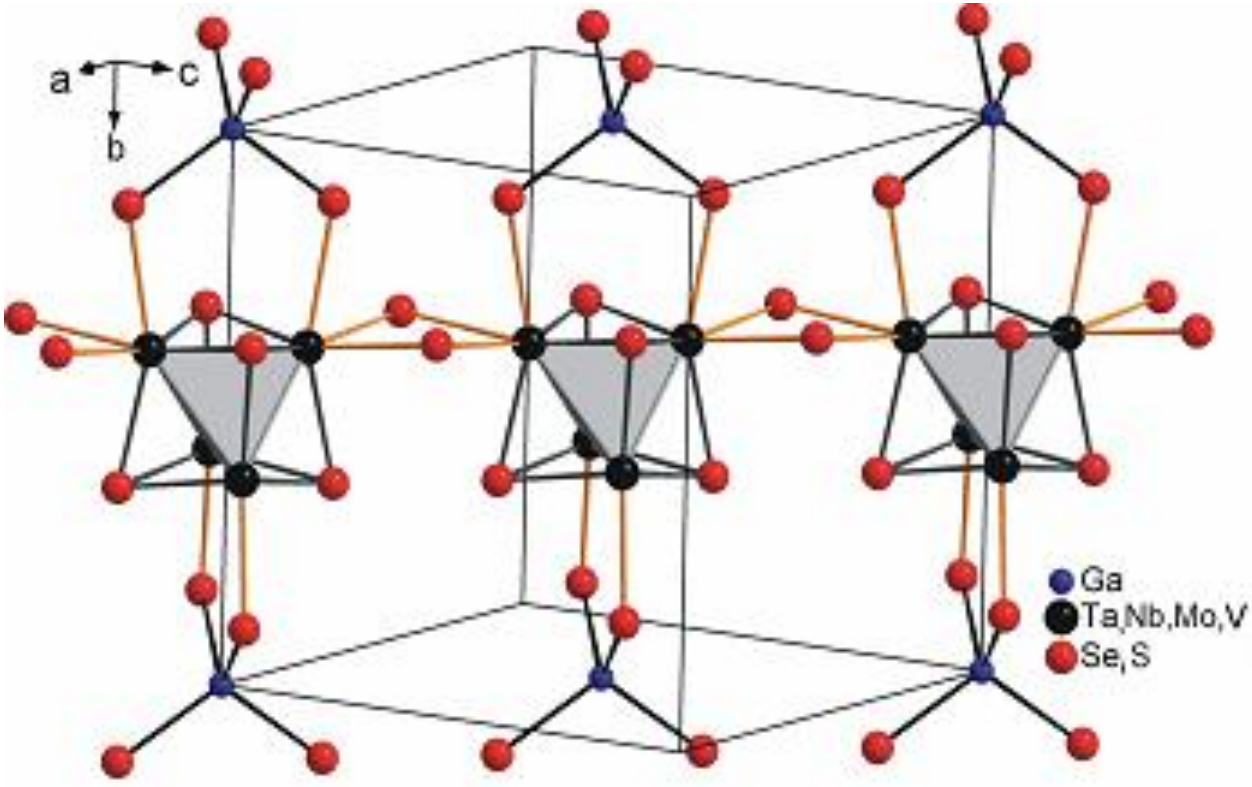
Selected correlated oxides



Metal-Insulator transition is driven by interplay between the degrees of freedom ⇒ **anomalous metallic state**

Metal Cluster compounds: AM_4X_8 (A=Ga,Ge; M=V,Mo,Nb,Ta; X=S,Se)

$GaMo_4S_8$ (fcc structure) $Ga^{3+}\left(M^{3.25+}\right)_4\left(S^{2-},Se^{2-}\right)_8$

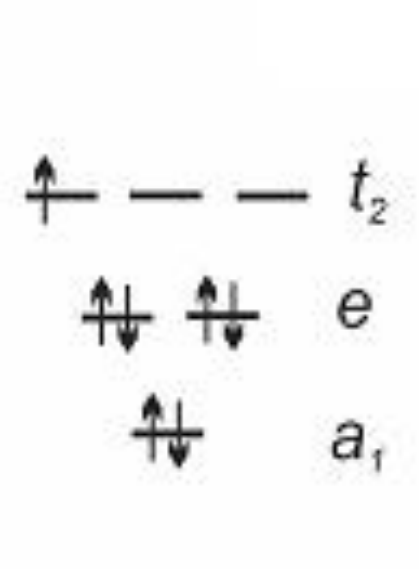


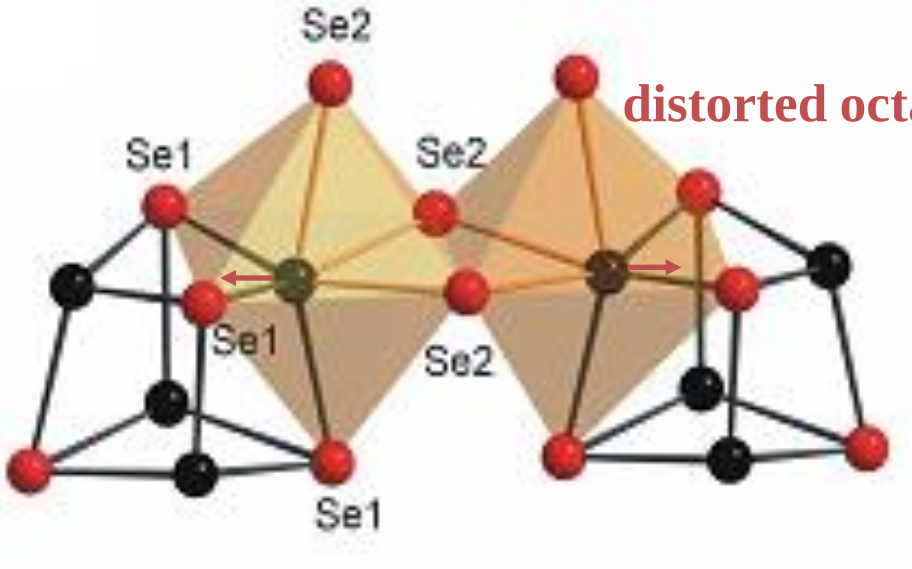
Tetrahedral M_4X_4-metal clusters separated by large distances ³ 4 Å and weakly coupled through S, Se anions. ⇒ localization of electronic states in the clusters

$GaMo_4S_8$ (fcc structure)

$$Ga^{3+}\left(M^{3.25+}\right)_4\left(S^{2-},Se^{2-}\right)_8$$

Mott-Insulators: with S = ½ (Ga^{3+})





distorted octahedra!

Ground state properties strongly depend on the local structure of the M_4-cluster; mainly on the number of valence electrons per cluster.

Consequences?

Consequences: localization of the electronic states in the clusters

(a) non of these compounds show metallic conductivity, instead the electronic conduction takes place by hopping of carriers among the clusters.

⇒ semiconducting systems with a small energy gap (~ 0.1 eV);

(b) Magnetic suseptibility is typical for localized spins (e.g. GaV_4Se_8 and GaV_4S_8 R. Pocha et al., Chem. Mater. (2000)).

Mott Insulators in which the **„correlated units“** are M_4-metal clusters!!

with extra internal degree of freedom?

Aim: Search for superconductivity under high pressure in the proximity to a Mott transition.

Mott Insulators $GaNb_4(S,Se)_8$ and $GaTa_4Se_8$

1. **Electrical resistance under high pressure up to 30 GPa and in external magnetic field up to 10 T using the Diamond Anvil Cell technique.**
2. **Energy-Dispersive x-ray diffraction up to 30 GPa (Hasylab).**
3. **Angle resolved x-ray diffraction on single crystal of $GaTa_4Se_8$ up to 15 GPa.**
4. **Raman spectroscopy up to 20 GPa**

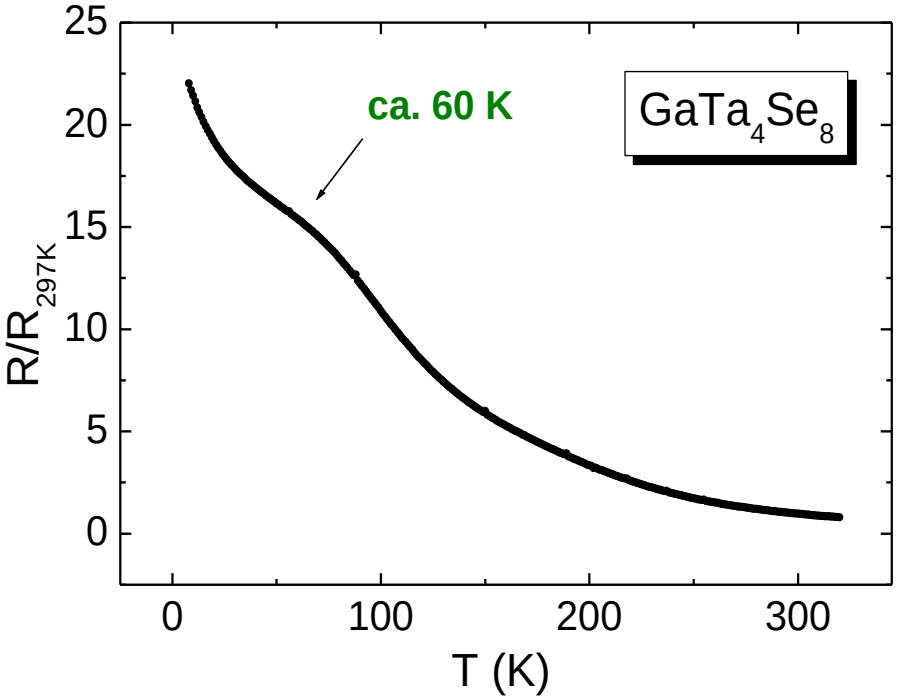
x-ray diffraction @300 K:

	a (Å)	V (Å^3)	d_{mm} (Å)	d_{cc} (Å)
$GaNb_4Se_8$	10.420(1)	1131.37	3.026(1)	4.320(1)
$GaTa_4Se_8$	10.358(2)	1111.29	3.002(2)	4.322(1)
$GaNb_4S_8$	9.985(2)	995.51	2.975(1)	4.085(1)

