

Lecture Notes

Introduction to Strongly Correlated Electron Systems

WS 2014/ 2015

Mohsen Abd-Elmeguid

II. Institute of Physics, University of Cologne, Germany

Introduction to strongly correlated electron systems

I. Introduction

Brief summary of electrons in solids, origin of strong electron correlations

II. Classes of strongly correlated electron systems

(a) Transition metal compounds: 3d-electrons

- Hubbard model, Mott insulator, metal-insulator transition
- Spin, charge, and orbital degrees of freedom and ordering phenomena, selected materials
- Pressure effect on the ground state properties of transition metal compounds

(b) Heavy fermion systems: 4f (5f) – electrons

- Landau Fermi-liquid model, Kondo effect, heavy fermion systems, non-Fermi liquid, quantum phase transitions, selected materials
- Pressure effect on the ground state properties of heavy fermion compounds

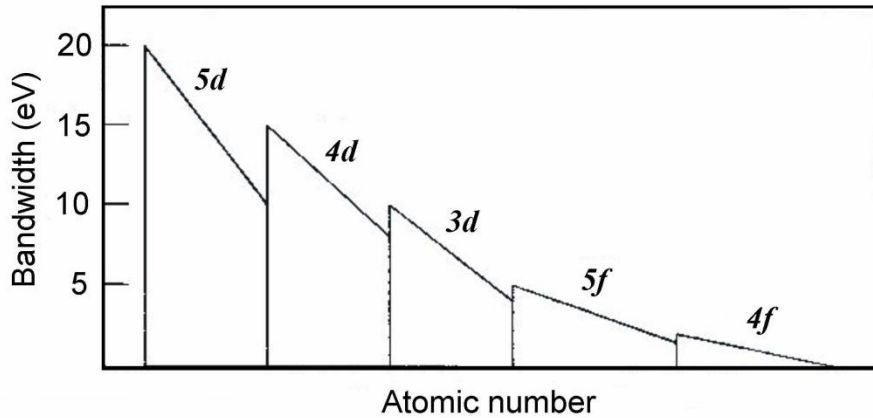
(c) Nanoscale structures:

- Quantum confinement, unusual properties for potential applications

III. Summary and open discussion

**Some applications to the emergence of unusual ground states
under high pressure**

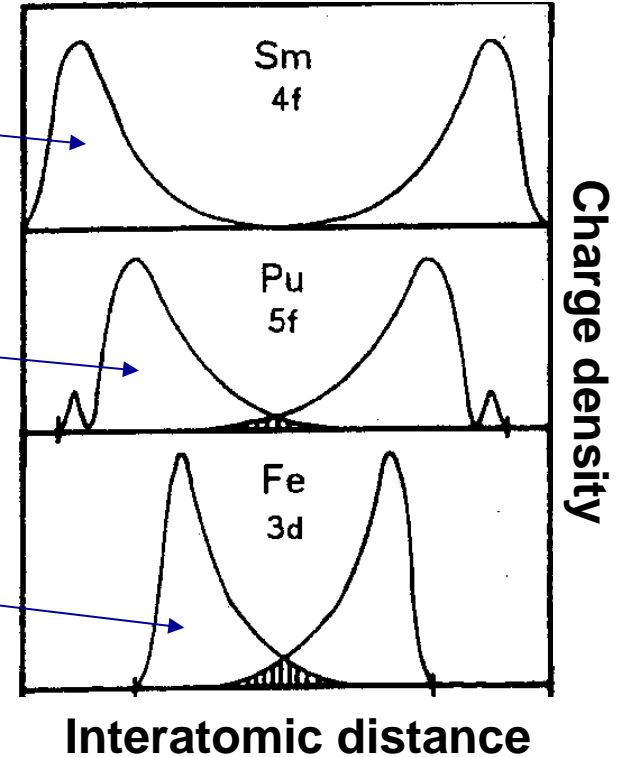
Local versus Itinerant magnetic moments



local moment magnetism

localized / itinerant

itinerant electron magnetism



Bandwidth (W) of the metallic state

$$W(\text{Fe}) \approx 4 \text{ eV}$$

$$W(\text{Pu}) \approx 2 \text{ eV}$$

$$W(\text{Sm}) \leq 1 \text{ eV}$$



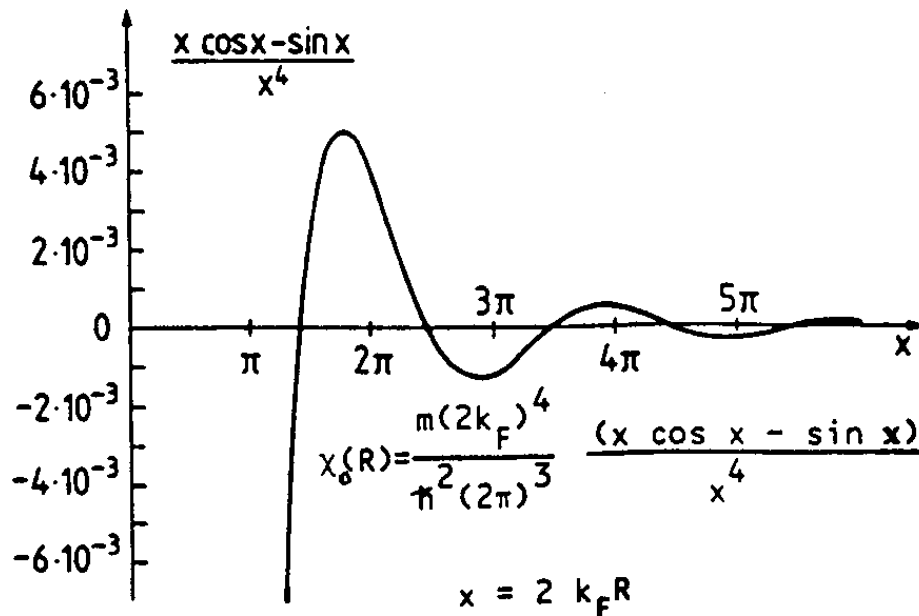
4f states are highly localized

No direct interaction possible!

RKKY interaction

Local moments (Spin S_i) in a sea of conduction electrons with itinerant spin $s(r)$

$$J(r) = 6\pi Z J D(E_F) \left[\frac{\sin(2k_F r)}{(2k_F r)^4} - \frac{\cos(2k_F r)}{(2k_F r)^3} \right]$$

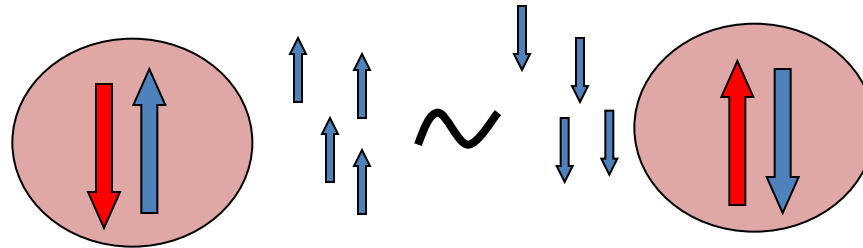


Z number of electrons / atom
 J s-d (f) exchange interaction
 $D(E_F)$ DOS at Fermi energy
 k_F Fermi momentum
 r distance between impurities

=> Oscillations of value and sign

Theoretical description

Kondo-lattice-system: periodical arrangement of localized **4f- moments** in a metallic matrix



Competition between:

Intrasite (on-site) interaction: **Kondo-Effect**

$$E_K = k_B T_K$$

⇒ screening of the magnetic moments

⇒ **nonmagnetic ground state**

$$T_K \sim \exp(-1/N(E_F)J)$$

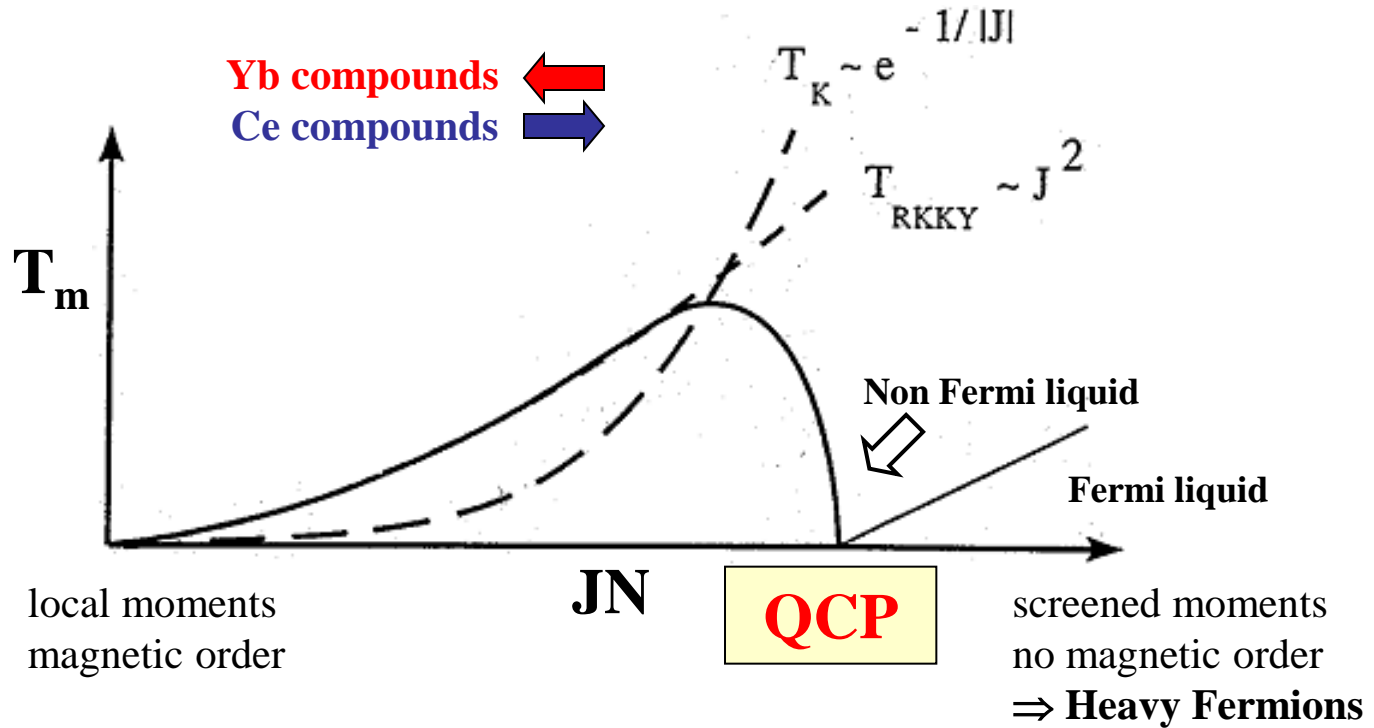
Intersite interaction: **RKKY** $E_{\text{RKKY}} = k_B T_{\text{RKKY}}$

⇒ **long range magnetic order**

$$T_{\text{RKKY}} \sim N(E_F) J^2$$

J: interaction between f- and conduction electrons

Doniach model



$T_m \rightarrow 0$

QCP: Quantum-Critical-Point

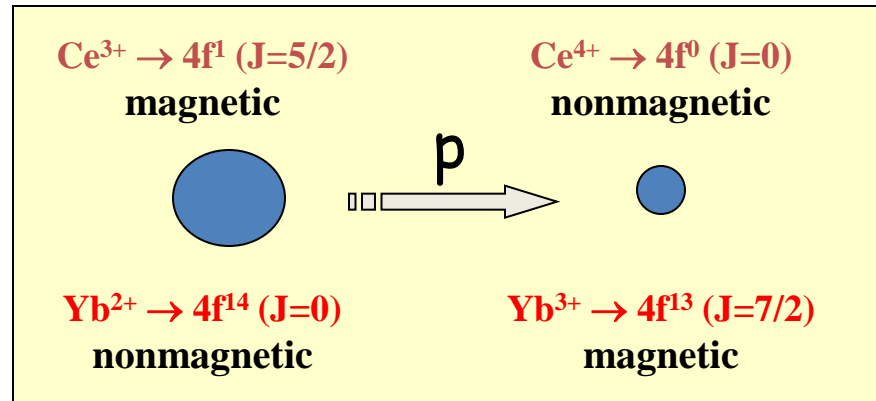
• Non-Fermi-Liquid (NFL):

$\Delta\rho \propto T^\epsilon \quad \epsilon = 1 - 1.5$

$\Delta C/T \propto -\ln T$

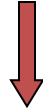
• Superconductivity possible

(e.g. $CeCu_2Si_2$, $CeRh_2Si_2$)



Yb heavy fermion compounds

analogy between $\text{Yb}^{3+}(4f^{13})$ and $\text{Ce}^{3+}(4f^1)$:



- nature of heavy fermion state?
- pressure effect is opposite ! → Same theoretical description ??

(4f-radius: 0.25\AA (Yb) < 0.37\AA (Ce))

^{170}Yb is a Mössbauer isotope !

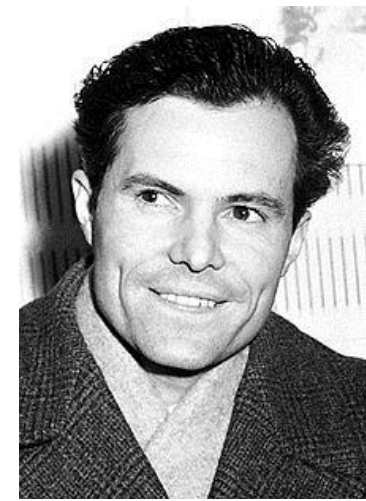


microscopic information on magnetic and electronic ground state properties

Mössbauer effect

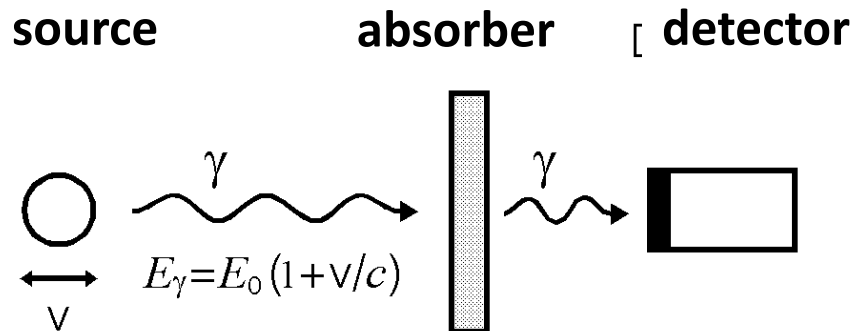
Rudolf Mößbauer (1929-2011)

Discovery 1957, Nobel Prize 1961

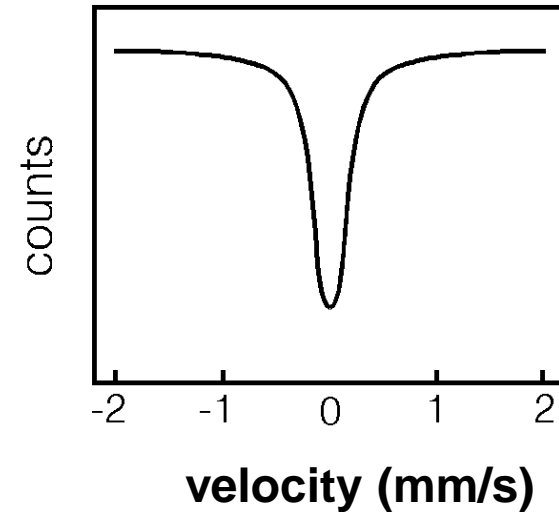


Mössbauer Spectroscopy

(a)



(b)



- recoilfree emission and absorption of γ -quanta of nuclei bounded in solids
- Doppler effect: $E = E_\gamma (1 + v/c)$

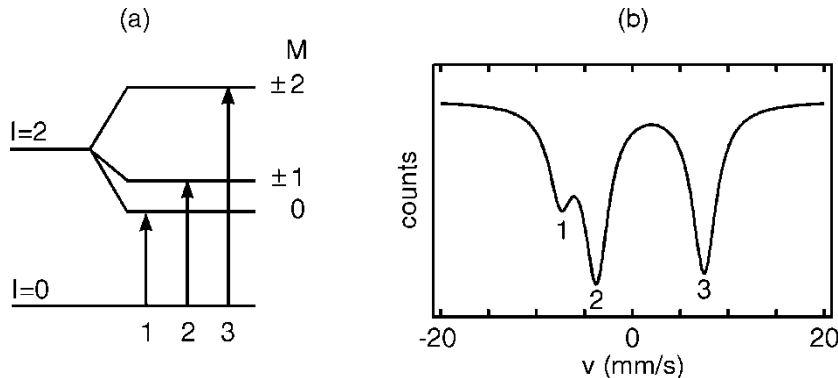
Hyperfine interactions between nucleus and electrons in solid