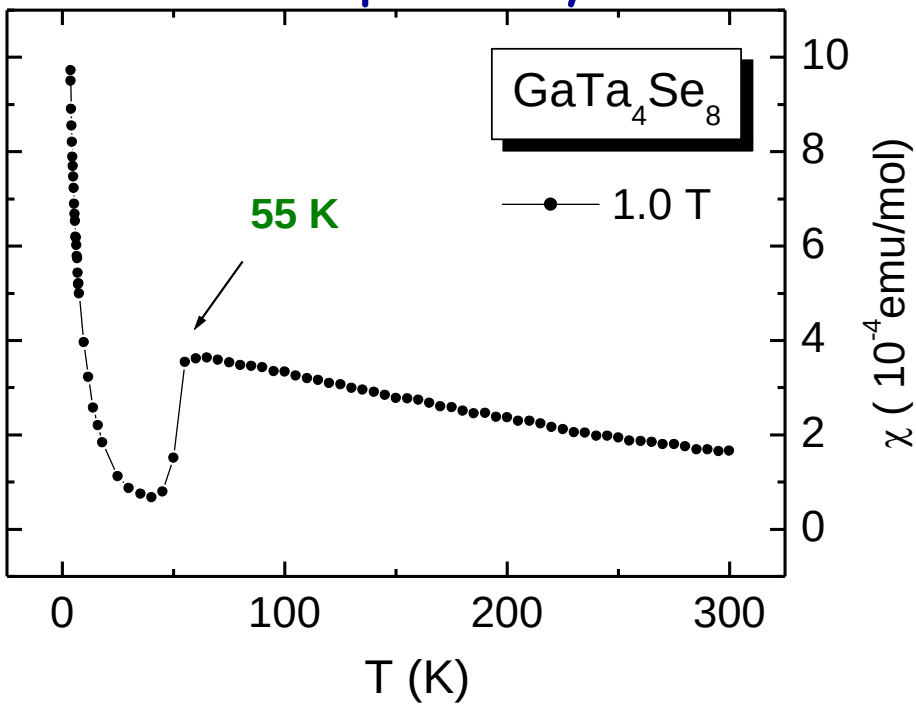
$$d_{cc} >> d_{mm}$$

Results at ambient pressure:

Electrical resistance



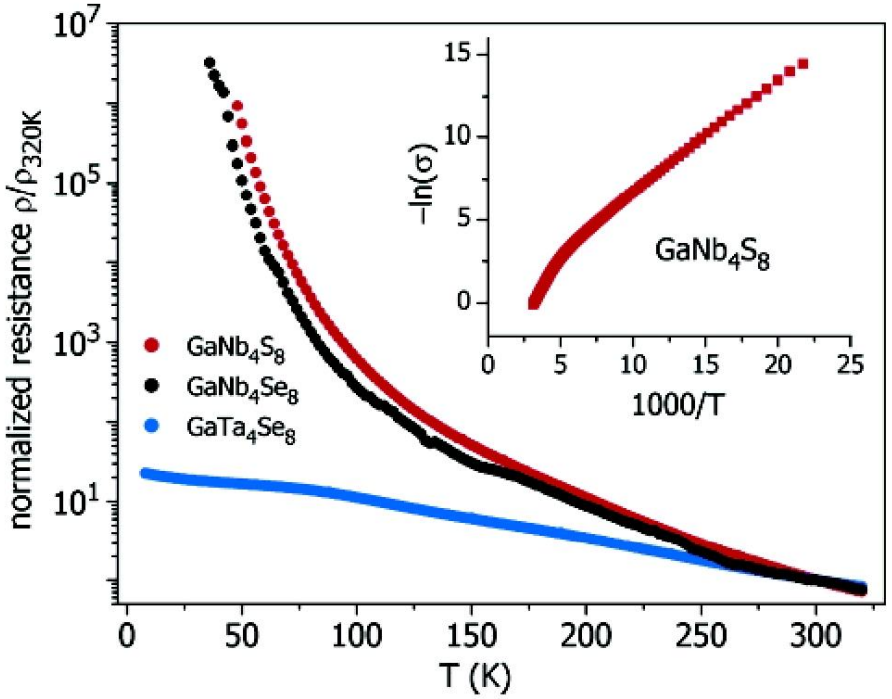
Magnetic susceptibility

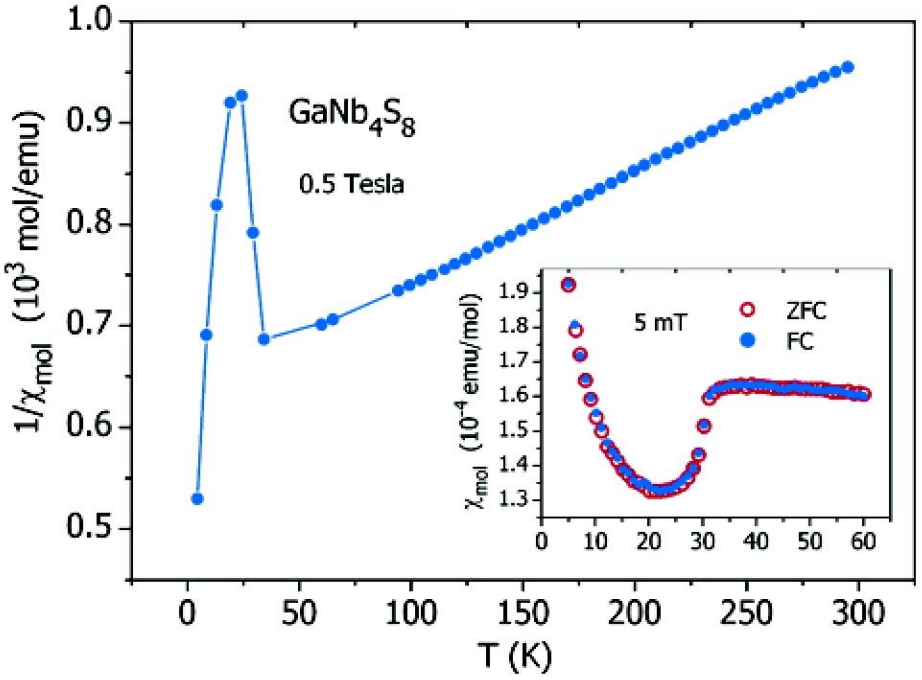


R(T) ⇒ small energy gap ~ 0.1 eV

χ(T) ⇒ sharp anomaly at low temperatures

Results at ambient pressure





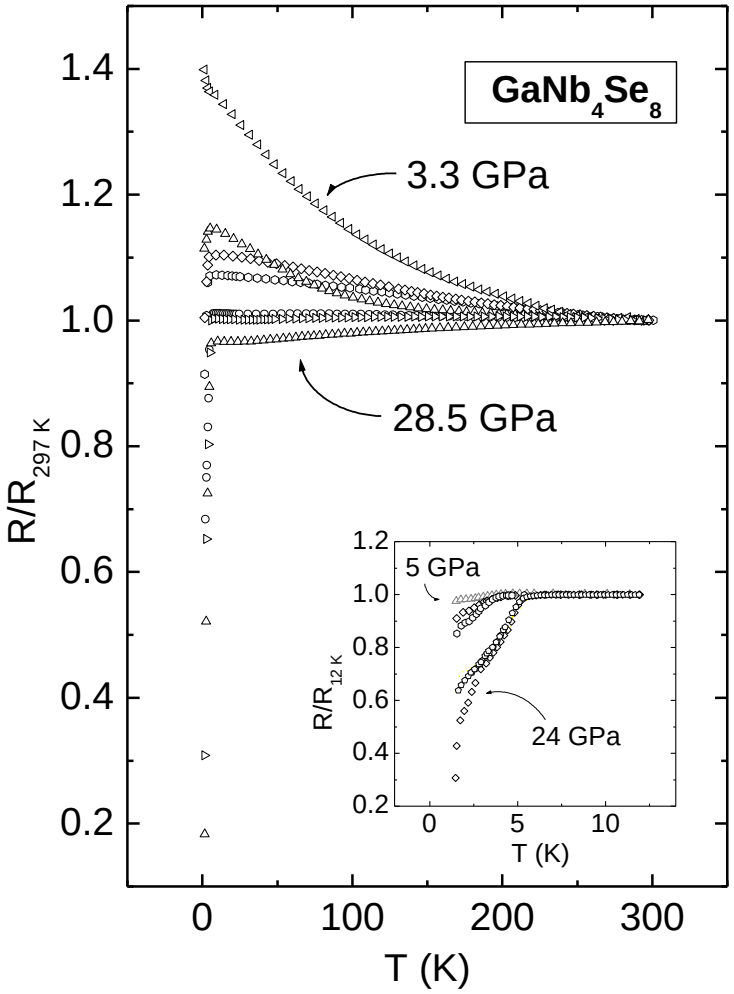
R. Pocha et al., JACS 2005

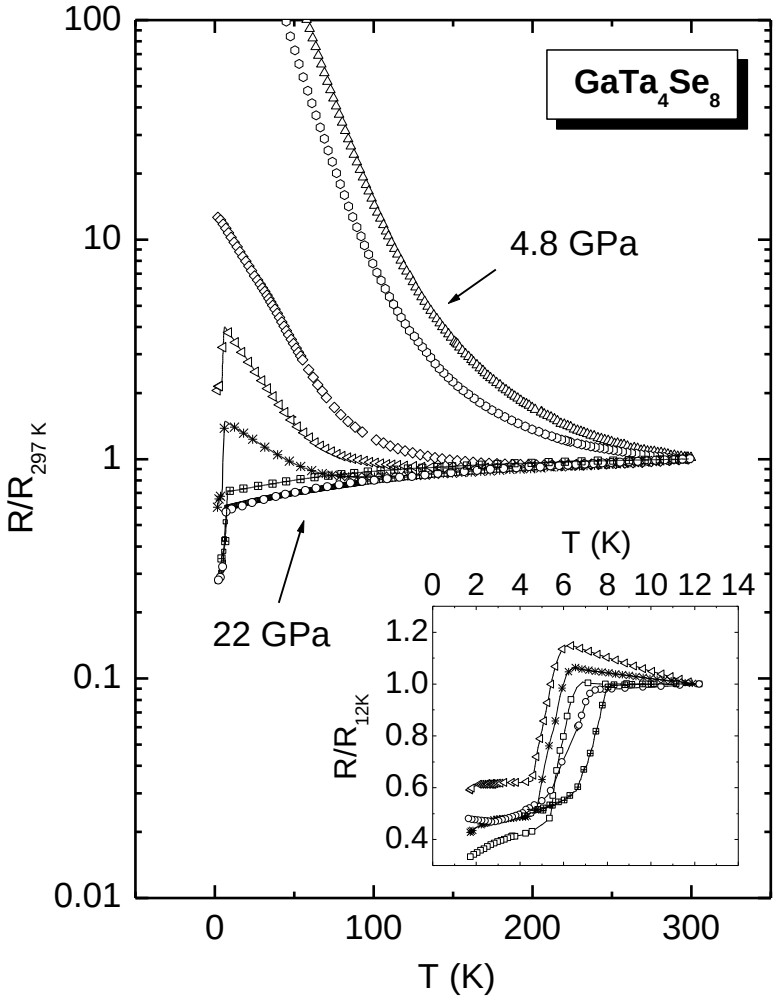
- small energy gap ~ 0.1eV

- Curie-Weiss behavior (100 K ≤ T ≤ 300 K), Θ_{CW} = - 298 K ! Indicating the existence of strong magnetic correlations, but no magnetic ordering is found down to 1.6 K (neutron scattering).

- values of the effective magnetic moments are 1.6 μ_B per Nb_4-cluster (close to theoretical values 1.73 μ_B for S = ½) and 0.7 μ_B per Ta_4-cluster.

electrical resistance:



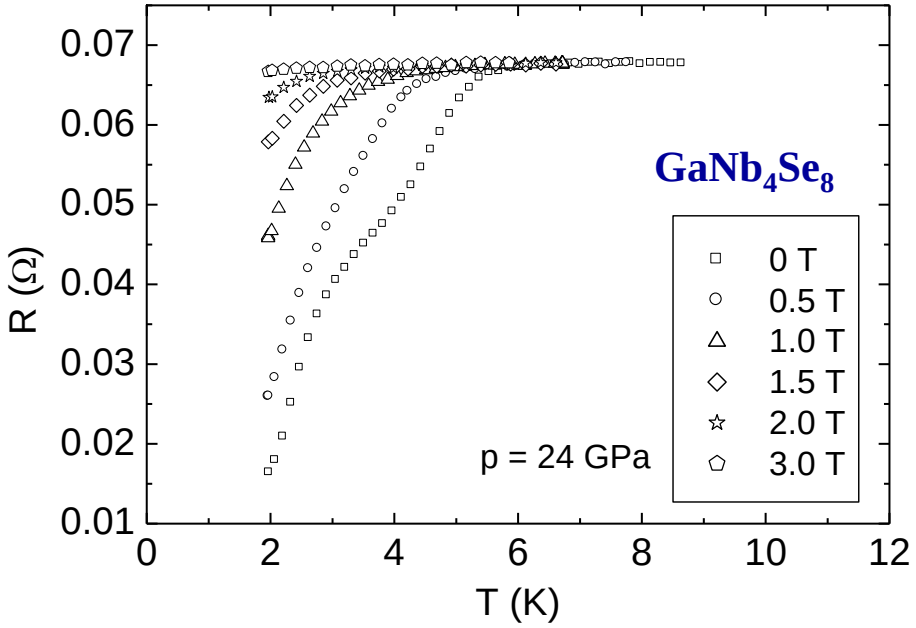


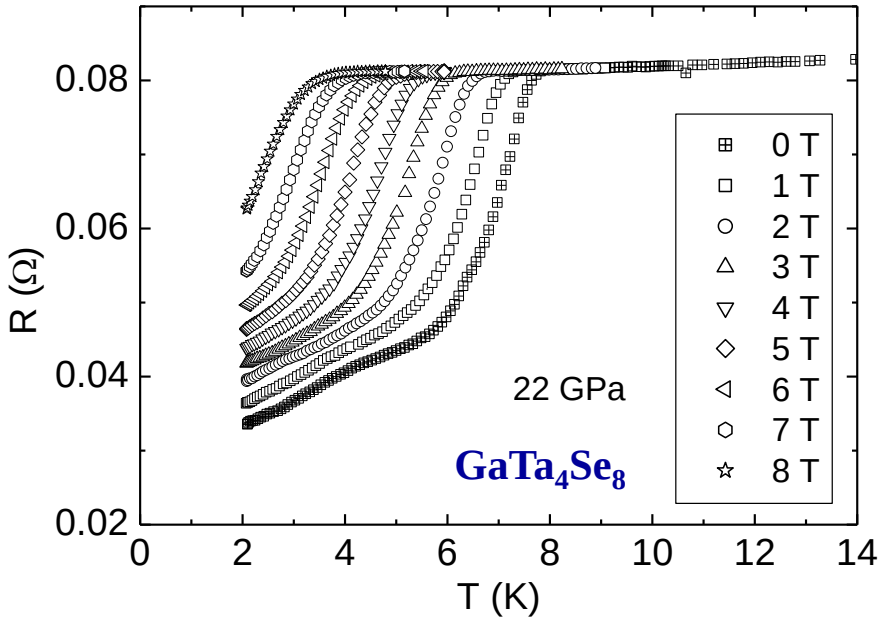
Semiconductor-Metal-Transition in $GaNb_4Se_8$ and $GaTa_4Se_8$