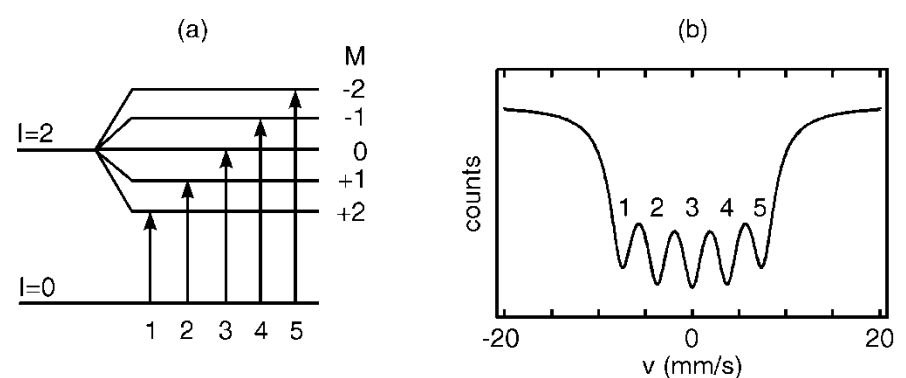
shift and splitting of nuclear energy levels

^{170}Yb :

electric quadrupole splitting



magnetic hyperfine splitting



- $E_\gamma = 84.25 \text{ keV}$
 - natural abundance of ^{170}Yb only 3%
- \Rightarrow very small effect \Rightarrow very long measuring time**

Pressure effect on Mössbauer parameters

paramagnetic state

only quadrupole splitting

$$\text{Yb}^{3+}, 4f^{13} \Rightarrow \text{max. } eQV_{zz} \approx 47 \text{ mm/s}$$

$$\text{Yb}^{2+}, 4f^{14} \Rightarrow eQV_{zz} = 0 \text{ mm/s}$$

\Rightarrow Possible change of the Yb valence state with p

magnetically ordered state

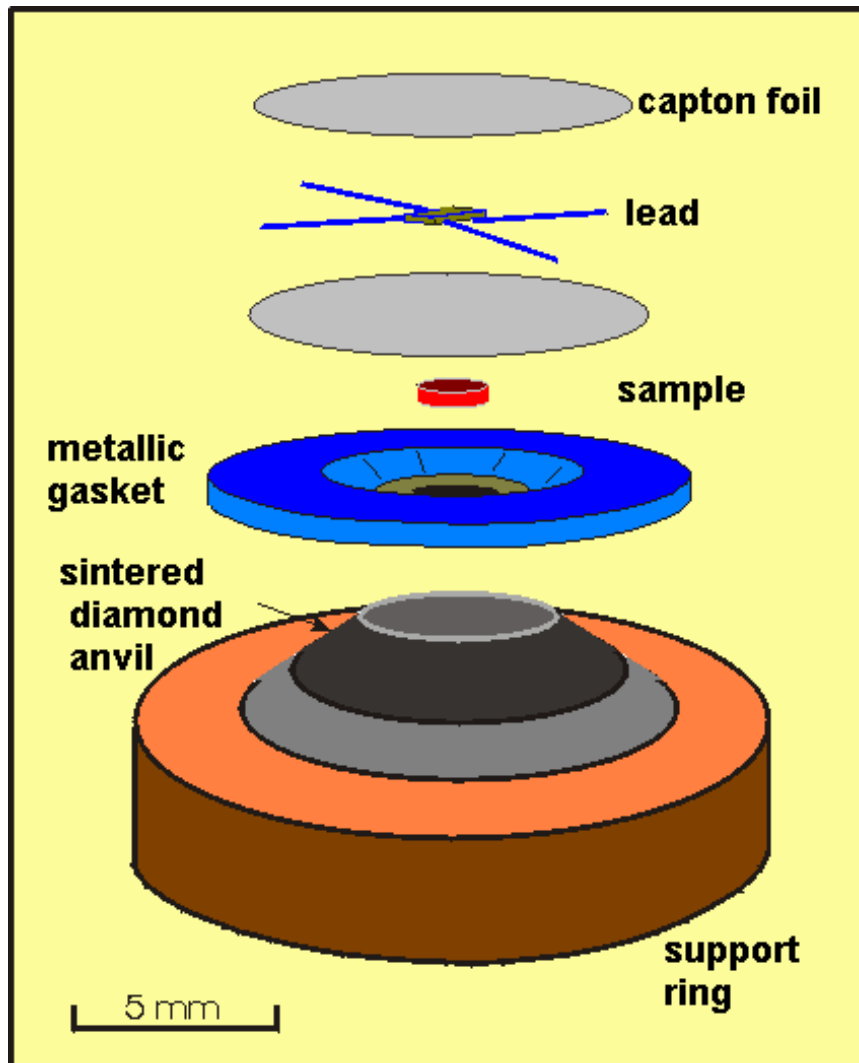
magnetic hyperfine splitting

contribution of the 4f moments is dominating

$$\mathbf{B}_{\text{eff}} = (102 \text{ T} / \mu_{\text{B}}) \mu_{\text{Yb}}$$

\Rightarrow information on $\mu_{\text{B}}(\text{p})$, $T_{\text{m}}(\text{p})$, change of spin structure with p

High pressure cell for ^{170}Yb -Mössbauer-spectroscopy



Requirements:

- large amount of sample – **large sample volume** necessary
 $d = 2.5 \text{ mm}$, $h = 0.5 \text{ mm}$
- higher pressure is needed
 $p \leq 20 \text{ GPa}$ (so far: $p < 9 \text{ GPa}$)

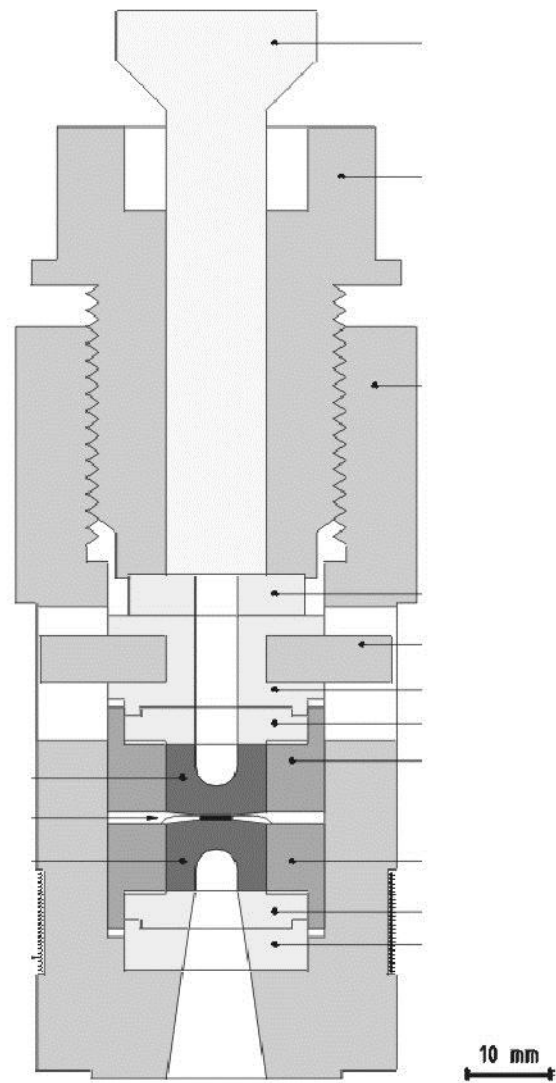
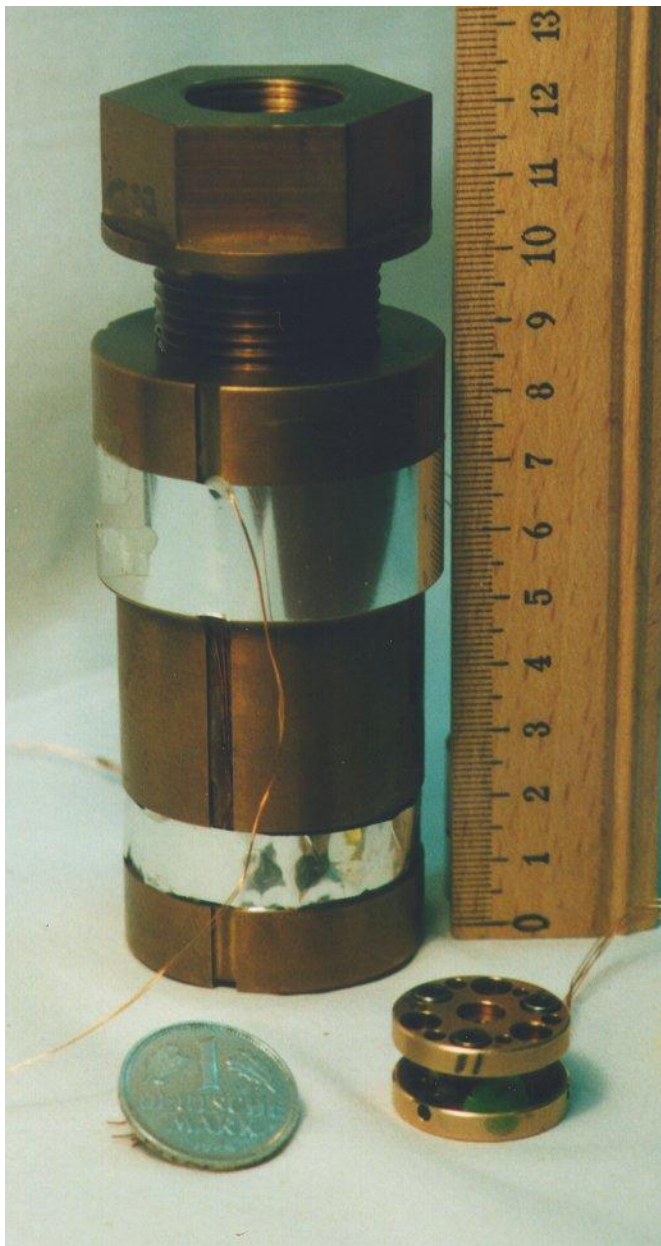


material must be
extremely hard

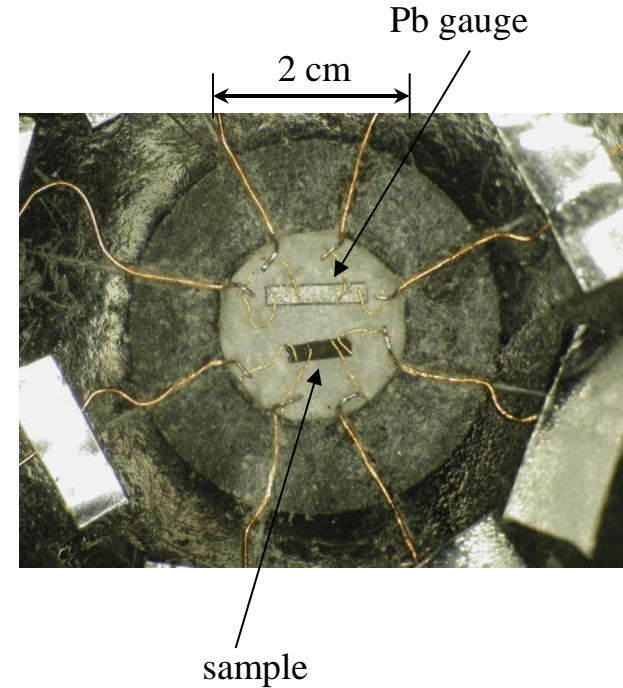
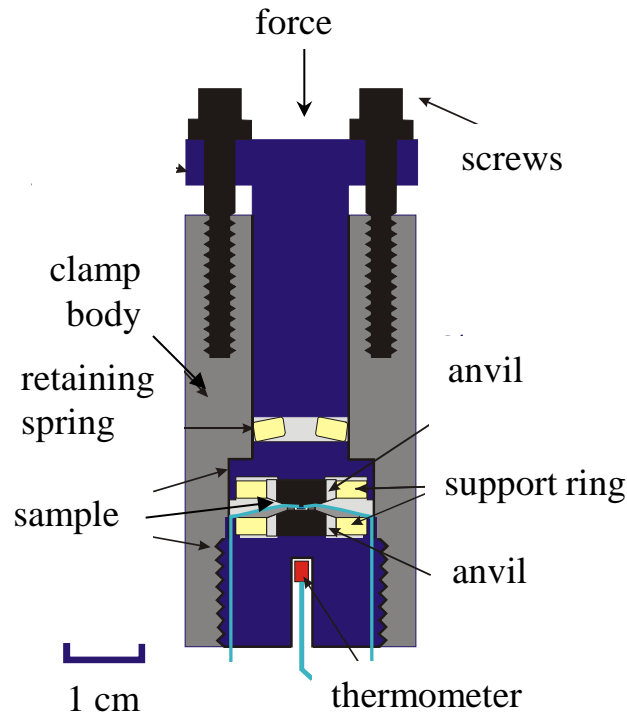
anvils made of
sintered diamonds

+

Re gasket



High pressure technique: large-volume clamp



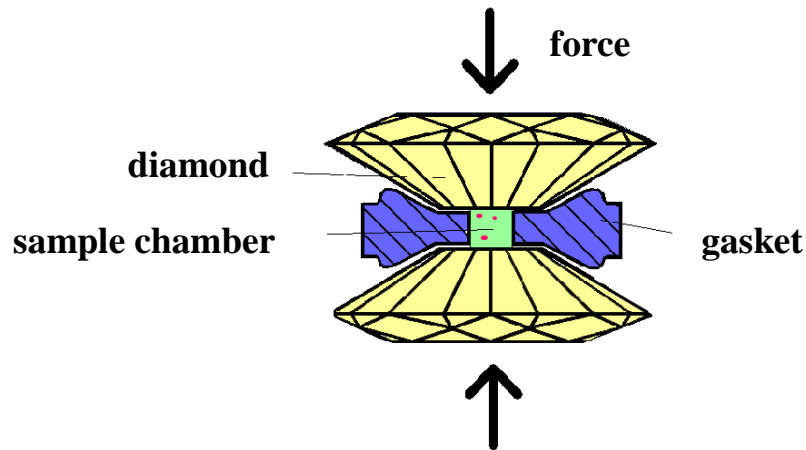
anvil culet: ~ 2 – 8 mm;
sample chamber: ~ 1 – 4 mm;
 p_{\max} ~ 40 GPa, quasihydrostatic

Benefits:

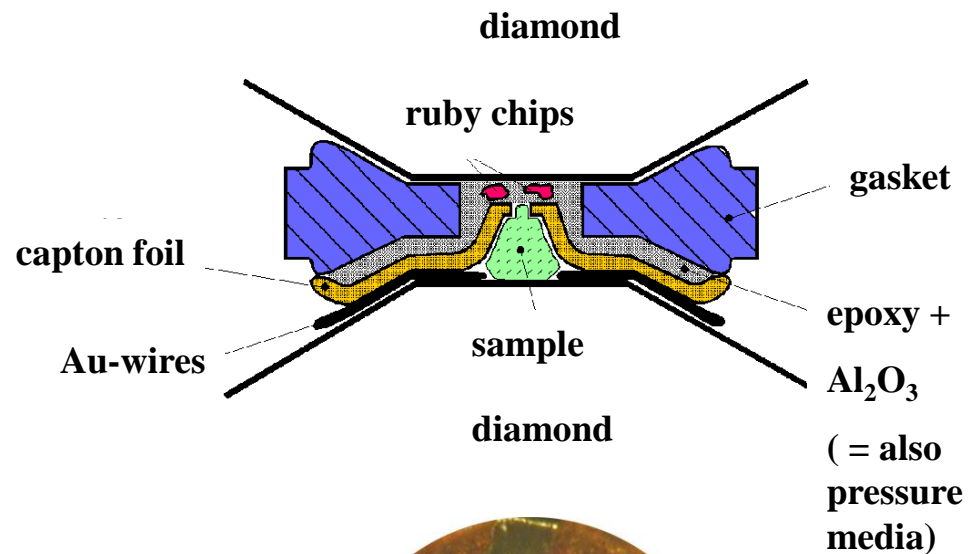
- large volume, large samples
- single crystals
- direction dependent electric transport