and superconductivity at high pressures

electrical resistance in magnetic field

⇒ type II superconductor





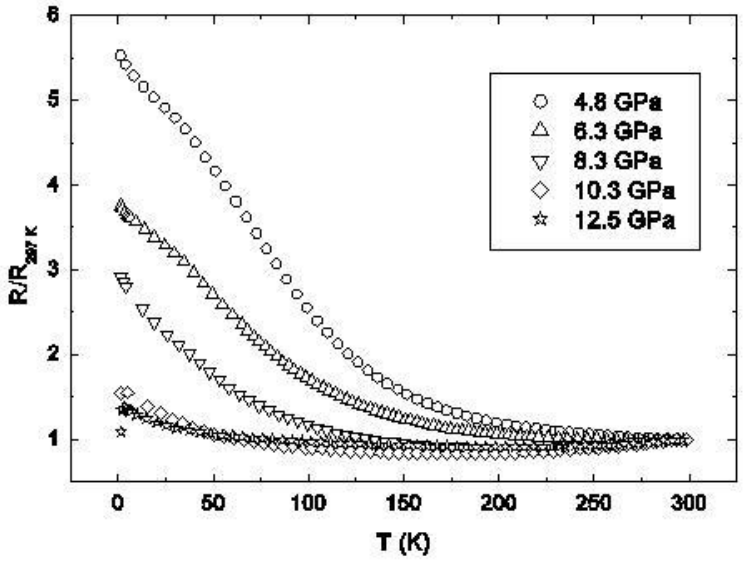
upper critical field B_{c2} ~ 2 T

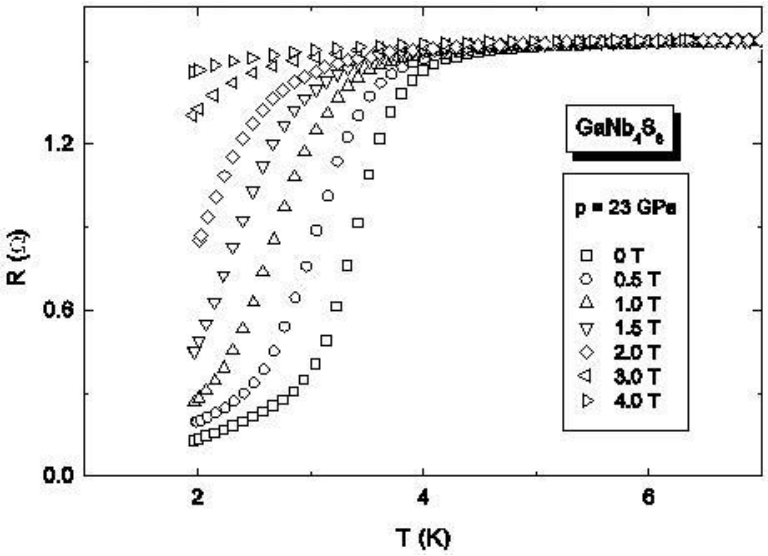
coherence lenght ζ ~ 130 Å

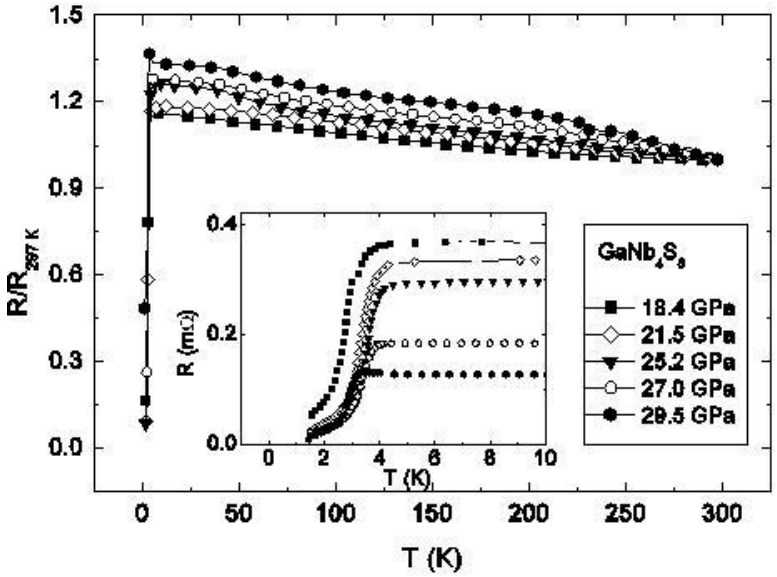
upper critical field B_{c2} ~ 10 T

coherence lenght ζ ~ 60 Å

Pressure-induced superconductivity in $GaNb_4S_8$





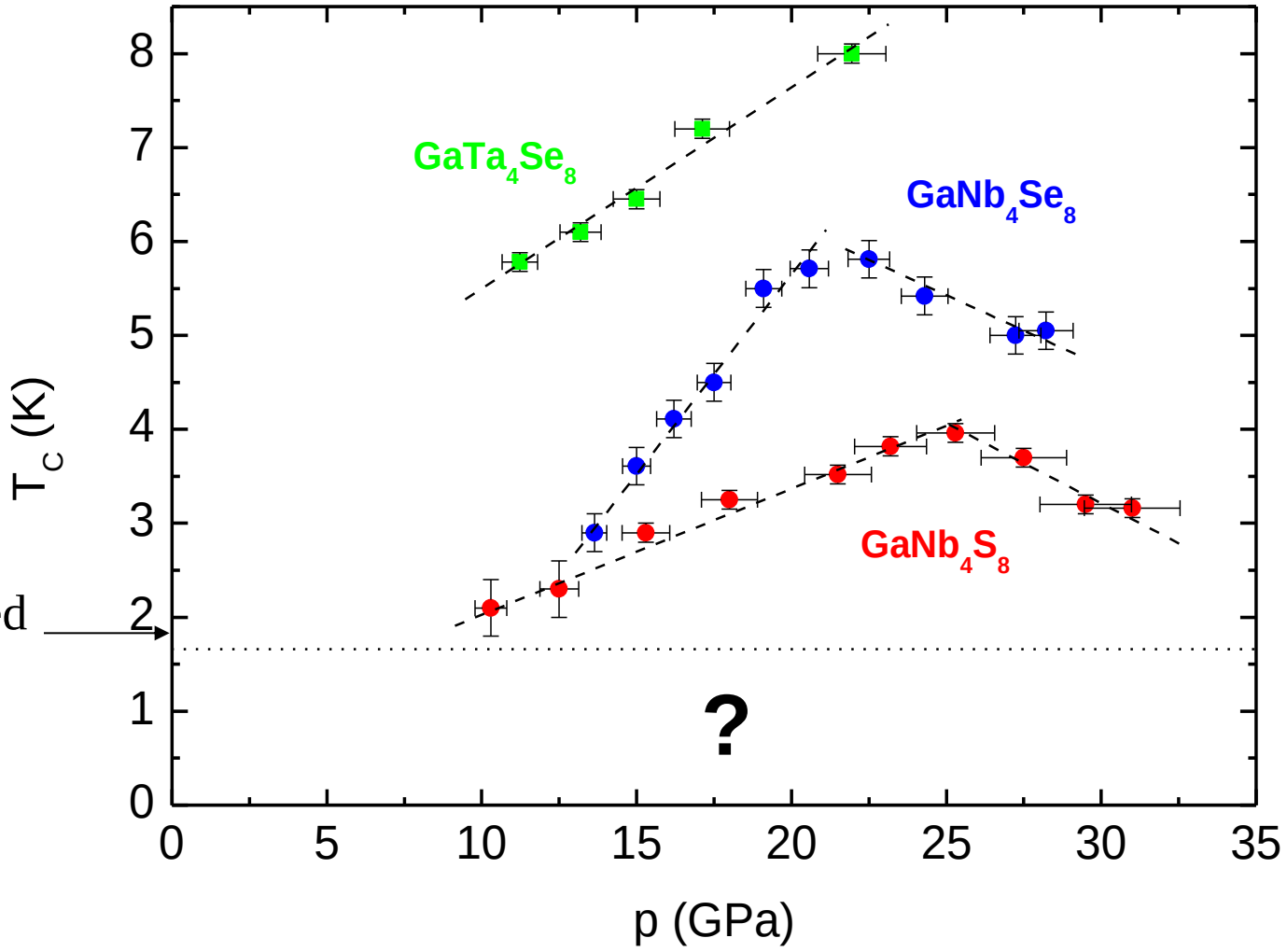


upper critical field $B_{c2} \sim 4.5$ T

coherence lenght $\zeta \sim 90$ Å

X. Wang et al. (to be published)

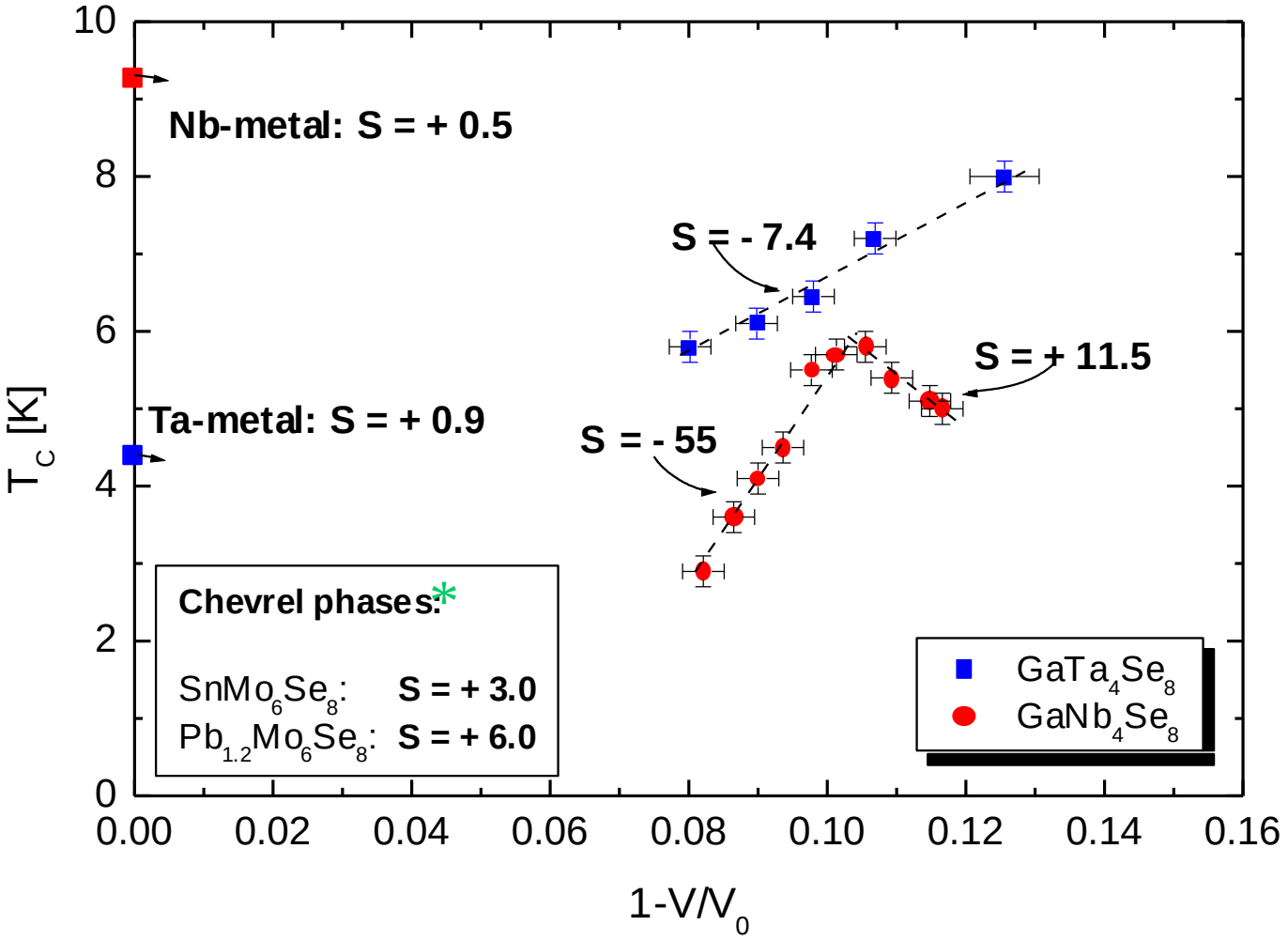
Pressure dependence of T_C



lowest measured temperature

decrease of T_C at higher pressure p > 20 GPa is connected with structural phase transition

volume dependence of T_C

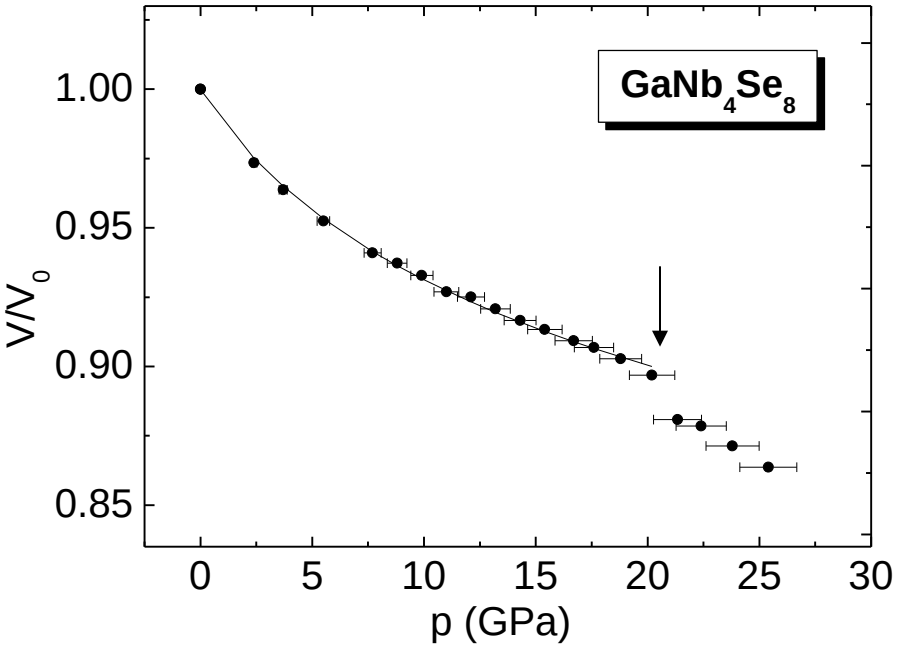


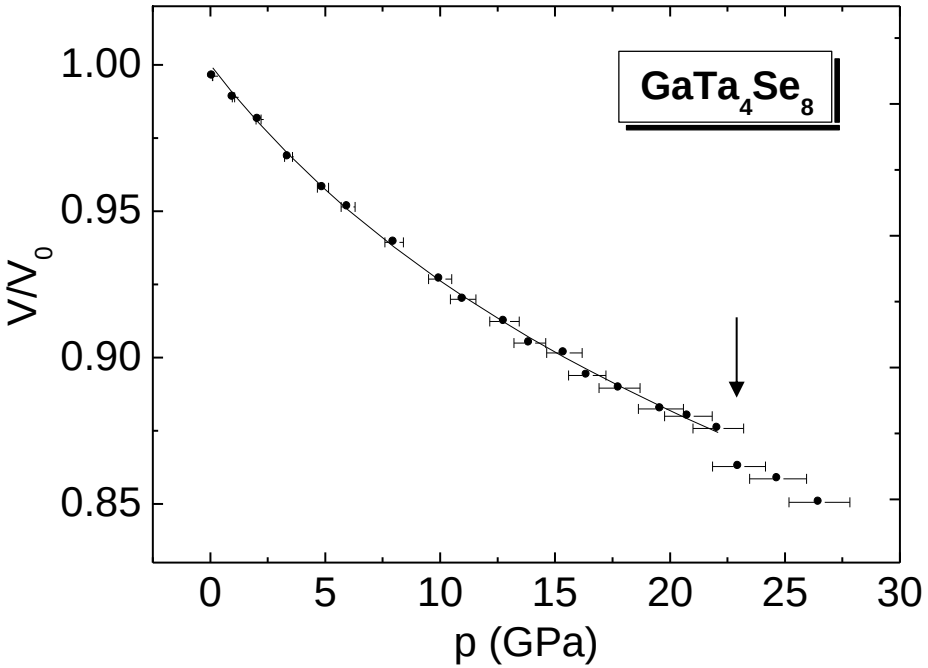
$$S = \frac{\partial \ln T_C}{\partial \ln V}$$

S = Slope

* Calculated from A.W. Webb and R.N. Shelton, J. Phys. F **8**, 261 (1978)

Crystal structure at high pressure





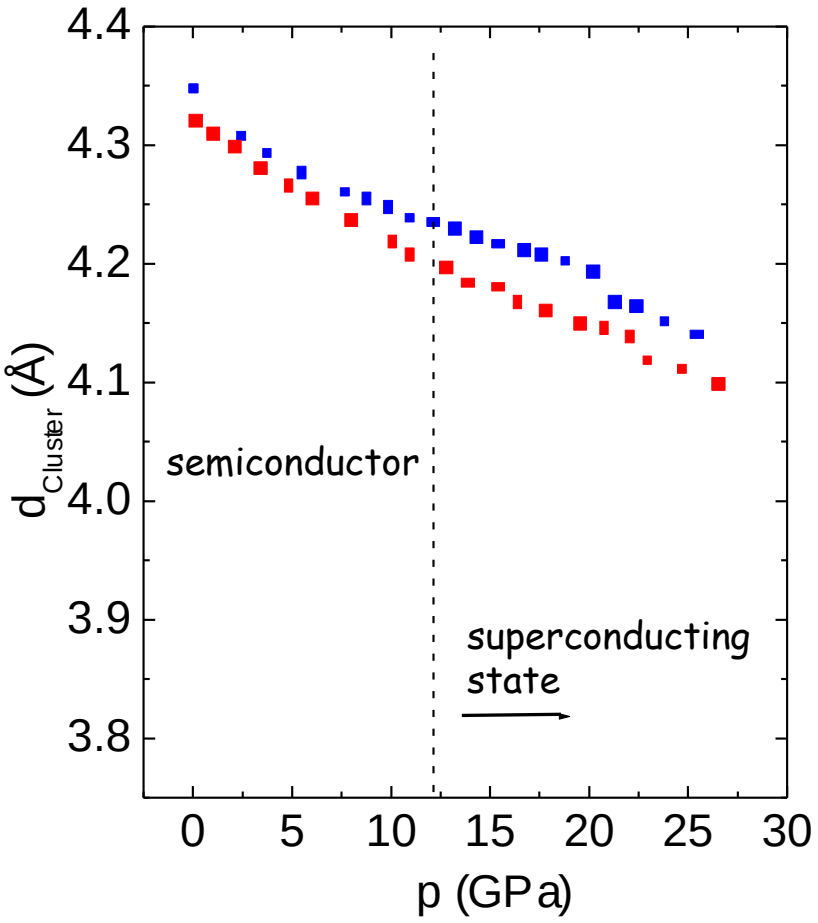
Bulk modulus

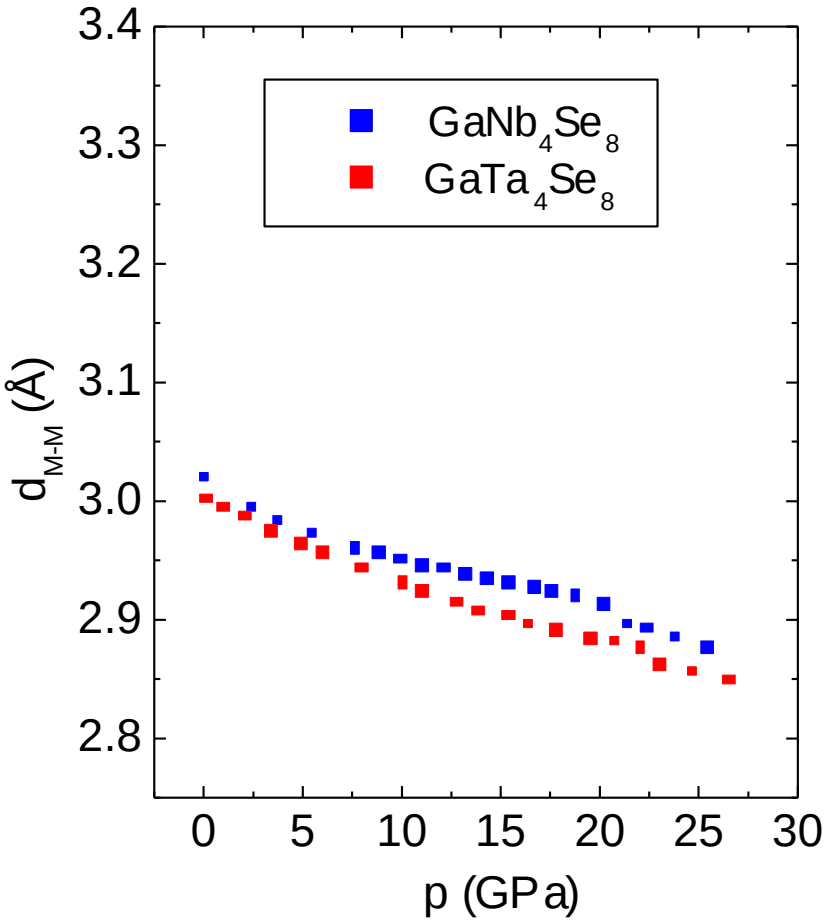
$GaNb_4Se_8$ $B_0 = 78(3)$ GPa; $B_0' = 15.0(0.6)$

$GaTa_4Se_8$ $B_0 = 98(2)$ GPa; $B_0' = 7.2(0.6)$

origin of superconductivity

origin of superconductivity

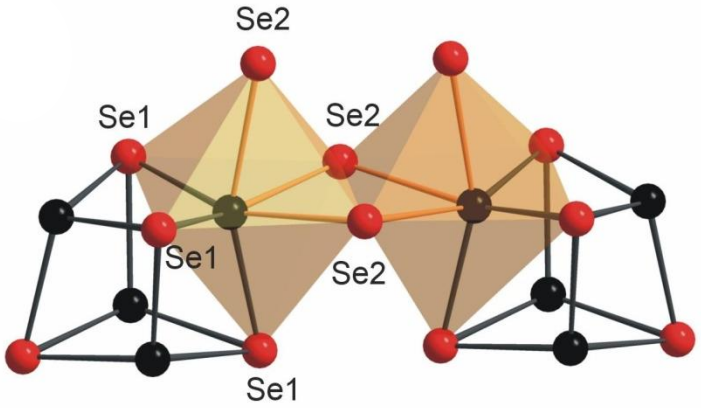


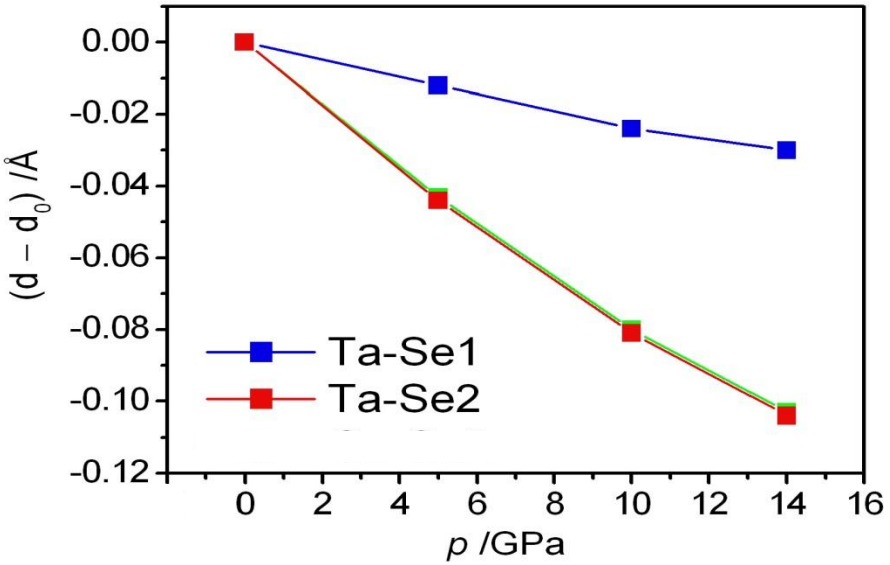


for p > 10 GPa $d_{Cluster} >> d_{M-M}$!!

The occurence of superconductivity is not related to a decrease of intercluster distances.

Change of local structure at high pressure





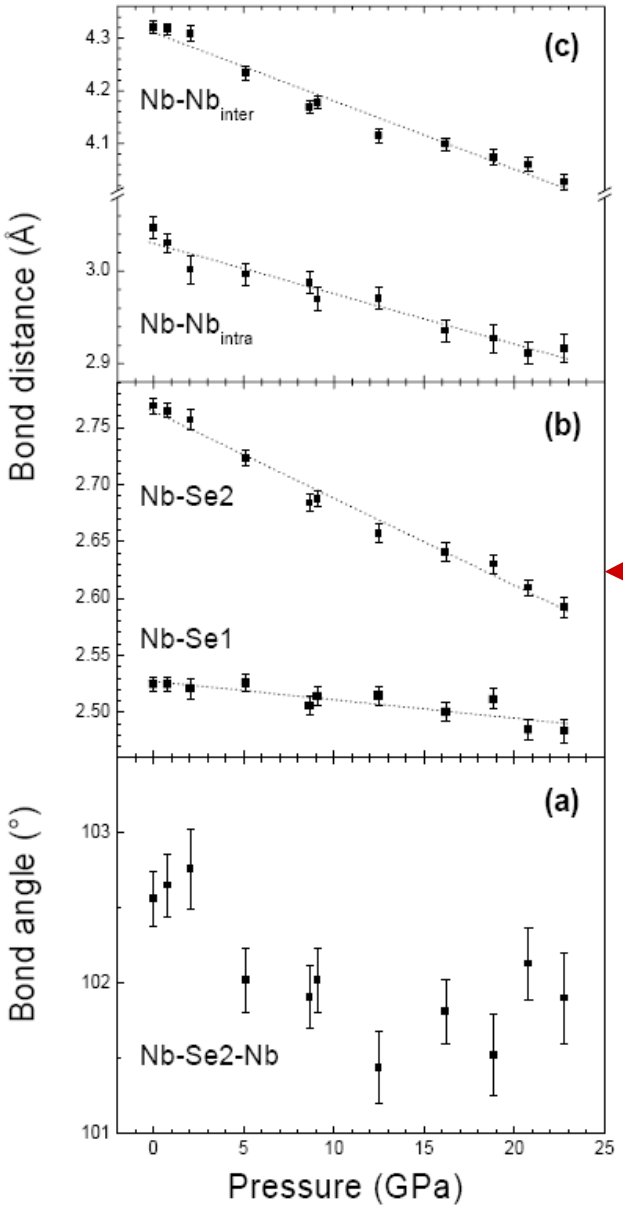
Ta atoms move towards the center of the octahedra. → **octahedral distortion is strongly reduced b increasing y pressure.**

Strong increase of the hybridization of the d-states of Ta with p-states of the bridging Se2-ions.