Experimental setup: Diamond Anvil Cell

i) x-ray diffraction



ii) resistivity measurements

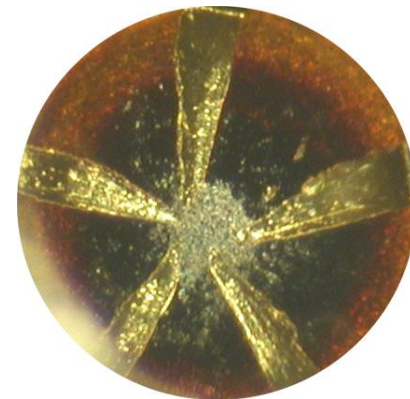


sample chamber: $\text{\O} = 100 - 300\mu\text{m}$;

height: 25-50 μm

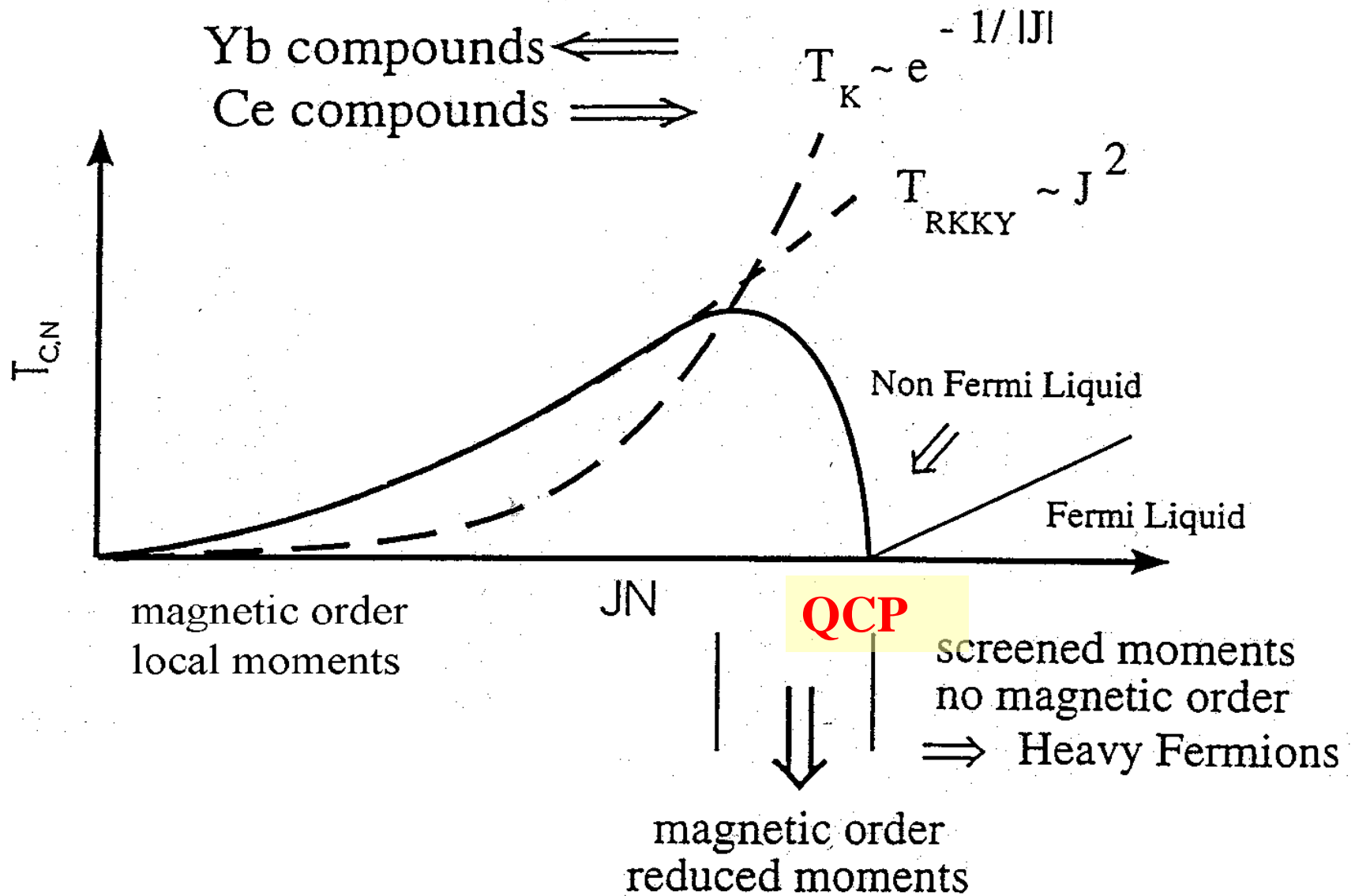
$p_{\text{max}} \approx 100 \text{ GPa} (= 1 \text{ Mbar})$

Pressure media: e.g. liquid Nitrogen, liquid Argon, liq. Helium, Oil, Epoxy, etc.

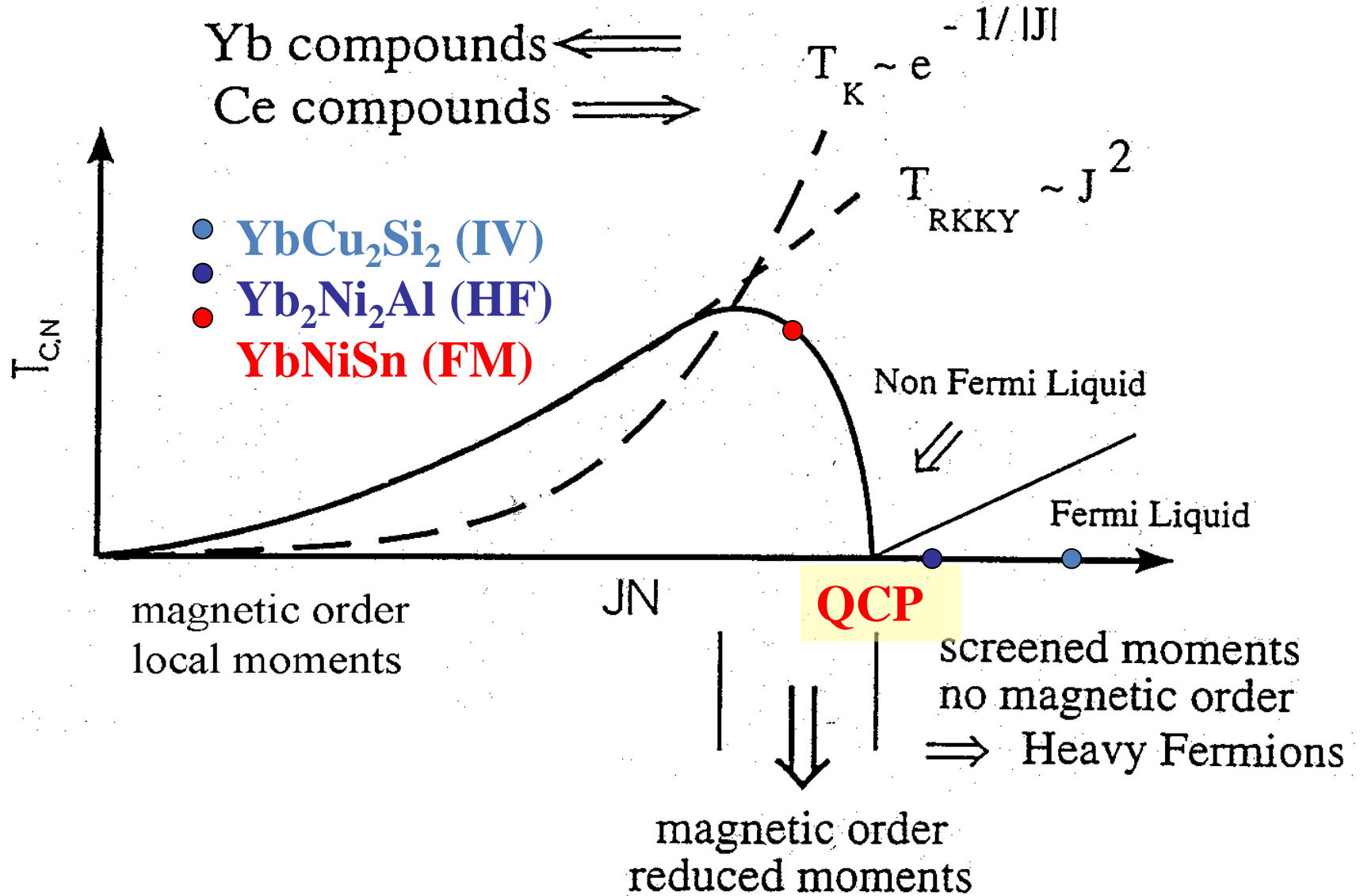


sample chamber $\text{\O} \approx 100 \mu\text{m}$

Some examples



Some examples



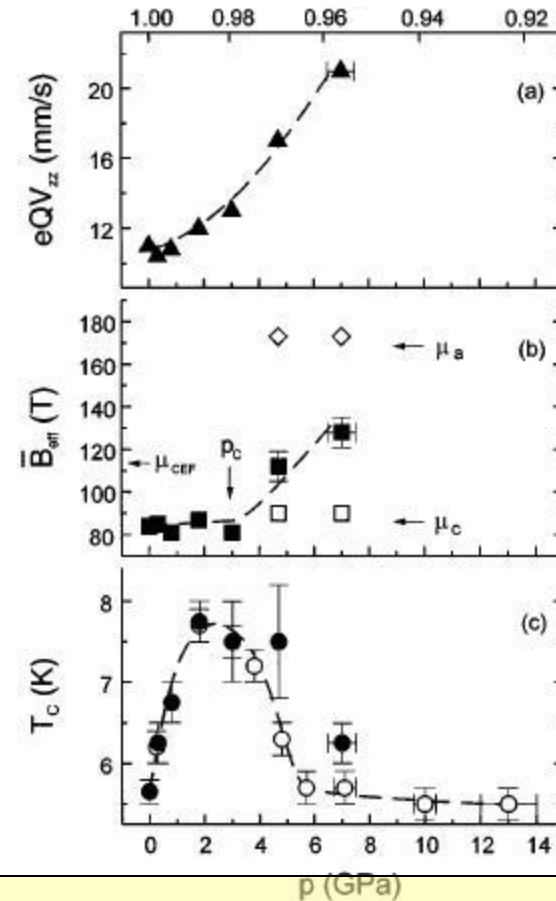
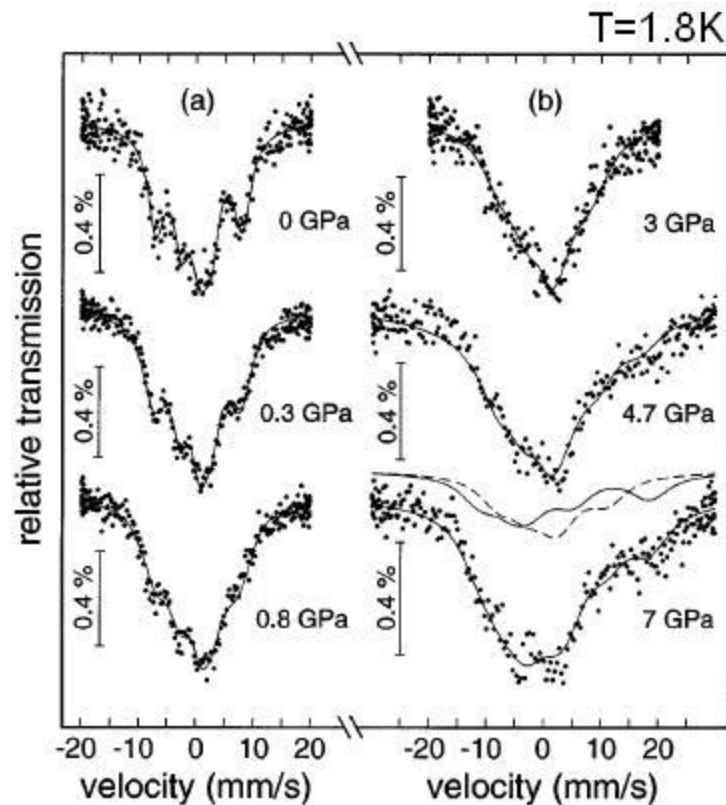
Competing Anisotropies in the Ferromagnetic Kondo-Lattice Compound YbNiSn: Observation of a Complex Magnetic Ground State under High Pressure

K. Drescher,¹ M. M. Abd-Elmeguid,¹ H. Micklitz,¹ and J. P. Sanchez²

¹*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany*

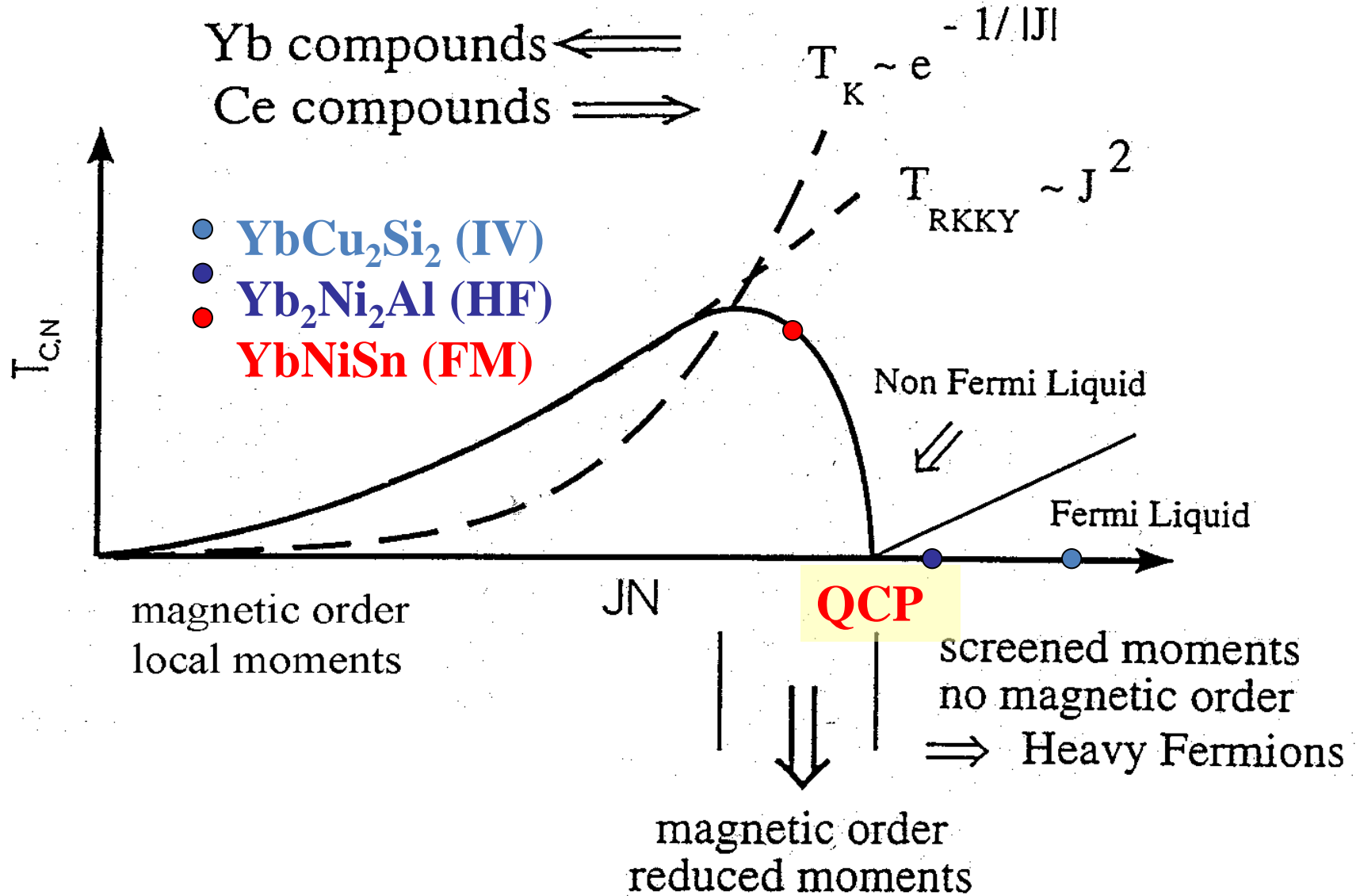
²*Département de Recherche Fondamentale sur la Matière Condensée, CEA/Grenoble,
17 Rue des Martyrs, 38054 Grenoble Cedex 9, France*

(Received 3 July 1996)



**Stable moment up to 3 GPa \Rightarrow no Kondo screening !
Pressure-induced complex magnetic state**

Some examples



Pressure-Induced Local Moment Magnetism in the Nonmagnetic Heavy Fermion Compound $\text{Yb}_2\text{Ni}_2\text{Al}$

H. Winkelmann, M. M. Abd-Elmeguid, and H. Micklitz

II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany

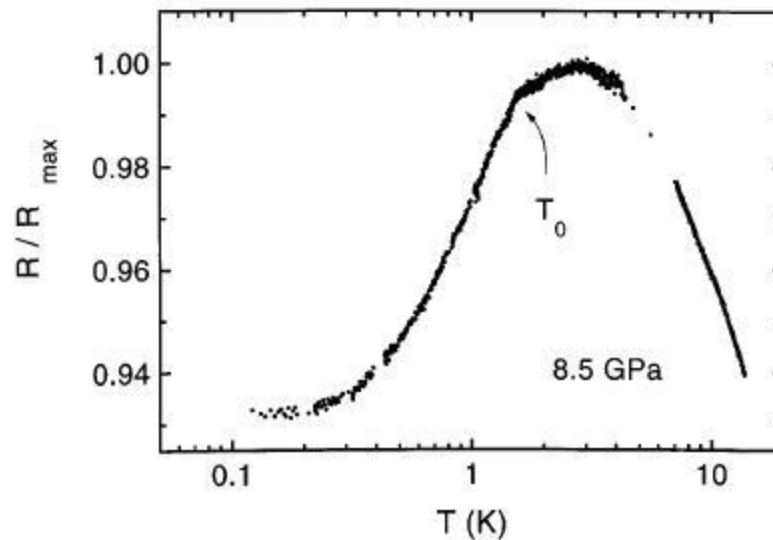
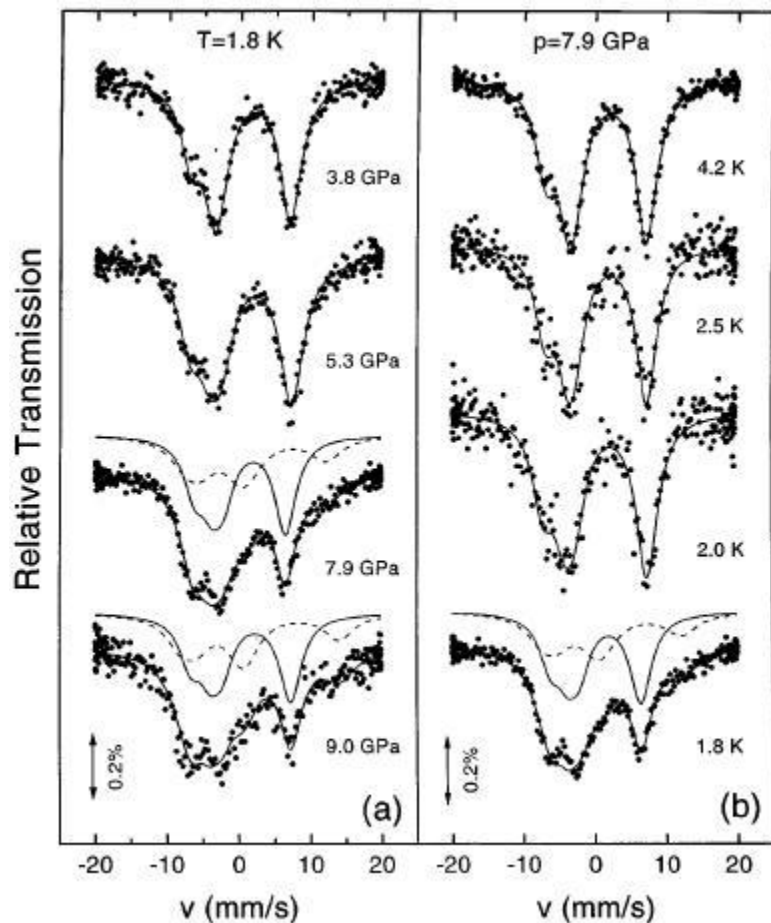
J. P. Sanchez

Département de Recherche Fondamentale sur la Matière condensée, CEA/Grenoble, 17 rue des Martyrs, 38054 Grenoble Cédex 9, France

C. Geibel and F. Steglich

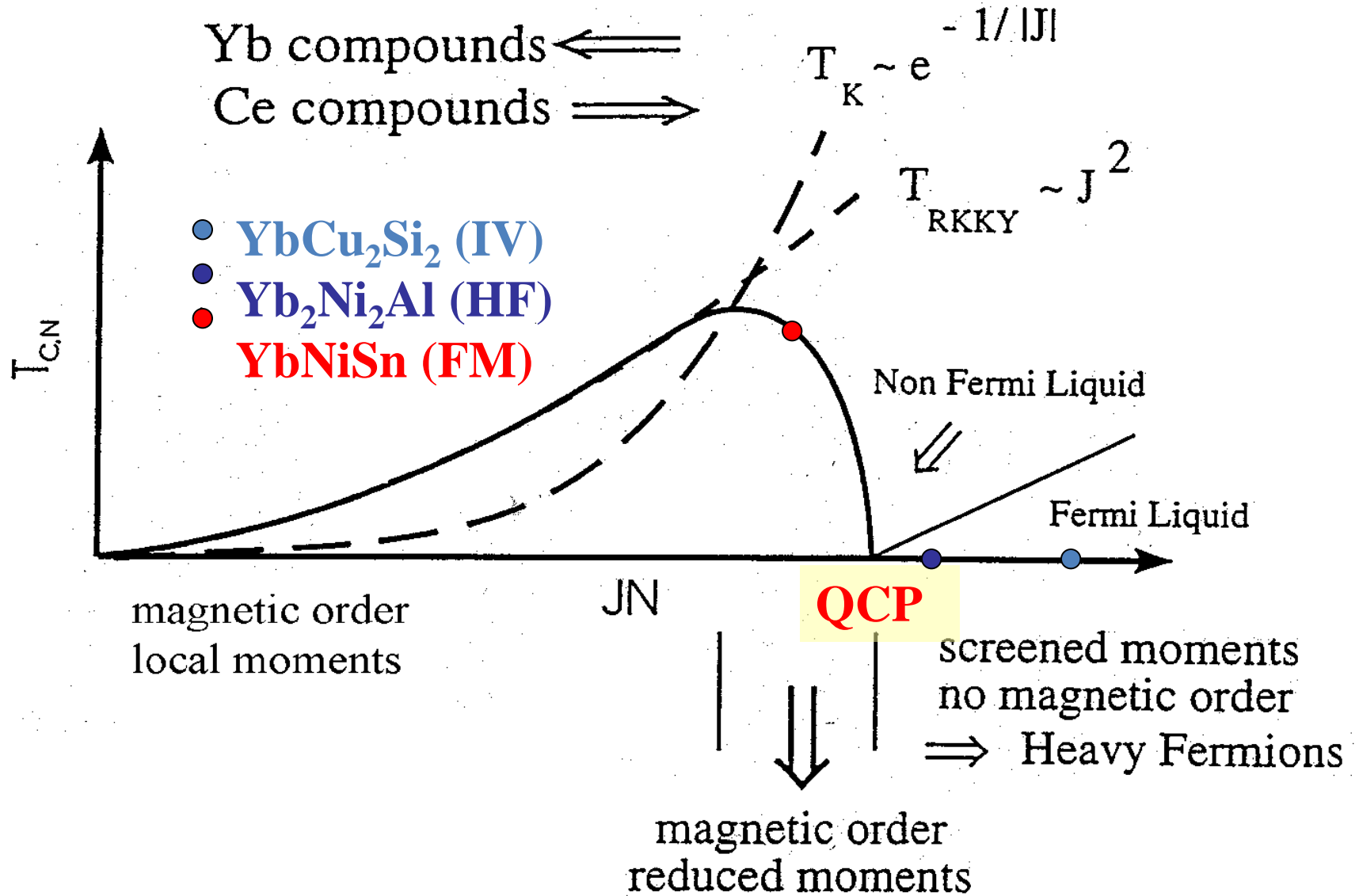
Max Plank Institut für Chemische Physik fester Stoffe, Bayreutherstrasse 40, Haus 16, 01159 Dresden, Germany

(Received 12 May 1998)

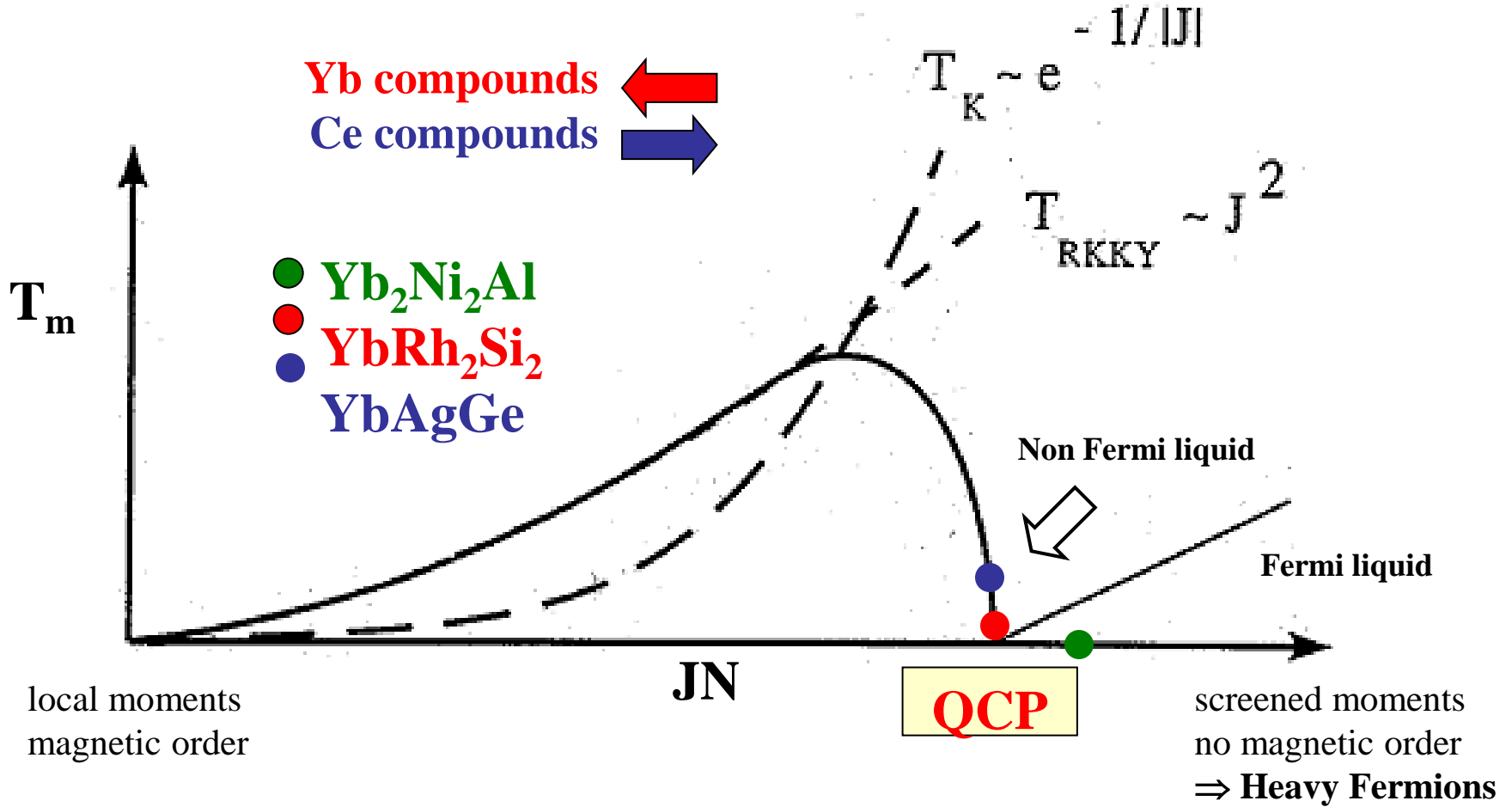


Pressure-induced first-order magnetic phase transition

Some examples



Some examples

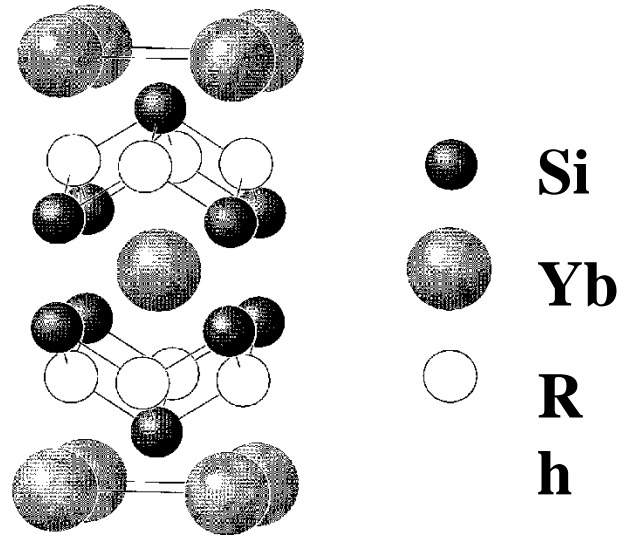


YbRh₂Si₂ - non Fermi liquid system near a QCP

tetragonal ThCr₂Si₂-type
structure (I4/mmm)

High quality single crystals (MPI Dresden)

O. Trovarelli; C. Geibel

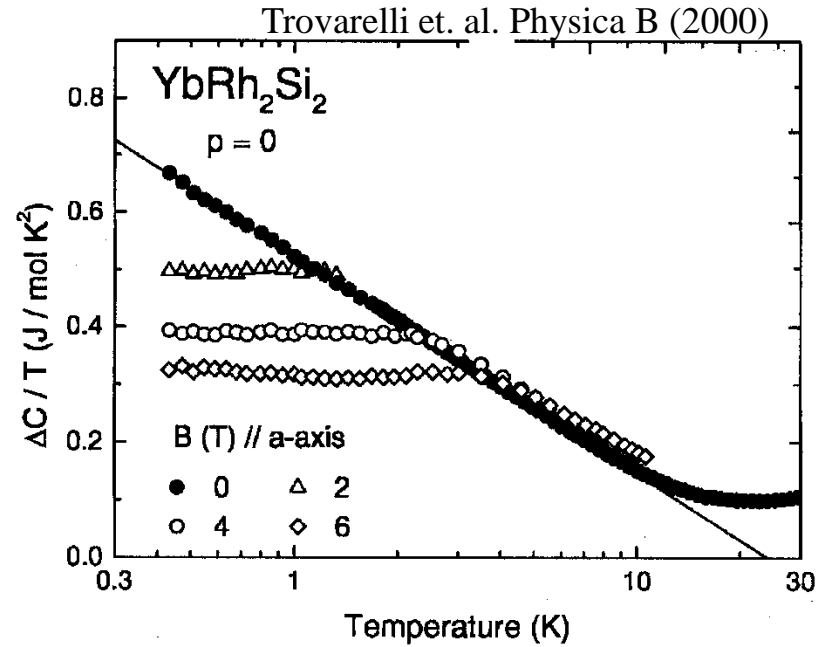
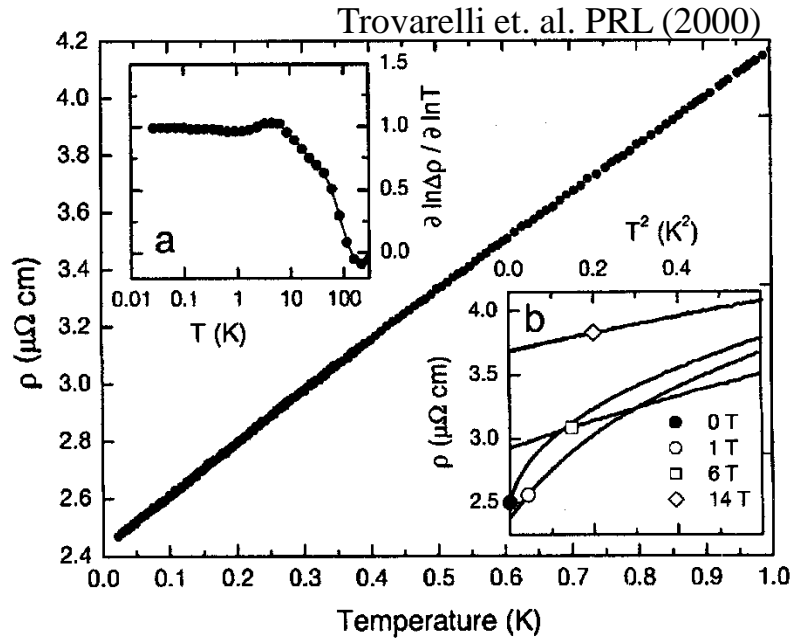


Model system for the observation of the evolution of the long range magnetic order out of the NFL state

Comparison with Ce-compounds possible

YbRh₂Si₂ - properties:

a) pronounced NFL-behaviour at low temperatures



NFL

$$\Delta \rho \propto T$$

$$\Delta C/T \propto -\ln T$$

FL

$$\Delta \rho \propto T^2$$

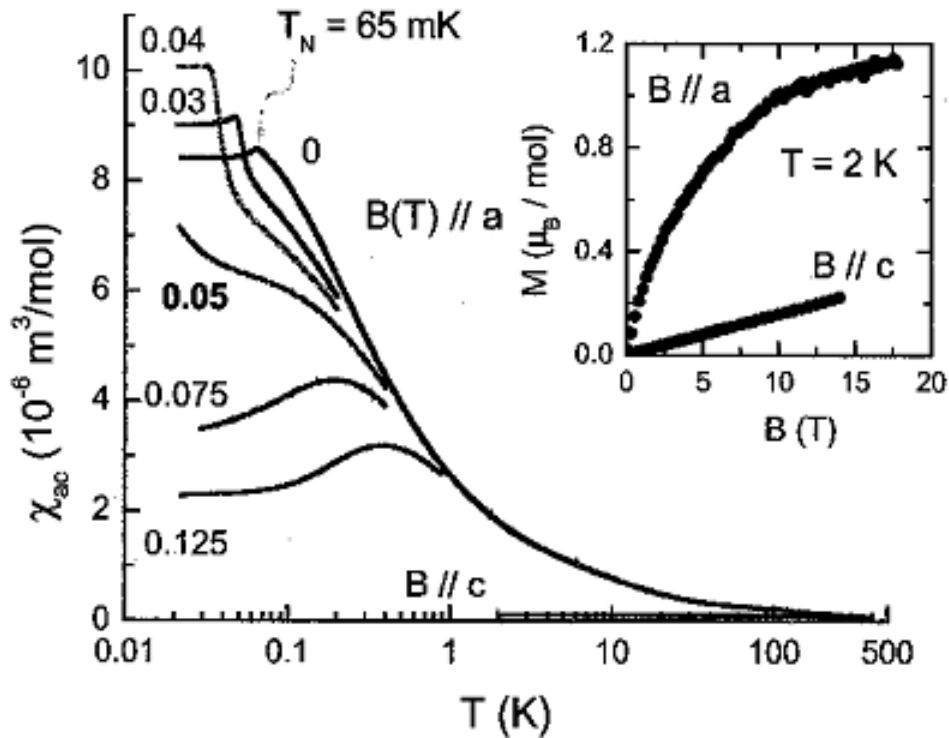
$$\Delta C/T = \text{const.}$$

B_{ext} suppresses NFL-behavior

NFL → FL

b) weak magnetic order at very low temperatures

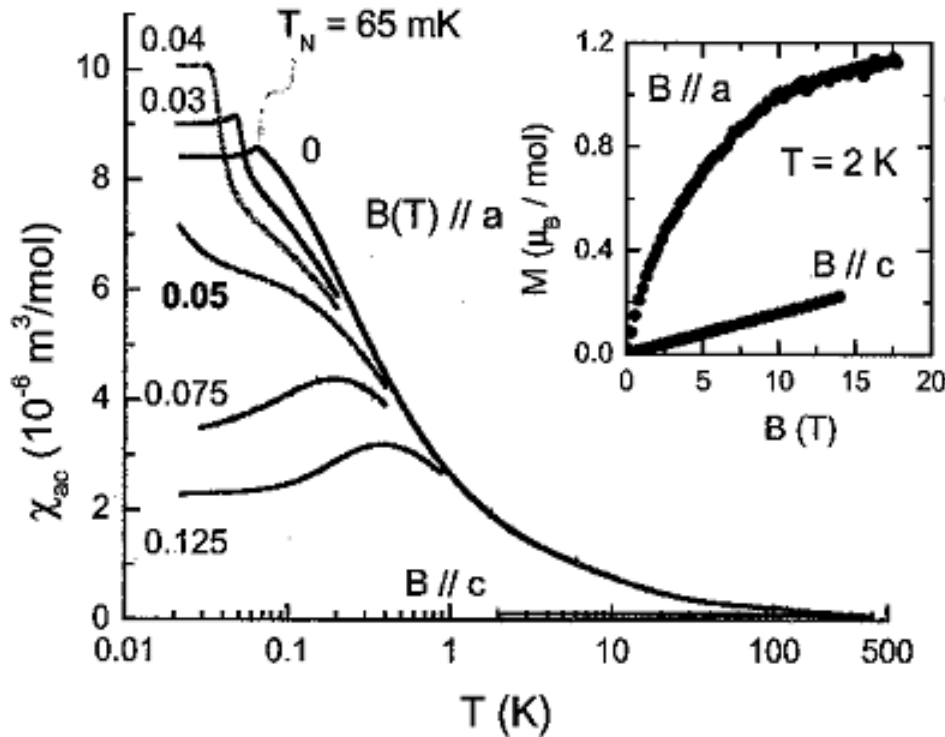
Trovarelli et al. PRL (2000)