↓

Increase of the effective intercluster coupling → pressure-induced metallic and superconducting state.

Change of local structure at high pressure

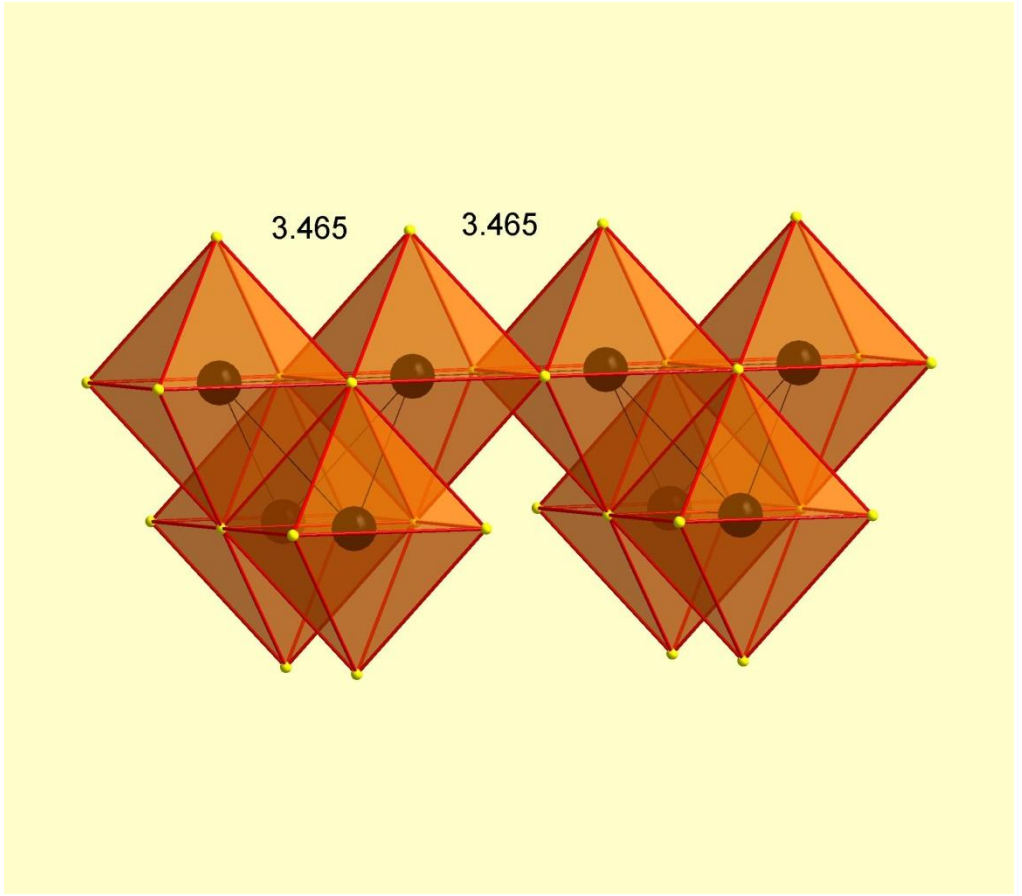


$GaNb_4Se_8$ - angle resolved x-ray diffraction (ESRF, Grenoble)

also here: octahedral distortion is strongly reduced by increasing pressure.

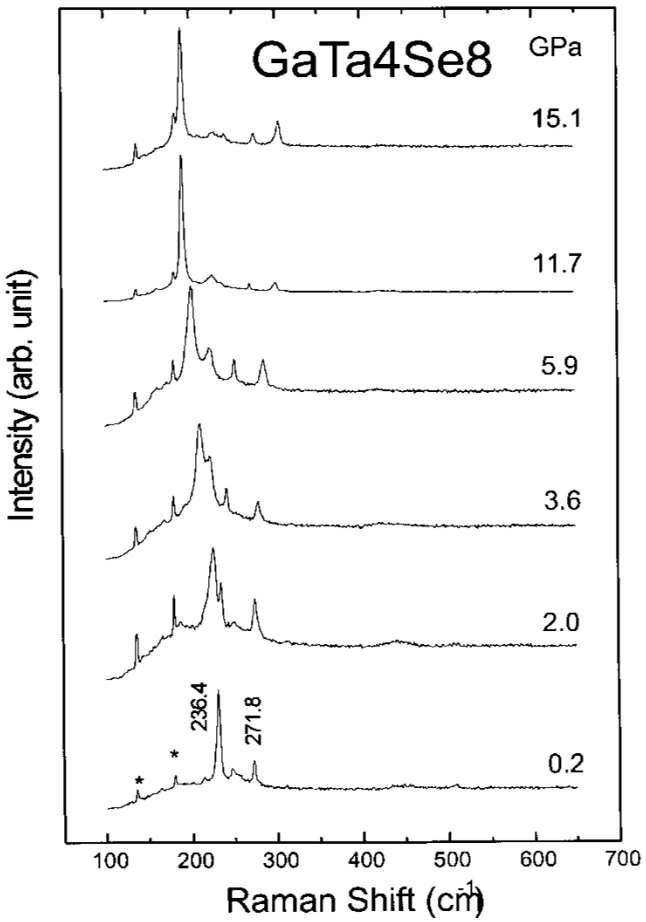
pressure-induced metallic and superconducting state.

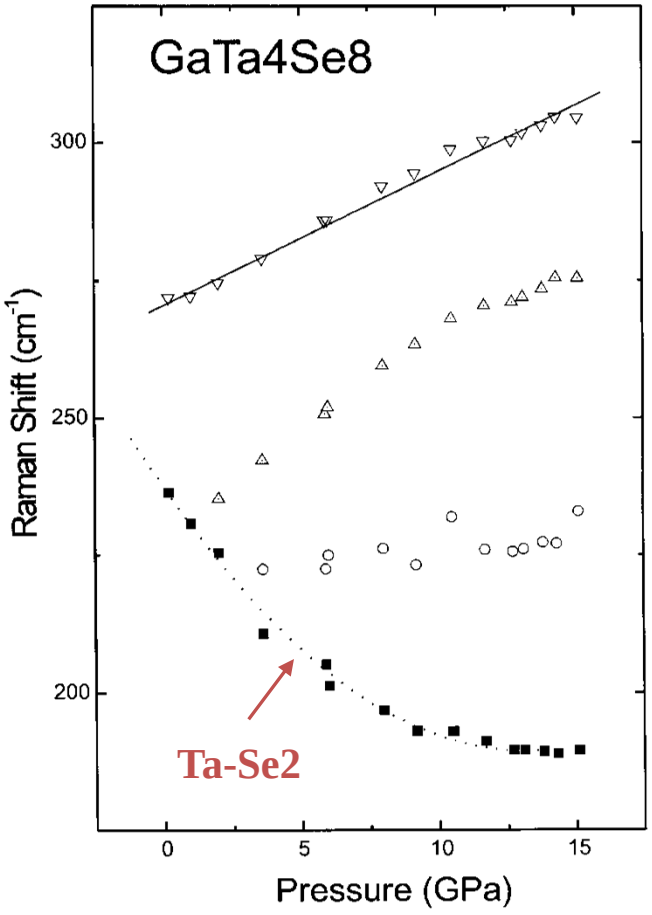
X. Wang et al. (to be published)


3.465
3.465

Lattice dynamics under high pressure

Raman spectra under high pressures





M.M.A. et al., PRL (2004)

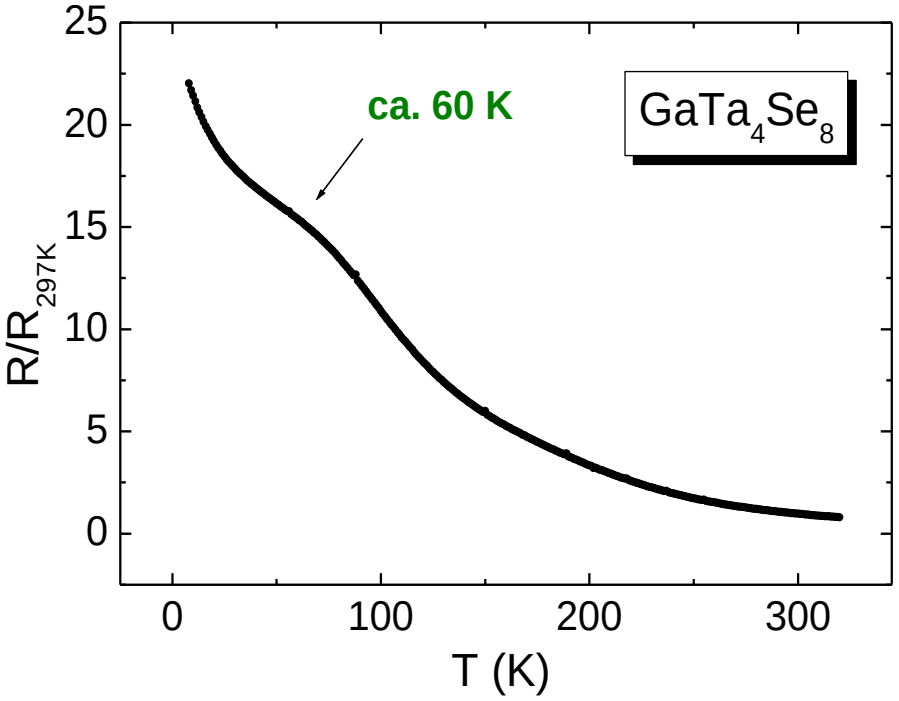
Phonon associated with Ta-Se2 becomes softer by increasing pressure and exhibits finite value at high pressures.

origin of superconductivity

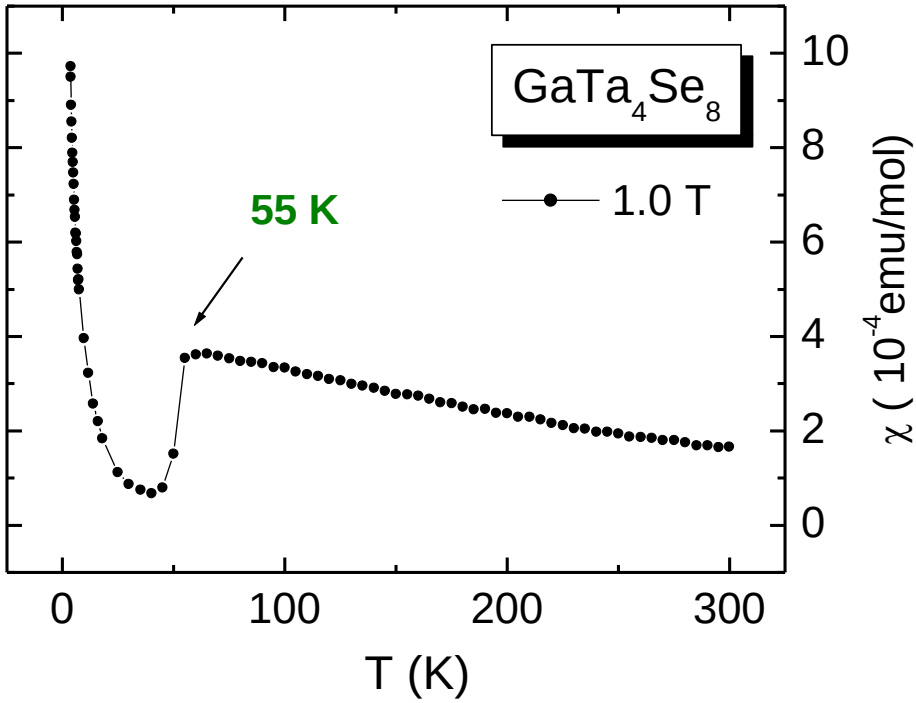
nature of the ground state

Results at ambient pressure:

Electrical resistance



Magnetic susceptibility

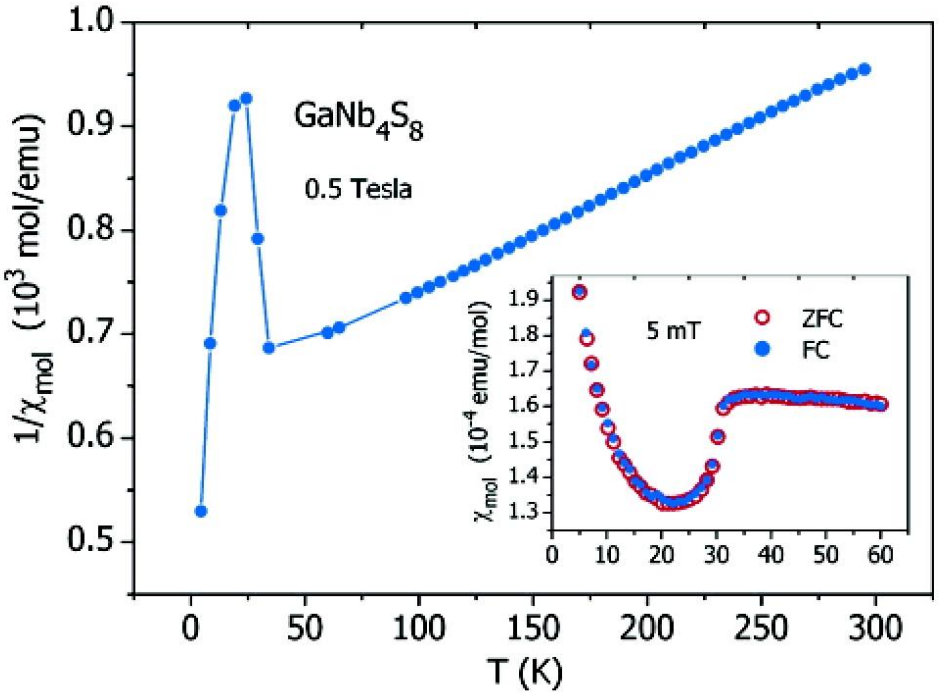


R(T) ⇒ small energy gap ~ 0.1 eV

χ(T) ⇒ anomaly at low temperatures;
propably connected with structural distortion?

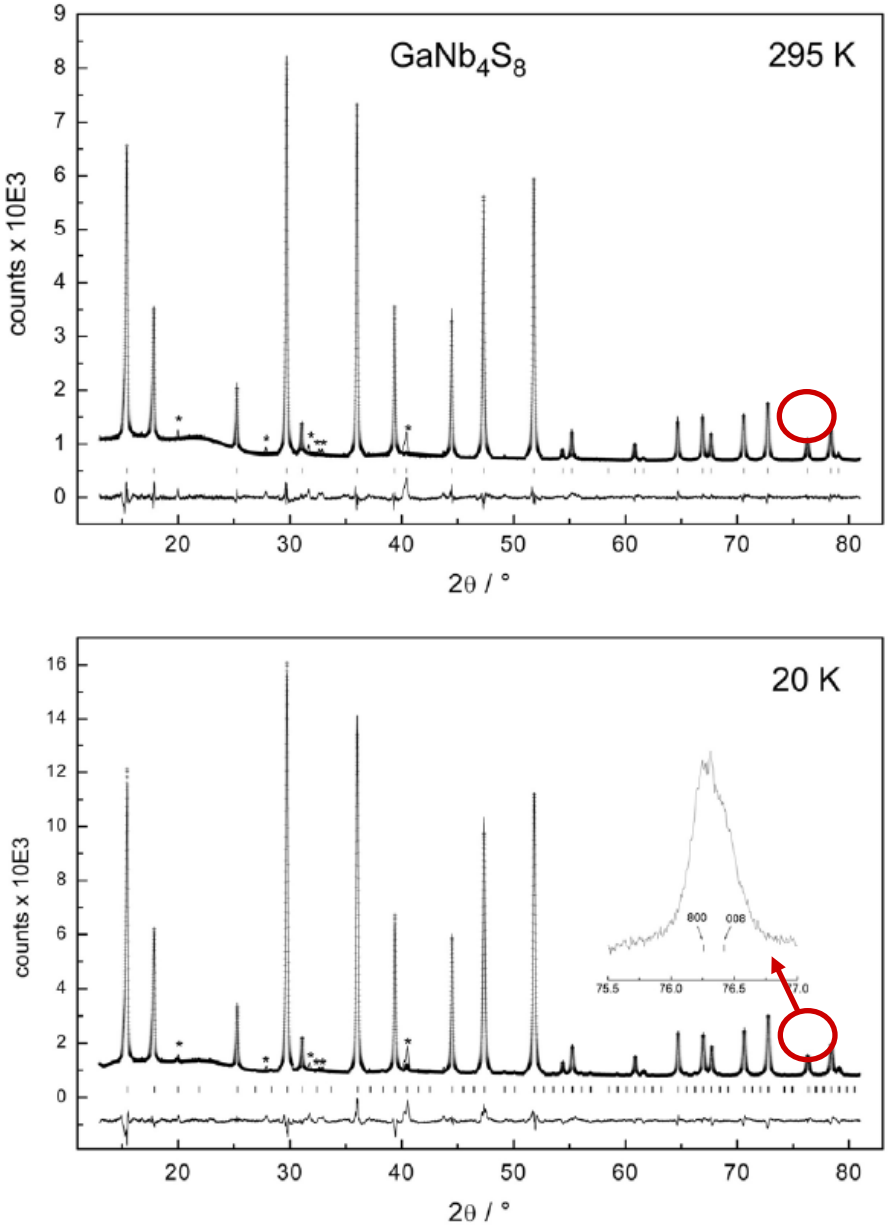
Results at ambient pressure

R. Pocha et al., JACS 2005



Curie-Weiss behavior (100 K £ T £ 300 K), Θ_{CW} = - 298 K ! Indicating the existence of strong magnetic correlations, but no magnetic ordering is found down to 1.6 K (neutron scattering).

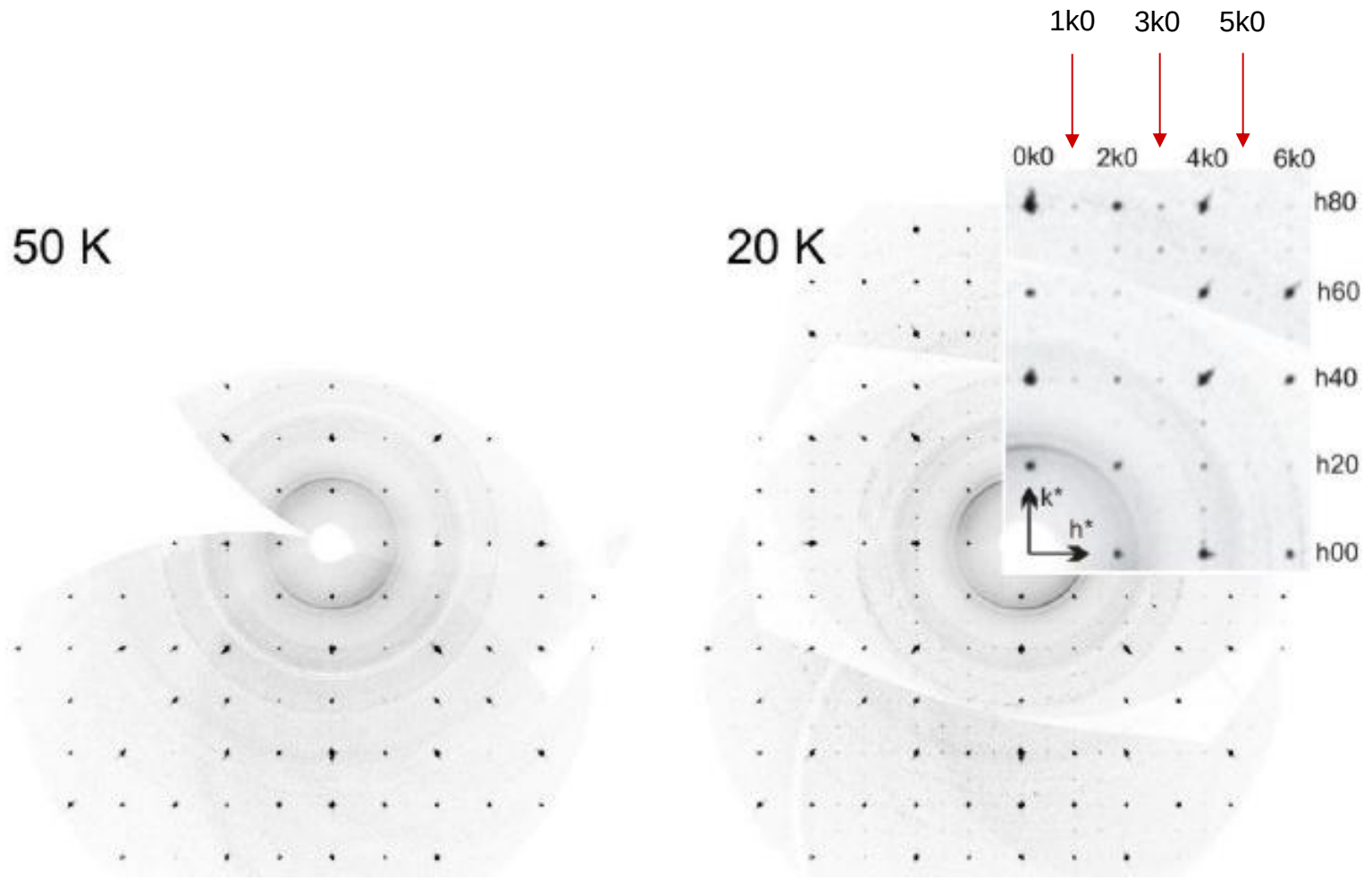
What causes the sharp drop in the susceptibility at about 30 K?