- $T_m \approx 65 \text{ mK}$
 - very weak magnetic order
 - B_{ext} suppresses magn. order
- $T_m < 20 \text{ mK}$ for $B_{\text{ext}} = 45 \text{ mT}$

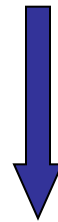
b) weak magnetic order at very low temperatures

Trovarelli et al. PRL (2000)



- $T_m \approx 65$ mK
- very weak magnetic order
- B_{ext} suppresses mag. order

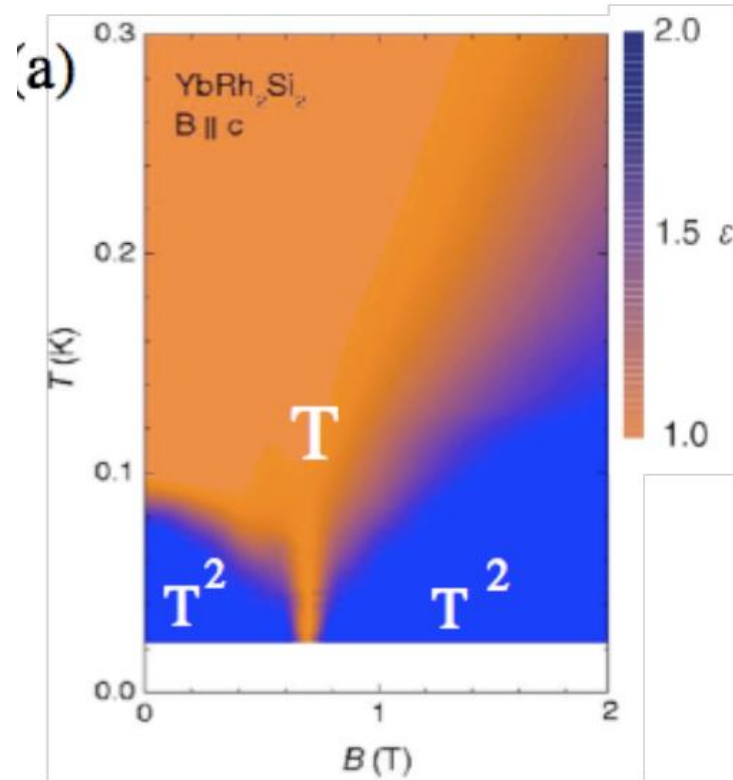
$T_m < 20$ mK for $B_{\text{ext}} = 45$ mT



Proximity of YbRh_2Si_2 to a QCP !

YbRh₂Si₂:

Field-induced quantum critical point



Custers et al; (2003)

c) effect of pressure and Ge-doping

Pressure

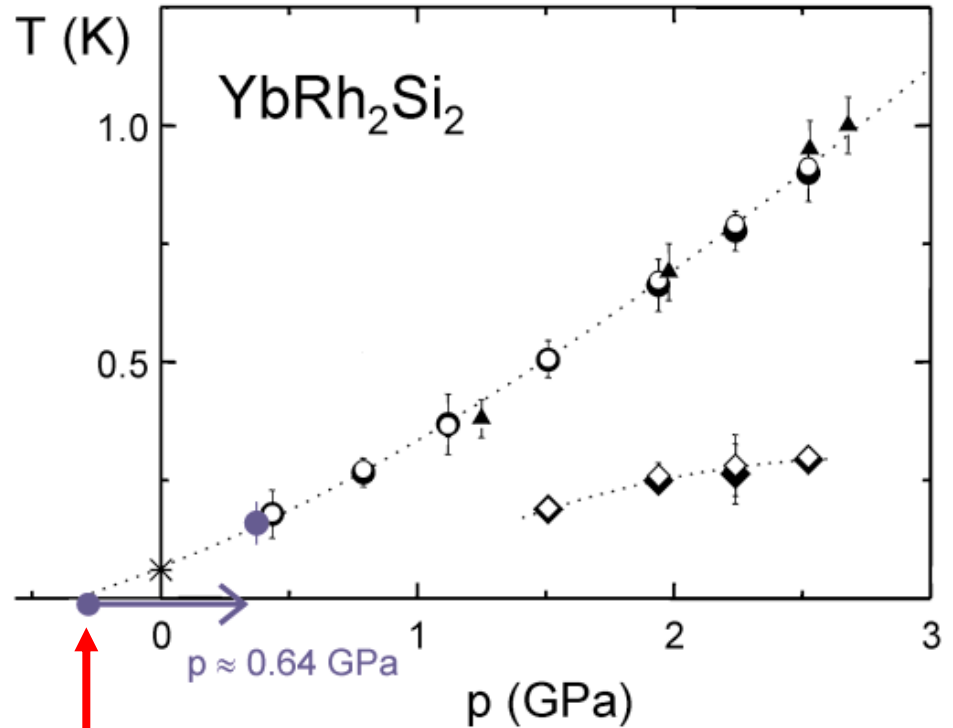
- T_m increases!
- $T_m \approx 1\text{K}$ at $p = 2.7$ GPa

Ge-doping \Leftrightarrow volume-expansion

5 % Ge
($T_m < 10\text{mK}$)

- mag. order suppressed

O. Trovarelli et al (2000)



YbRh₂Si₂ can be tuned to QCP

QCP: $p \approx -0.3$ GPa $\cong \sim$
4% Ge

QCP

YbRh₂Si₂ - magnetic ground state

P. Gegenwart et al. PRL (2002)

- **weak antiferromagnetic order below $T_N = 70$ mK**
 - **paramagnetic moment $T_N < T < 0.6$ K; $\mu_{Yb} = 1.4 \mu_B$**
 - **ordered antiferromagnetic moment $\mu_{Yb} < 0.1 \mu_B$**
- **antiferromagnetic fluctuations** (NMR, K.Ishida et al., PRL (2002);

μ SR, K. Ishida et al. Physica B (2003))



Low moment (LM) dynamic magnetic state at ambient pressure

Open questions

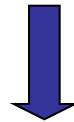
nature of the ground state near the QCP

- change of the magnetic moment μ_{Yb} and T_m with pressure?
- pressure-induced magnetic phase transition?

⇒ pressure-temperature magnetic phase diagram

experiment ↔ theory ?

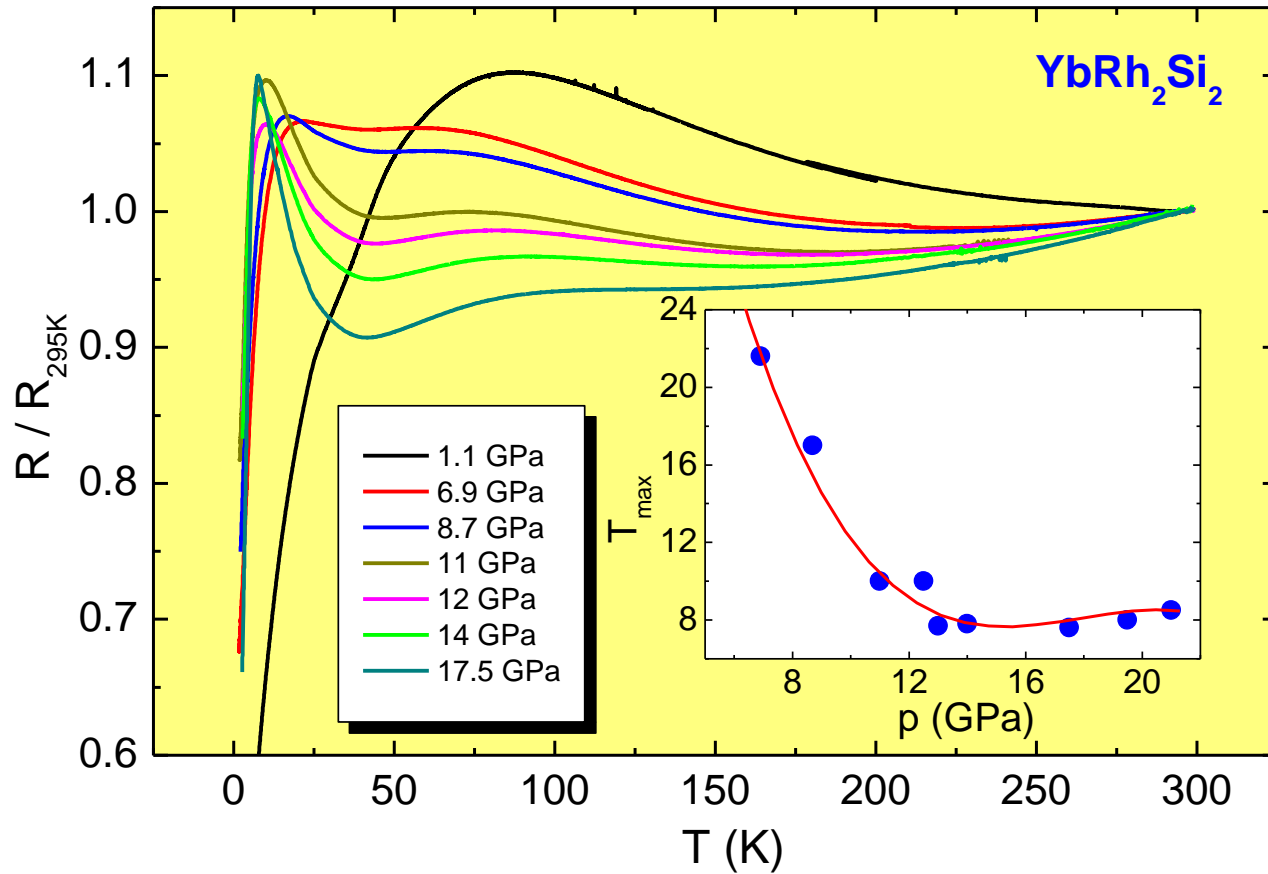
?



experimental approach

- ^{170}Yb -Mössbauer spectroscopy $p \leq 20 \text{ GPa}$, $T \geq 1.3 \text{ K}$
- electrical resistance $R(p,T,B)$ $p \leq 25 \text{ GPa}$, $T \geq 1.7 \text{ K}$ and mK-range
- x-ray diffraction $p \leq 25 \text{ GPa}$, $T = 300 \text{ K}$

YbRh₂Si₂ - electrical resistance under high pressure



**Hints for magnetic order
at $p \geq 11$ GPa !**

YbRh₂Si₂ - ¹⁷⁰Yb-Mössbauer spectroscopy

- observation of long range magnetic order for

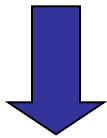
p > 10 GPa and **T < 1.5 K**

- for p ≥ 15 GPa:

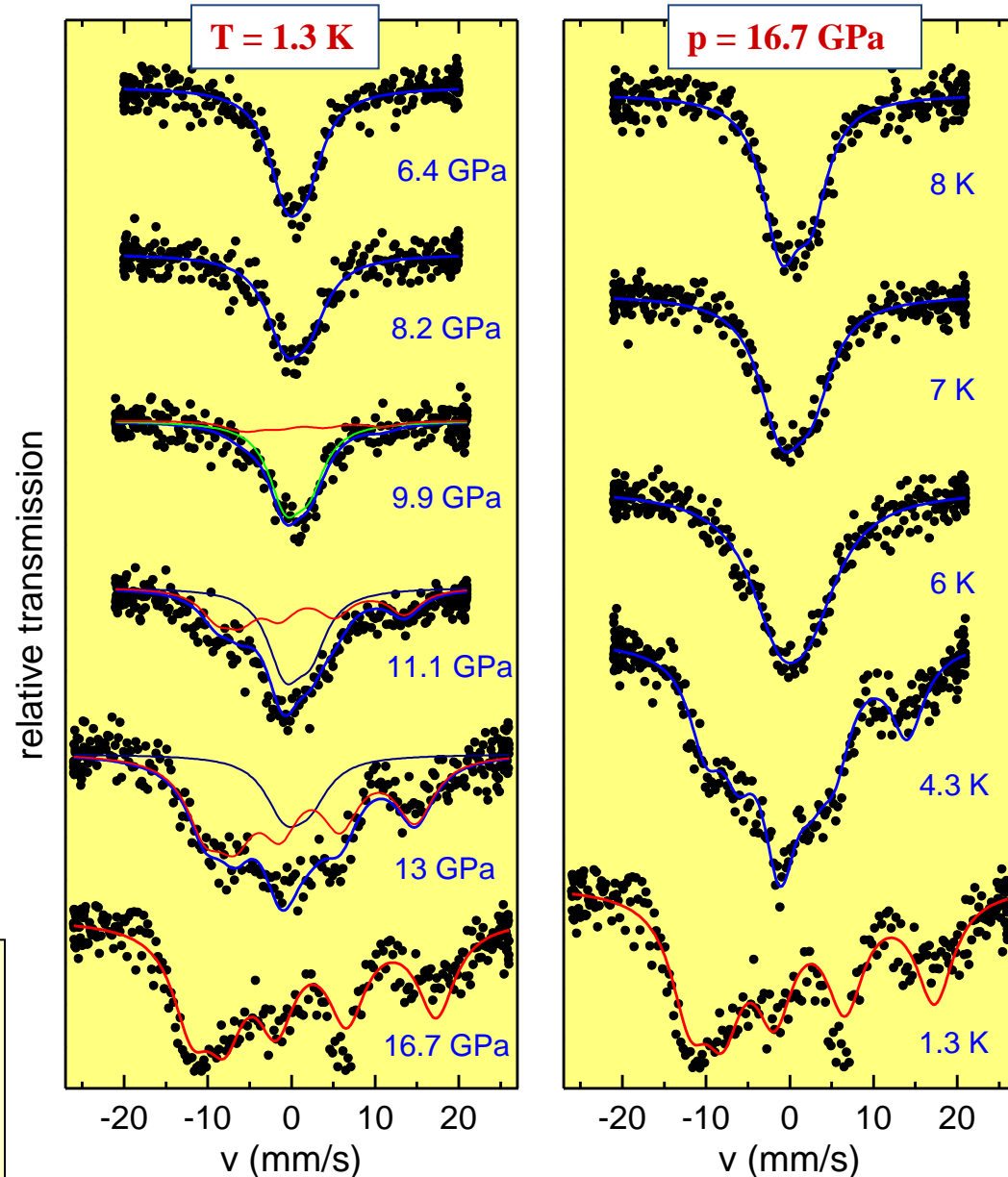
$$T_{\text{mag}} \geq 7 \text{ K}$$

$$\mu_{\text{Yb}} \sim 1.9 \mu_{\text{B}} \parallel \text{c-axis}$$

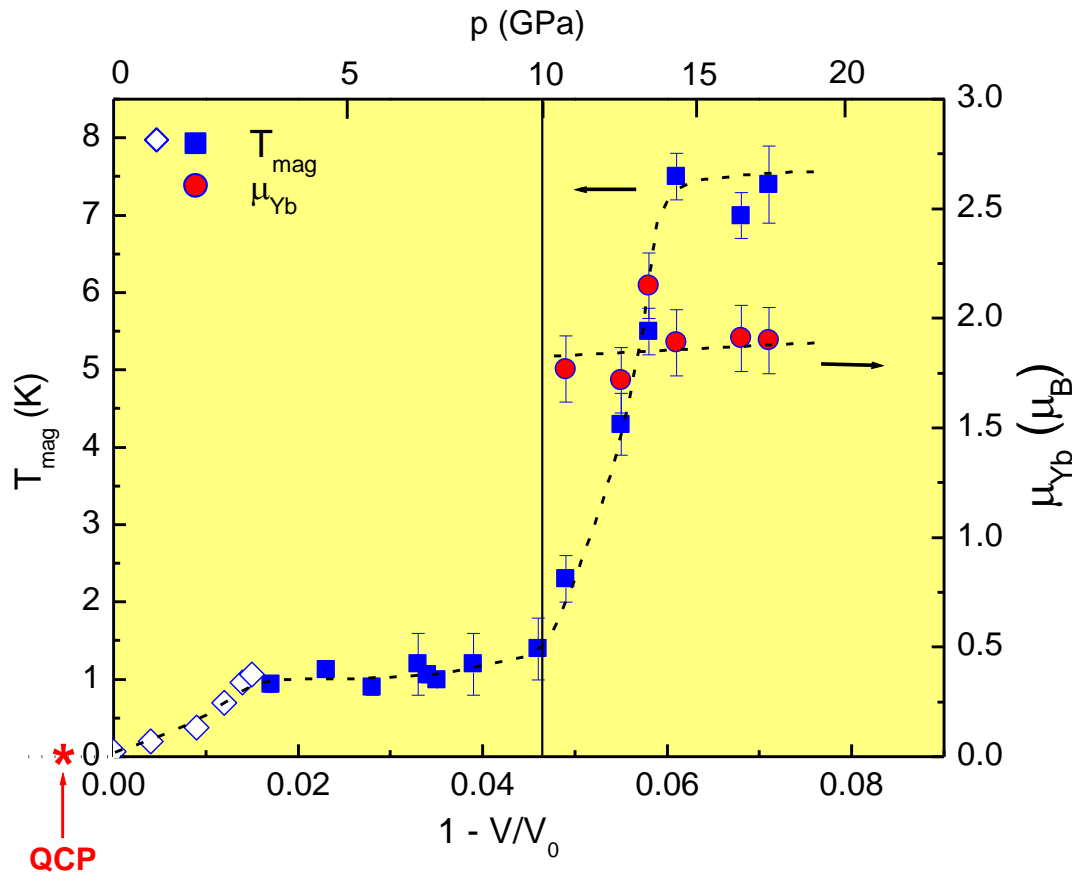
(low moment \perp c-axis)



first-order magnetic phase transition (**Low moment** → **High moment**)



YbRh₂Si₂ - pressure dependence of T_{mag} and μ_{Yb}

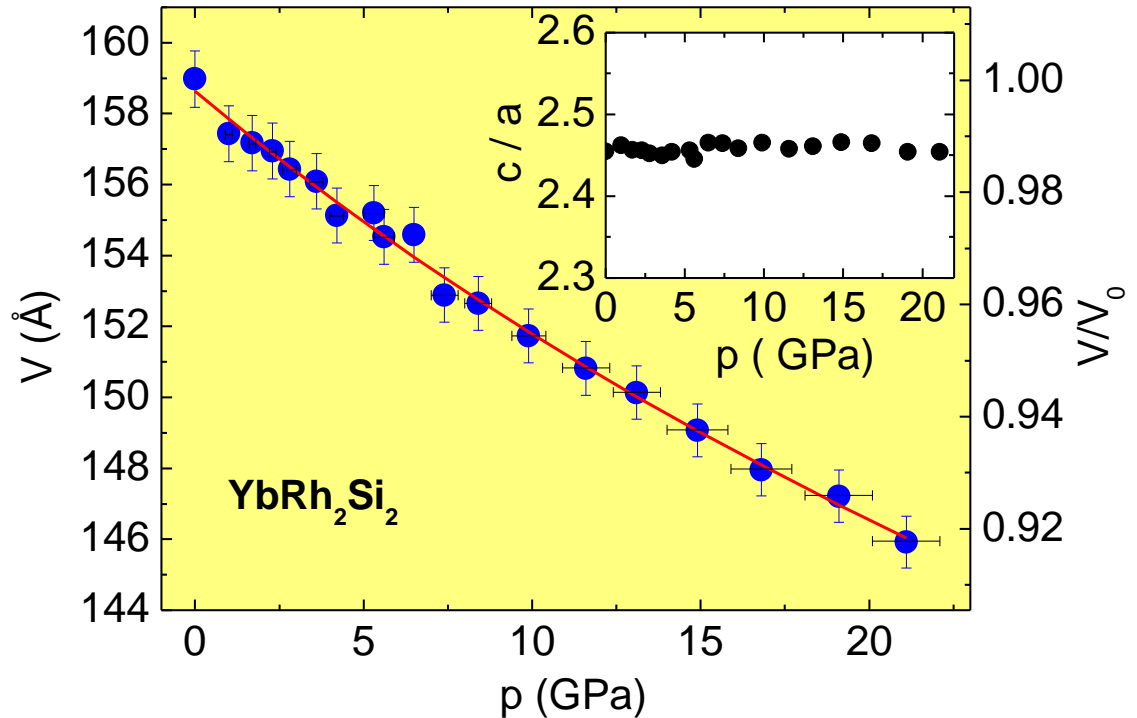


unusual pressure dependence of T_{mag}
First order phase transition at $p \approx 10$ GPa

structural phase transition?

YbRh₂Si₂ - x-ray diffraction under high pressure

**crystal structure
stable for
 $p \leq 21$ GPa !**



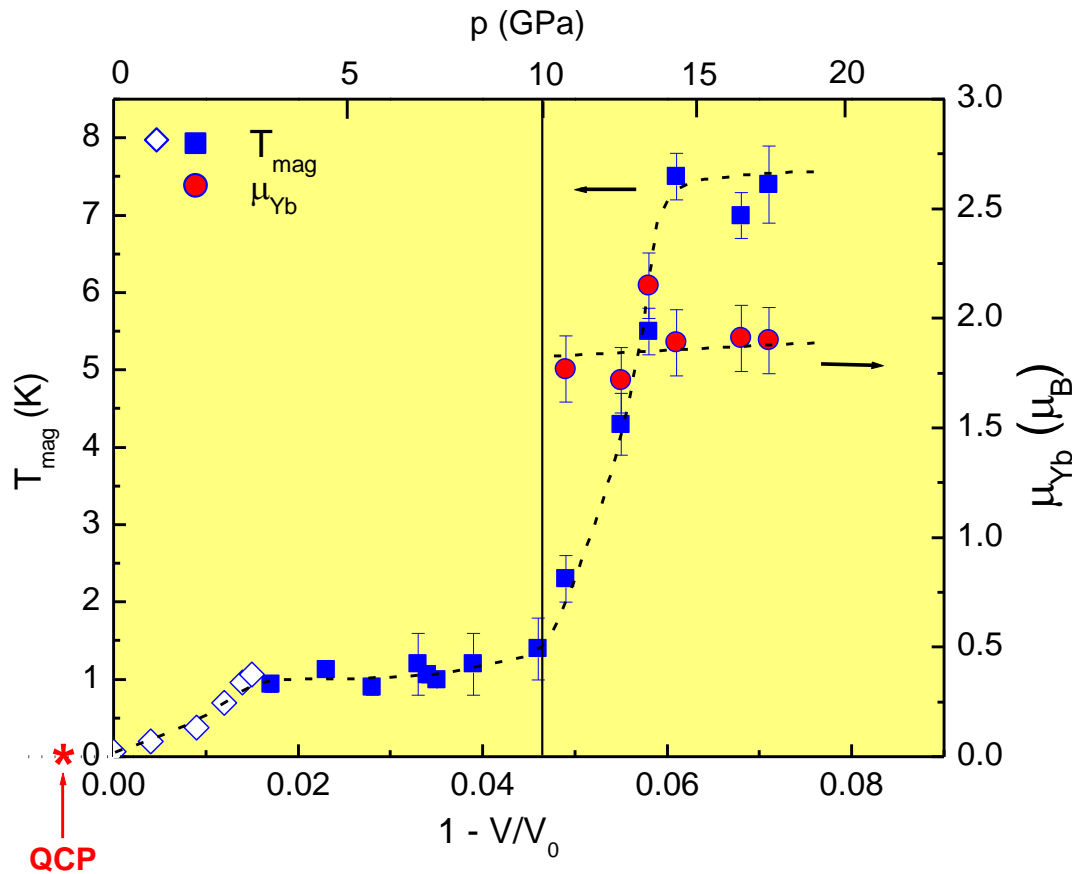
Bulk modulus: $B_0 = (198 \pm 15)$ GPa

comparison:

YbNiSn: $B_0 = (146 \pm 20)$ GPa

Yb₂Ni₂Al: $B_0 = (165 \pm 12)$ GPa

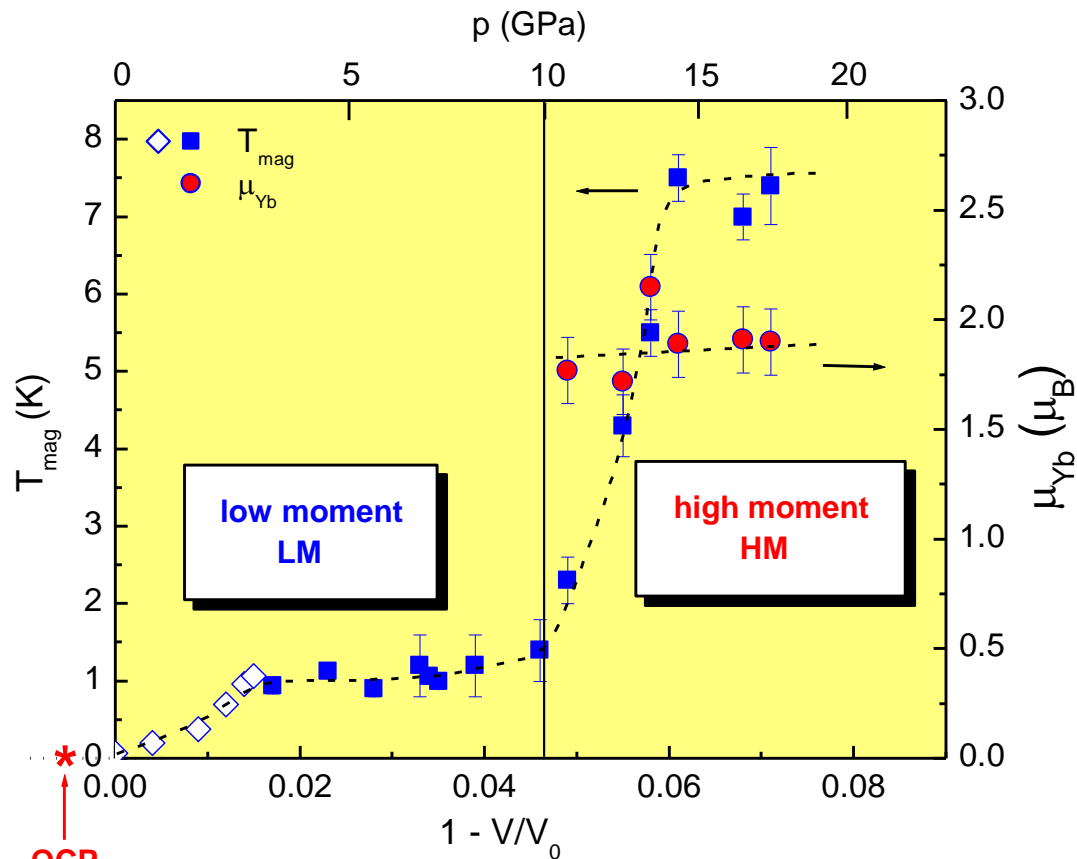
YbRh₂Si₂ - pressure dependence of T_{mag} and μ_{Yb}



unusual pressure dependence of T_{mag}

First order phase transition at $p \approx 10$ GPa

YbRh₂Si₂ - pressure dependence of T_{mag} and μ_{Yb}



$p < 10$ GPa : LM state
dynamic fluctuations

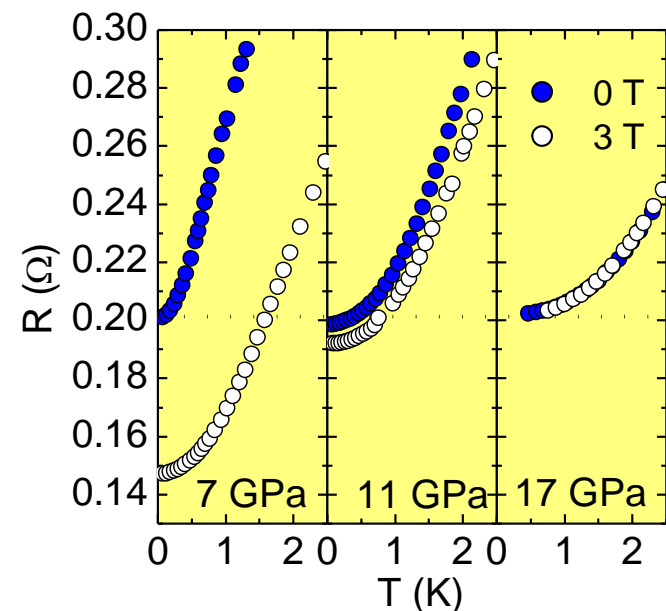
$p > 10$ GPa : HM state

- $\mu_{\text{Yb}} \approx 1.9 \mu_{\text{B}}$
- static magnetic order

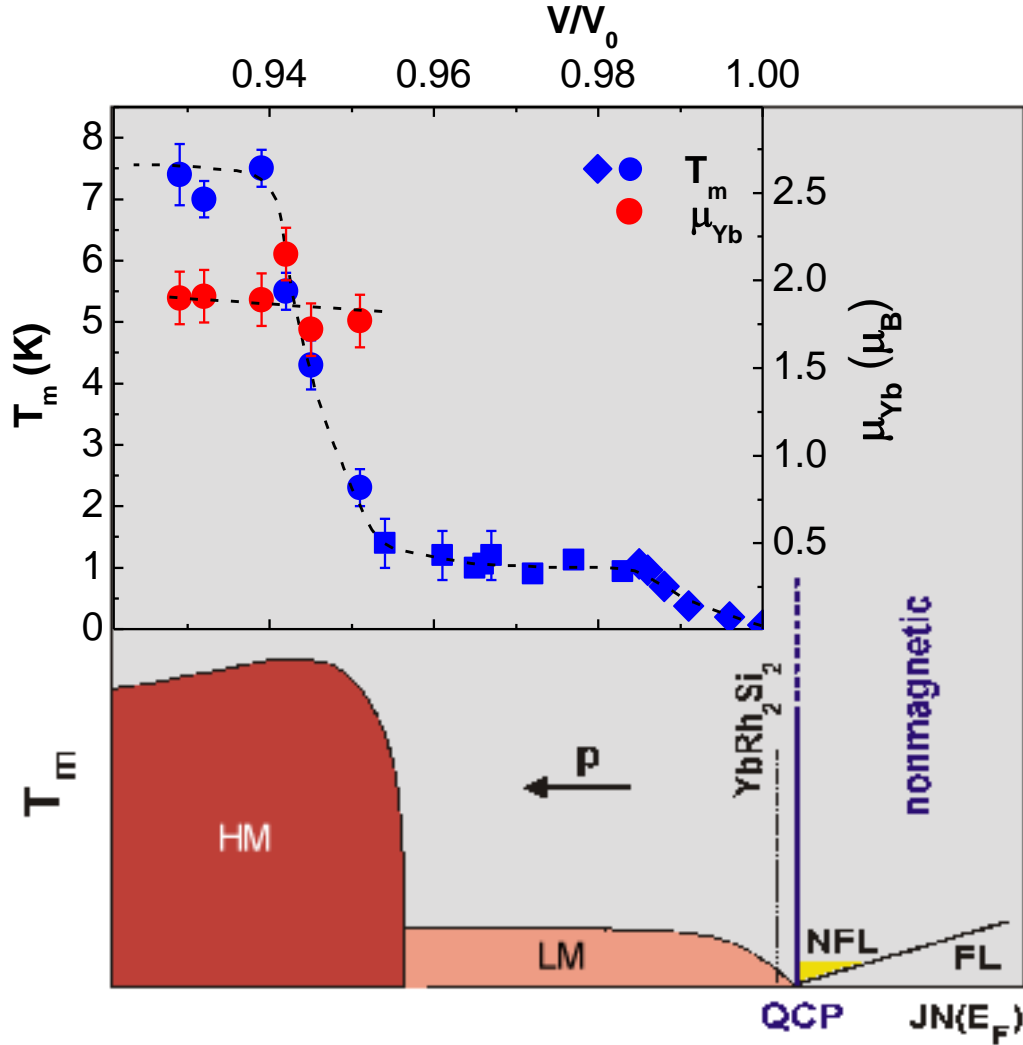
$R(p, T)$ in external magnetic field for $T \rightarrow 0$ K

negative magneto resistance in LM-state

→ evidence for spin fluctuations



Magnetic phase diagram - YbRh_2Si_2



LM: low moment

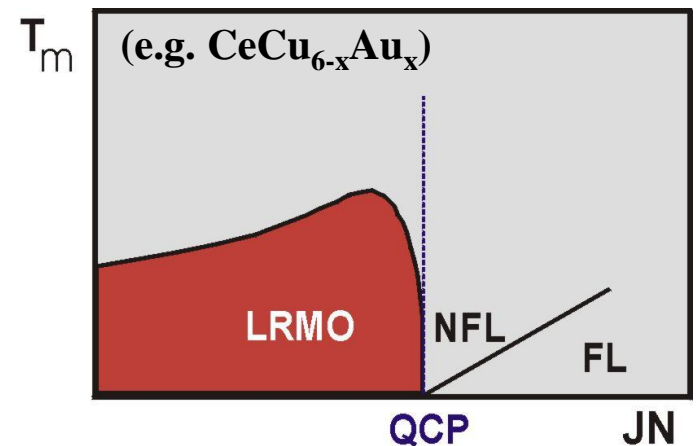
HM: high moment

Description within the Doniach model not possible!