Structural phase transition below 30 K!

Very small tetragonal distortion ($F43m \rightarrow P42_1m$).

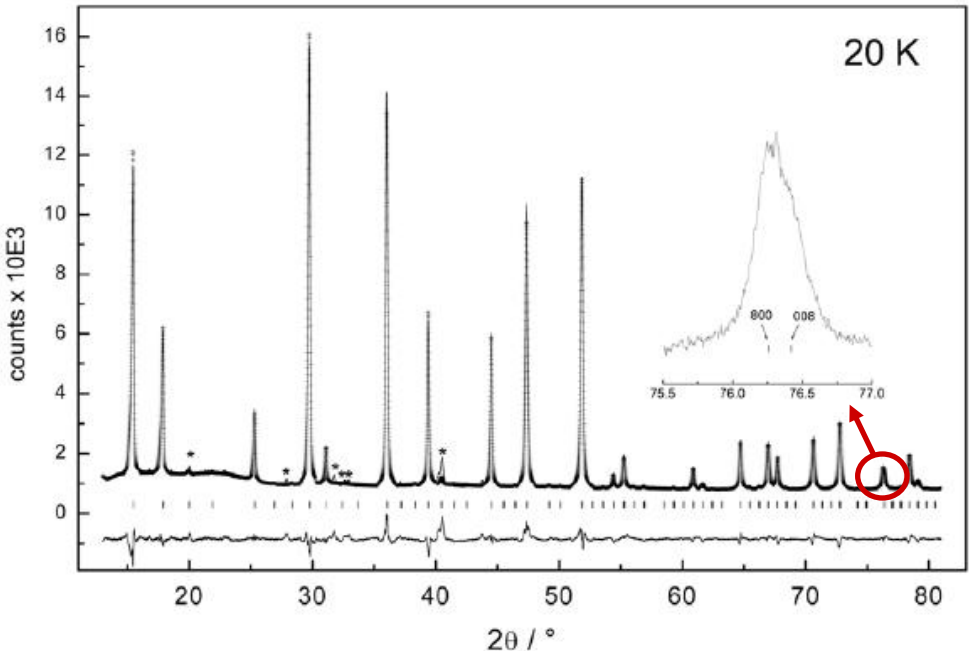
S. Jakob et al., J. Mater. Chem. 2007, 17, 3833 (2007)

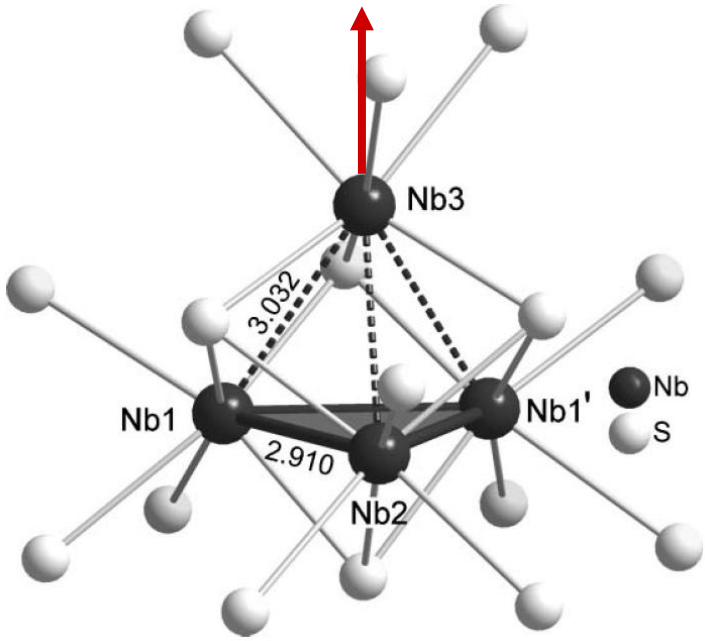


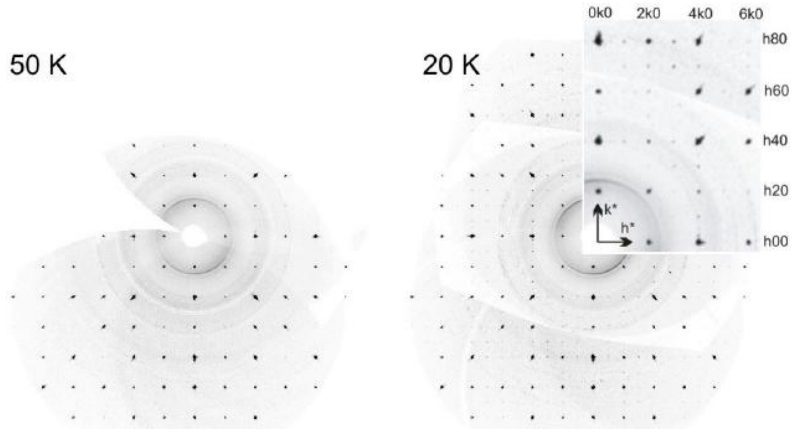
Reciprocal space *hk*0-sections of $GaNb_4S_8$.

S. Jakob et al., J. Mater. Chem. 2007, 17, 3833 (2007)

What causes the sharp drop in χ(T) at about 30 K?





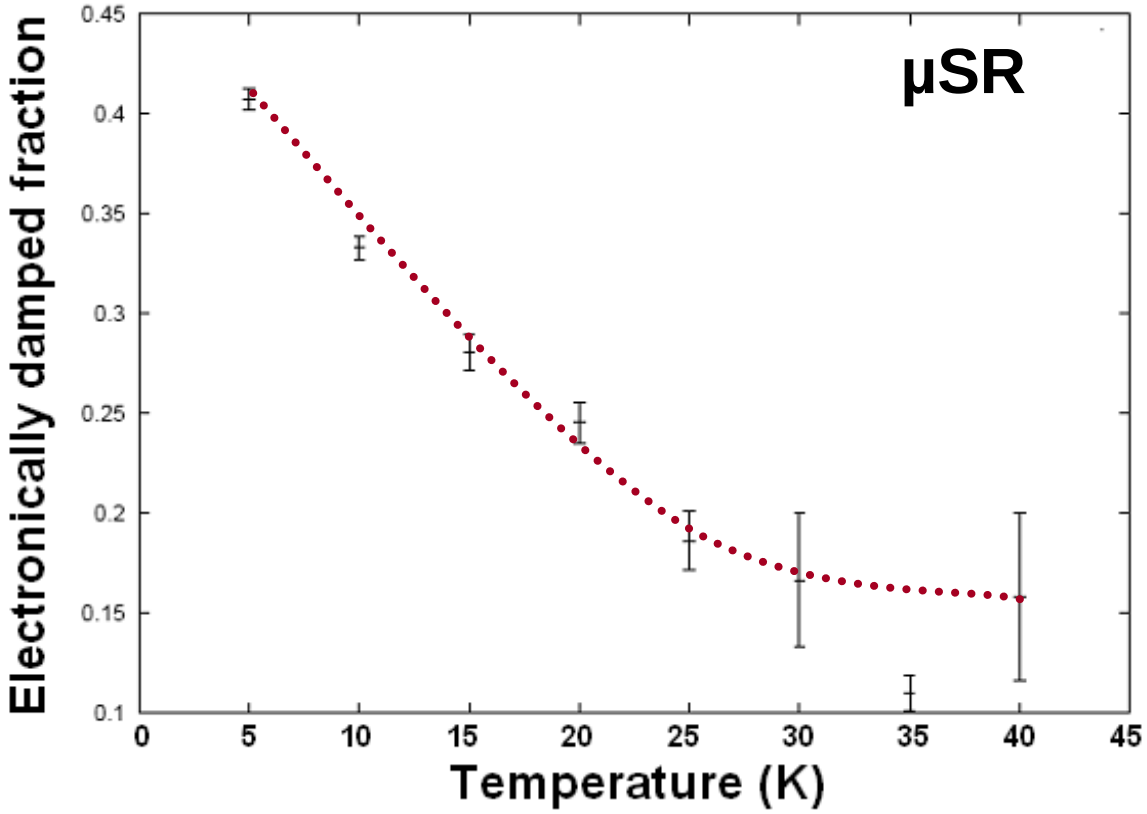


Structural phase transition below 30 K!

Very small tetragonal distortion ($F\bar{4}3m \rightarrow P\bar{4}2_1m$).

S. Jakob et al., J. Mater. Chem. 2007, 17, 3833 (2007)

Evidence for magnetic correlations below 30K



Structural phase transition is associated with the appearance of a damped signal fraction below 30 K, indicating magnetic correlations (no long-range static order down at least to 5 K).

Current scenario