↓

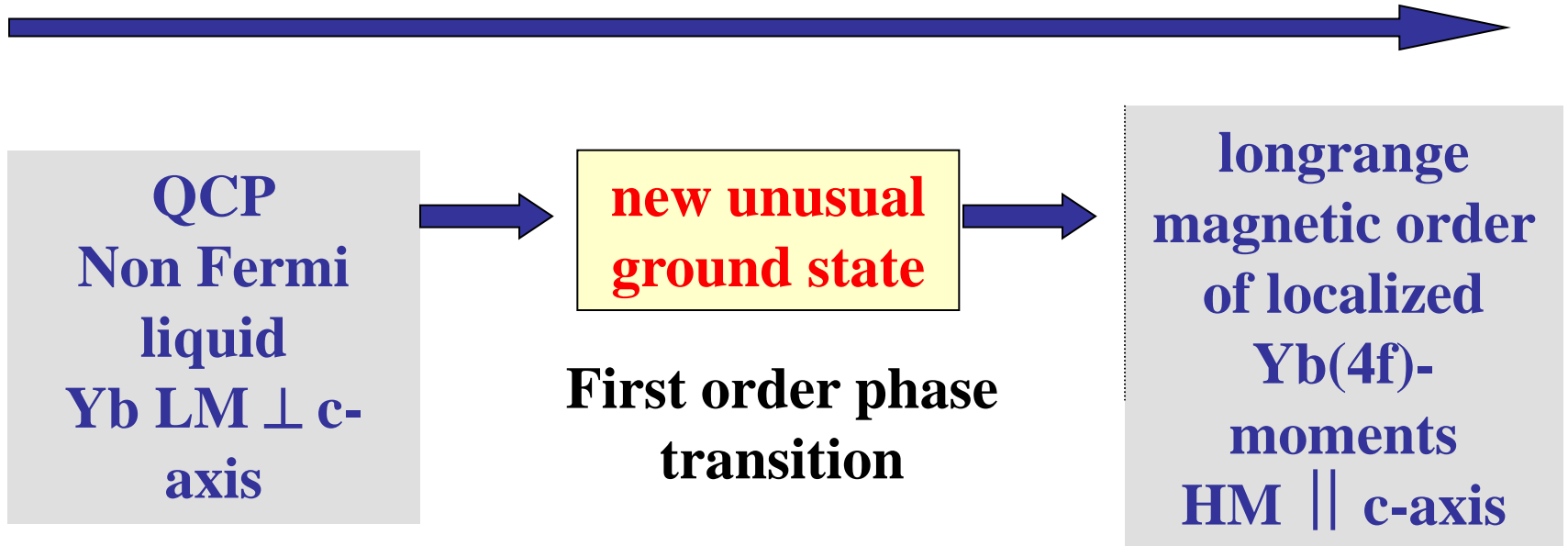
new unusual ground state in YbRh_2Si_2

stable up to $\Delta V/V_0 \approx 5\%$!!



Summary

pressure



- spin fluctuations along the pressure axis up to 10 GPa
- quite different behaviour than Ce heavy fermion systems

high pressure studies using Synchrotron Radiation

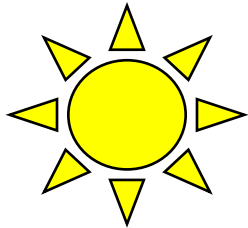
Mössbauer Spectroscopy with Synchrotron Radiation

Nuclear Forward Scattering of SR and some Applications

Why NFS?

Mössbauer Spectroscopy

1958 Mössbauer

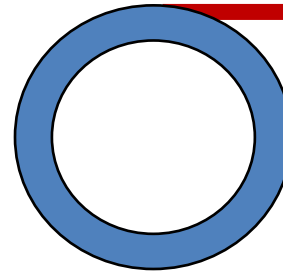


Radioactive source
→ 4 p emission

Nuclear Resonant Scattering of Synchrotron Radiation

1974 Ruby (proposition)

1986 Gerdau (first experiment)



Synchrotron Radiation:

- high intensity
- collimation
- broad energy range
- polarization
- time structure

Information about hyperfine interactions
between nucleus and surrounding
environment

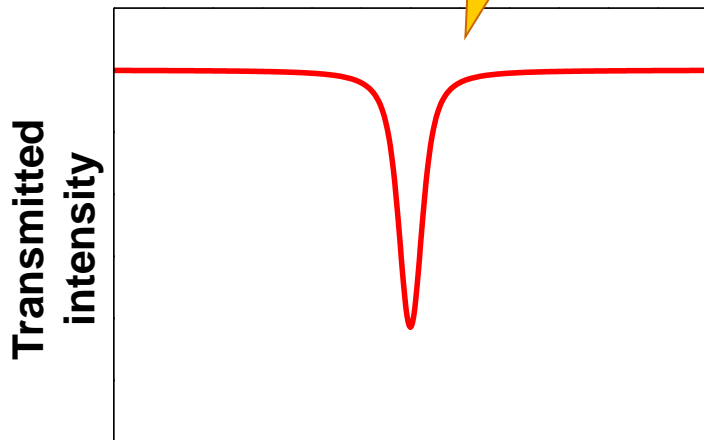
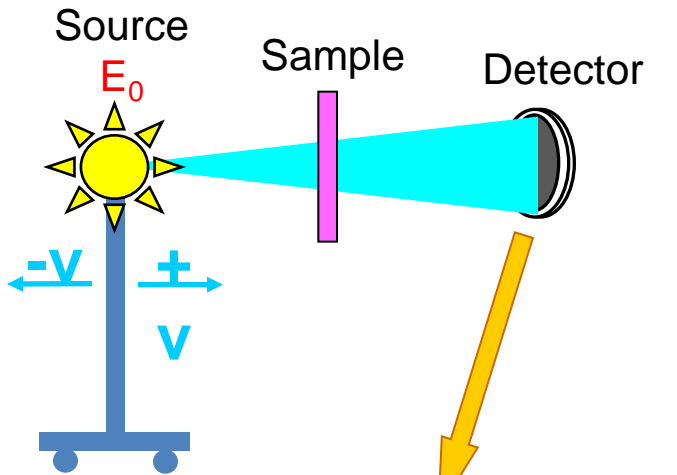
Magnetic and electronic properties

Well adapted to measurements under very high
pressure and in external magnetic field!!

Mössbauer Spectroscopy and Nuclear Resonance Scattering

techniques
based on the

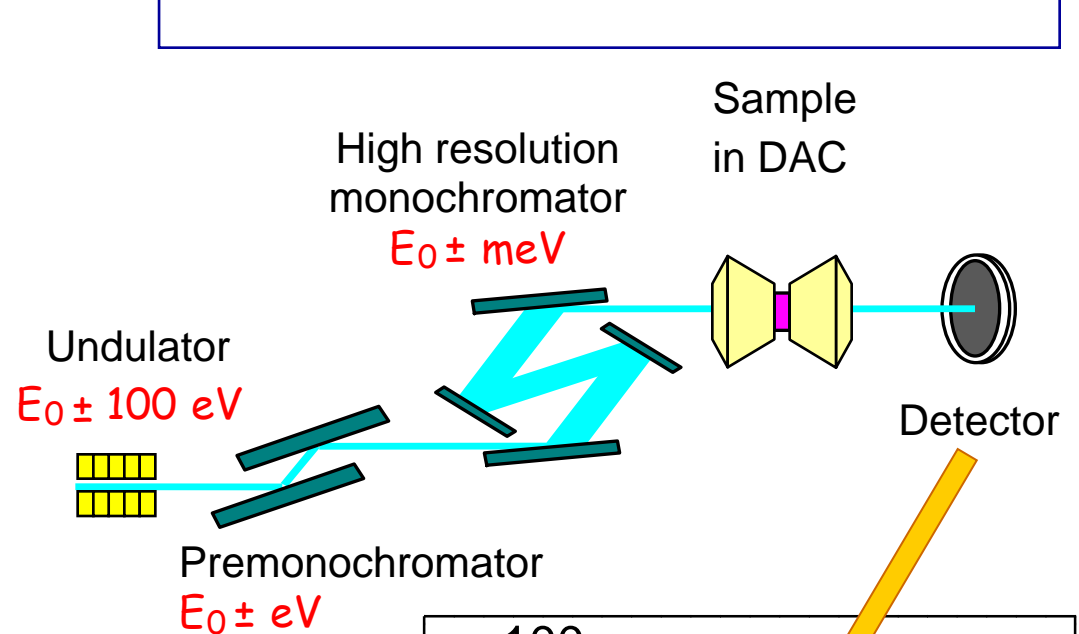
Mössbauer Spectroscopy



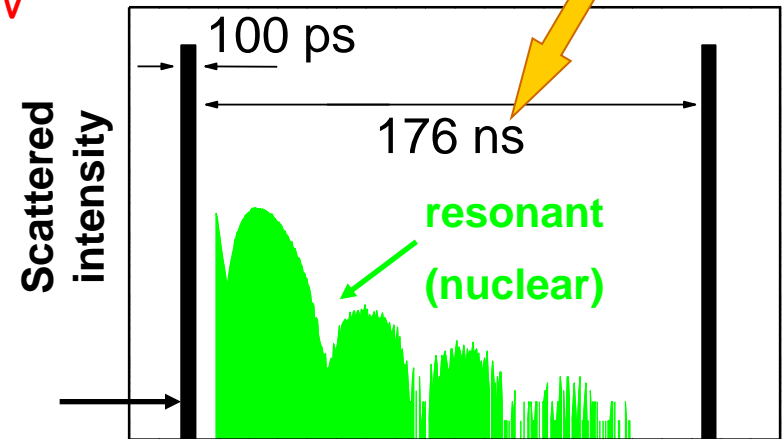
Energy (neV ... μ eV)



Nuclear Resonance Scattering (NRS)



non-resonant
(electronic)

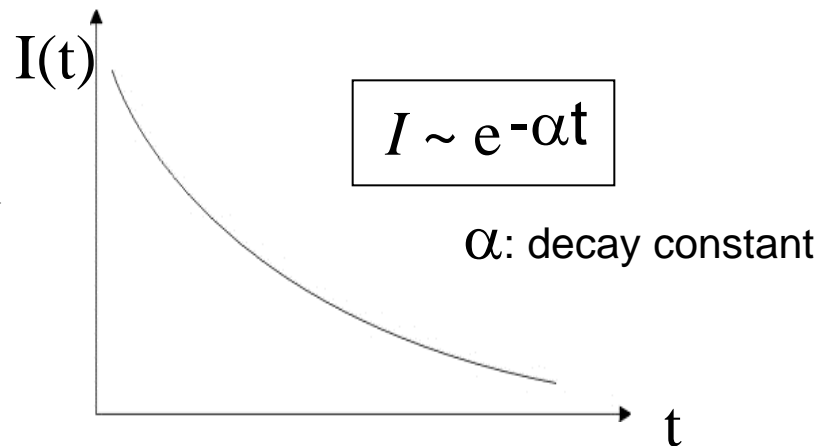
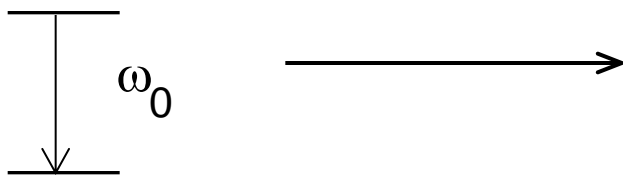


Time (ns)

(a)

excited state

ground state



no hyperfine interactions

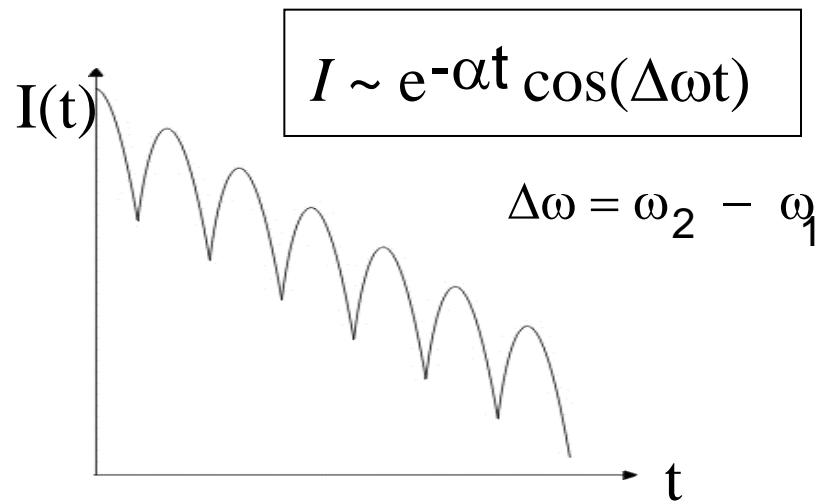
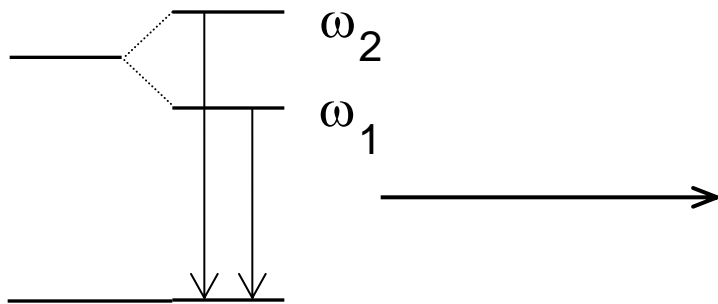


radiative decay

(b)

excited state

ground state

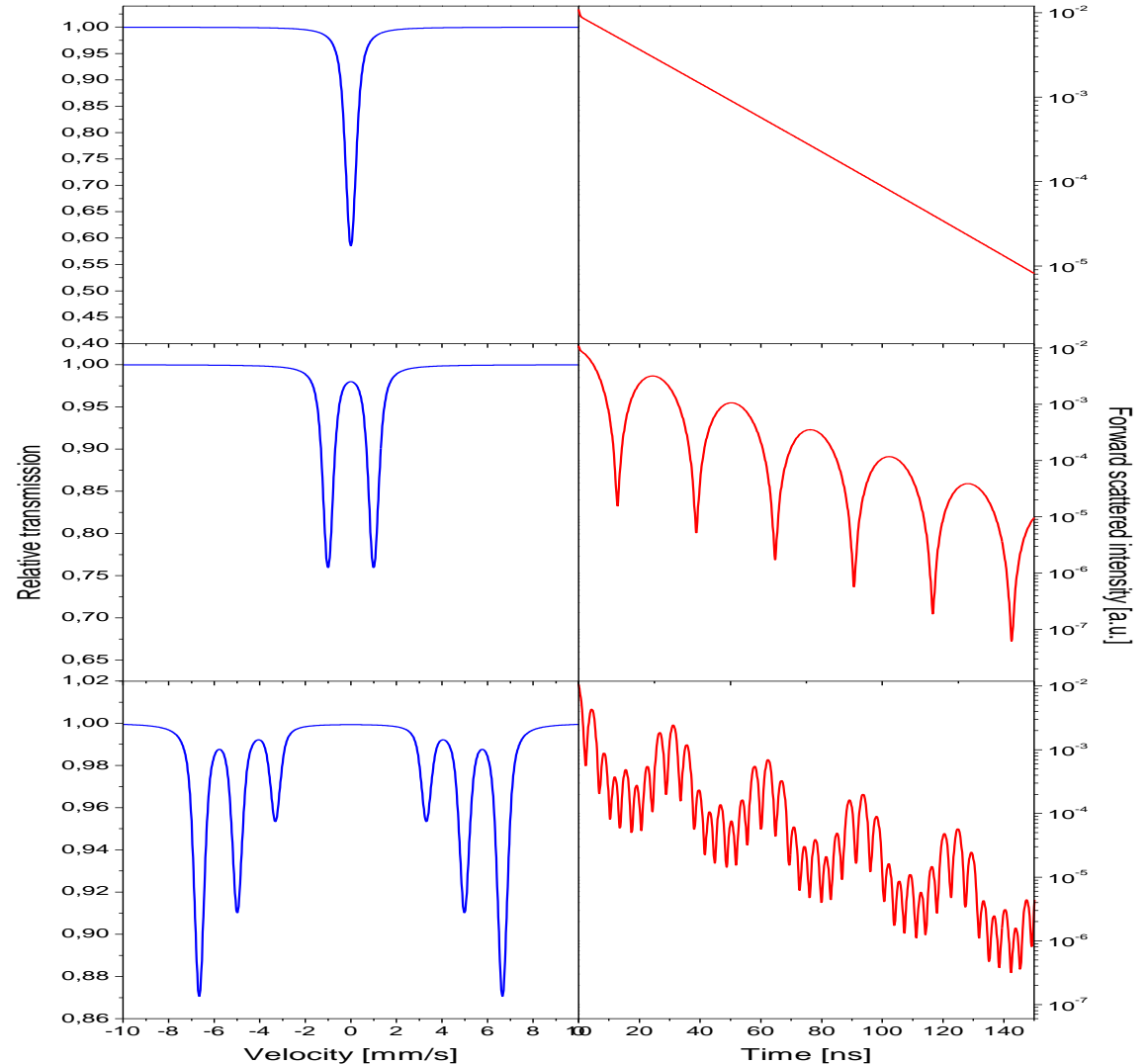
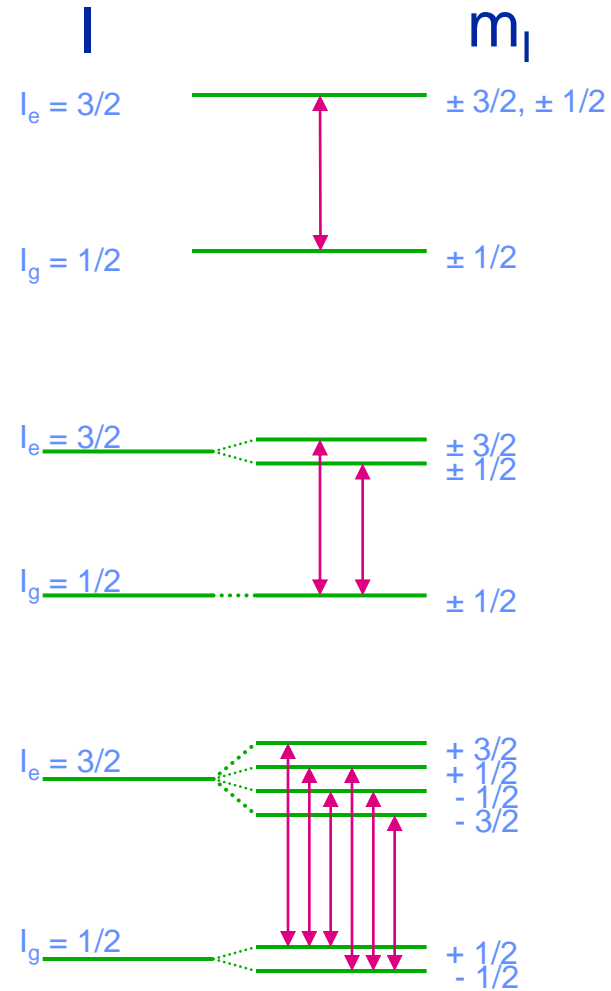


hyperfine interactions

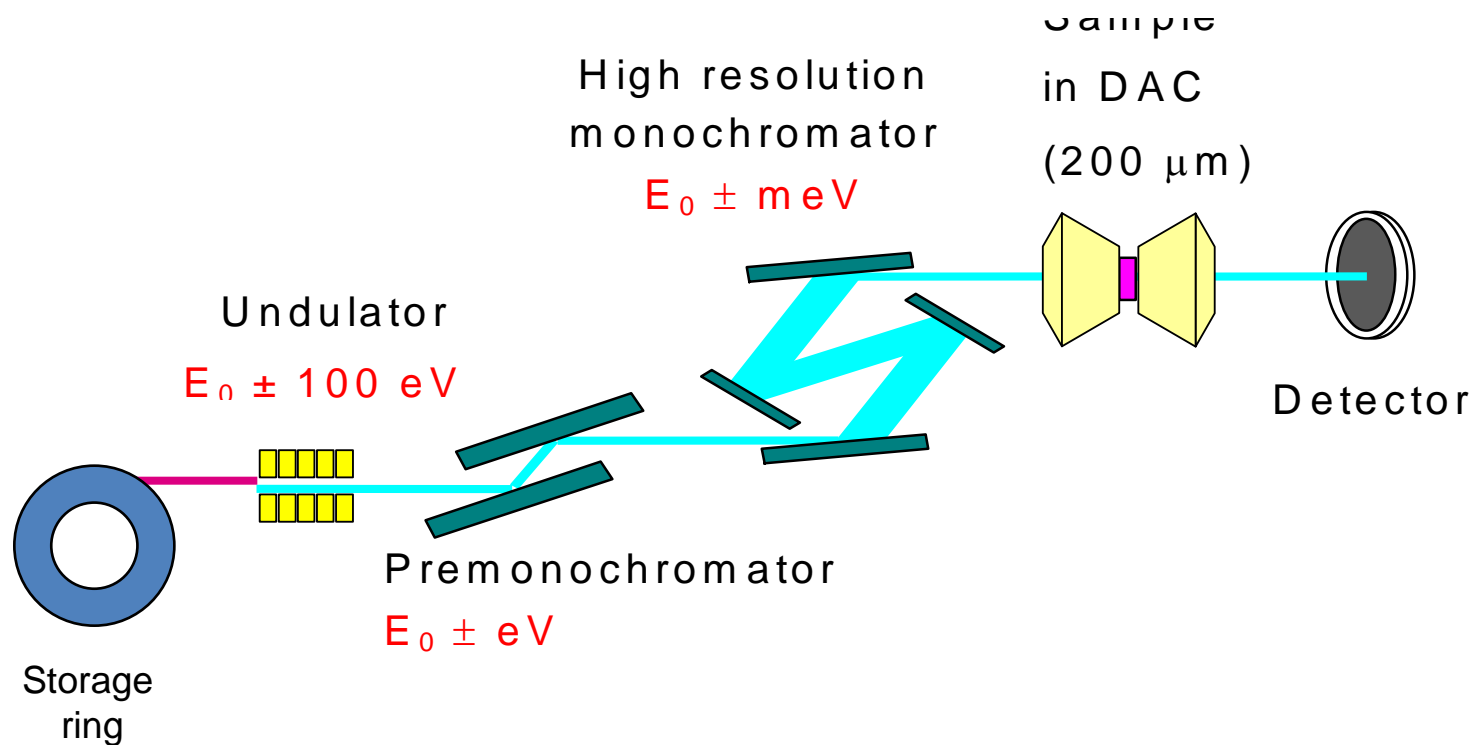


quantum beats

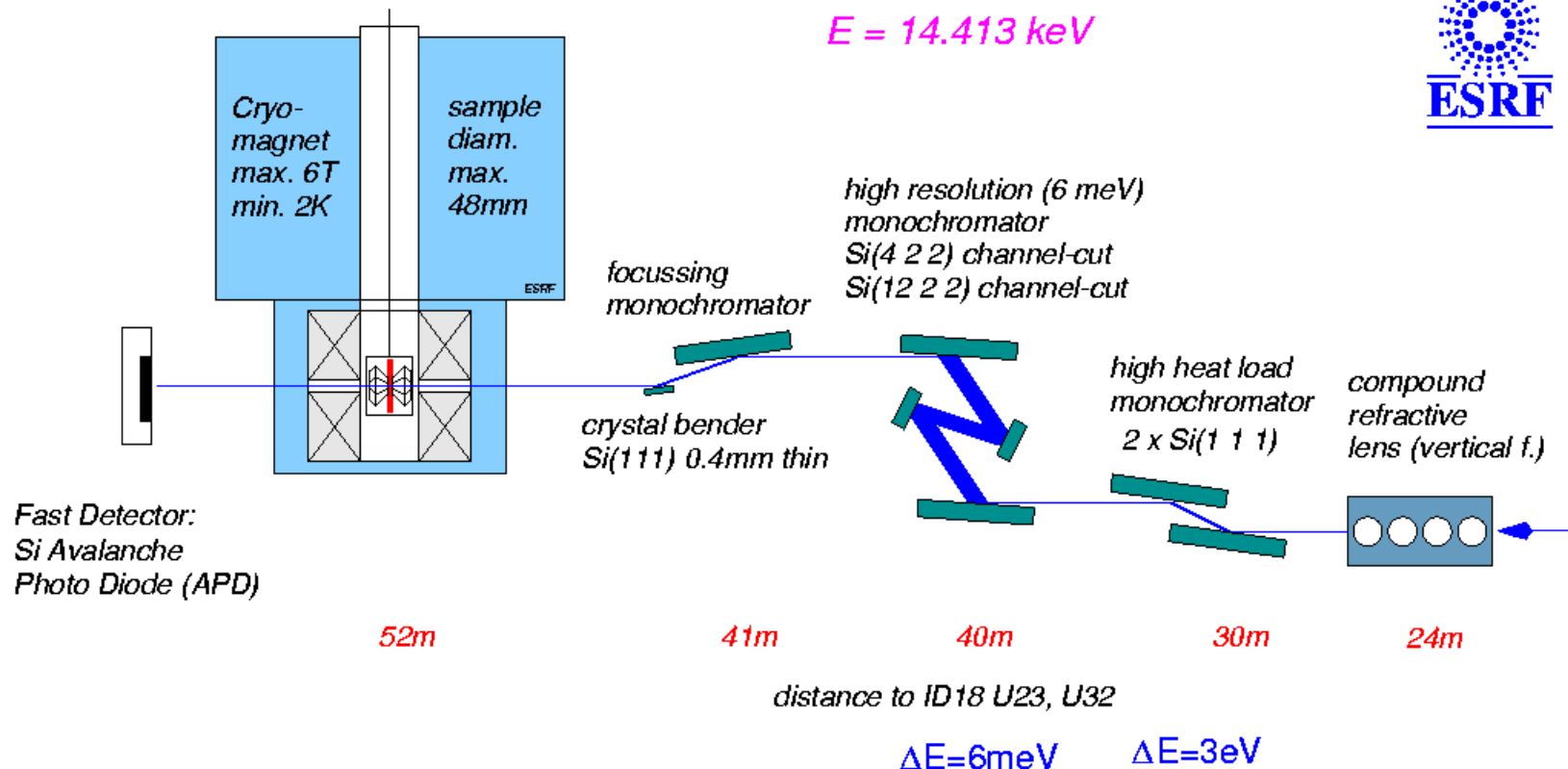
Comparison between Mössbauer spectroscopy and NFS for ^{119}Sn



Experimental setup for Nuclear Forward Scattering

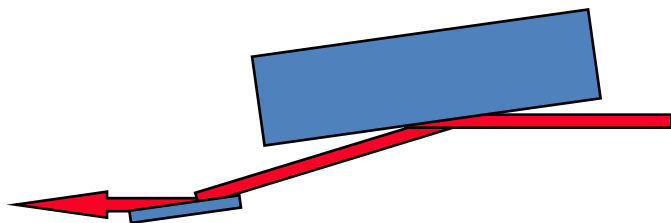


Experimental Setup for Nuclear Forward Scattering at ID18



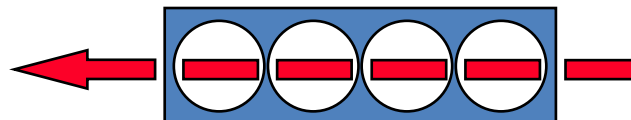
Optics for high pressure

HORIZONTAL
FOCUSSING

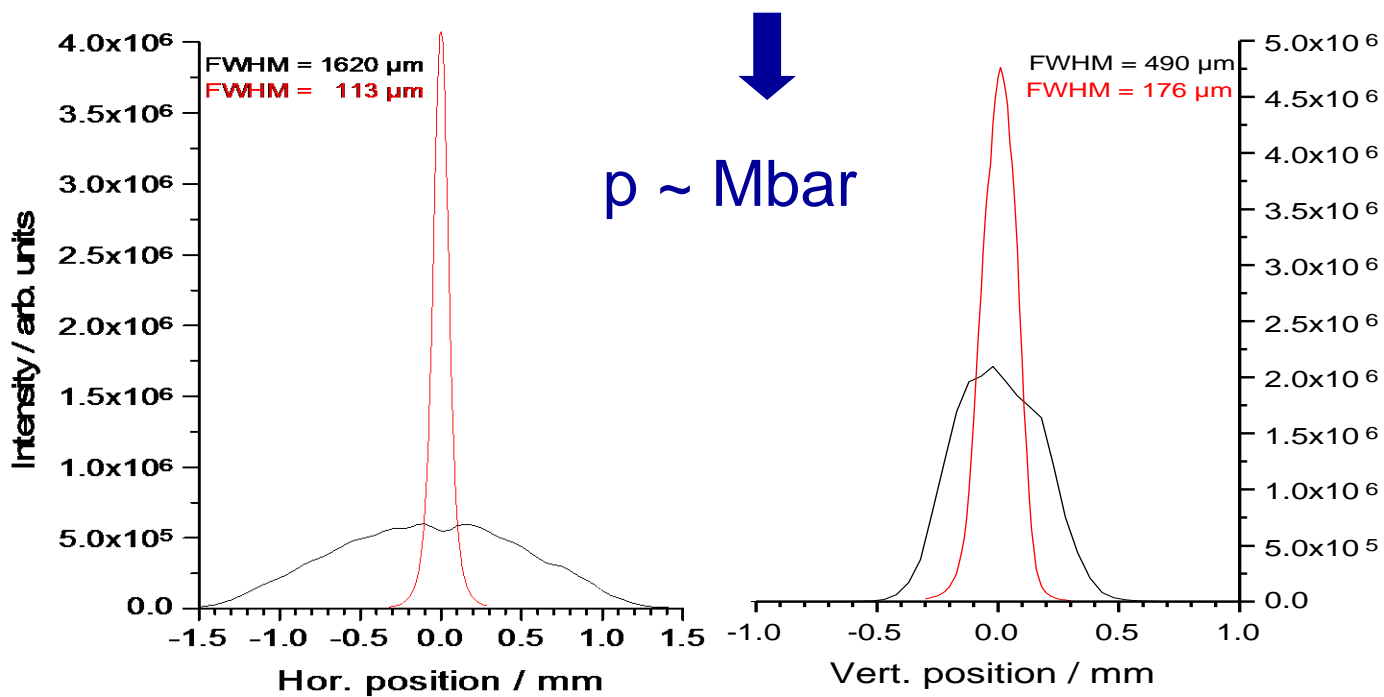


sagittally bent crystal

VERTICAL
FOCUSSING



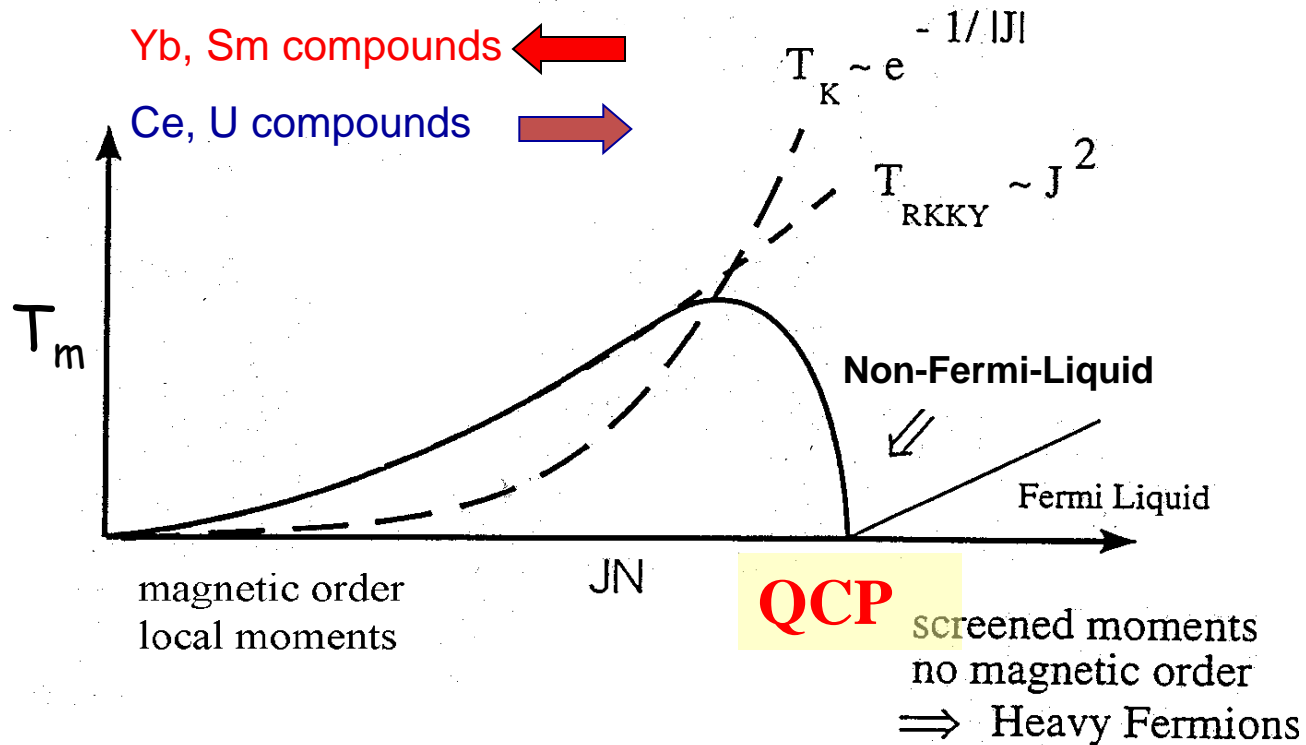
Be compound
refractive lens



Some Application of NFS
High pressure studies

Application to magnetic properties of SmS under high pressure

Extended Doniach Model



$$T_m \rightarrow 0$$

QCP: Quantum-Critical-Point

• **Non-Fermi-Liquid (NFL):**

$$\Delta\rho \propto T^\varepsilon \quad \varepsilon = 1 - 1.5$$

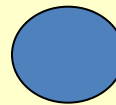
$$\Delta C/T \propto -\ln T$$

• **Superconductivity possible**

(e.g. CeCu_2Si_2 , CeRh_2Si_2)



magnetic



nonmagnetic



nonmagnetic

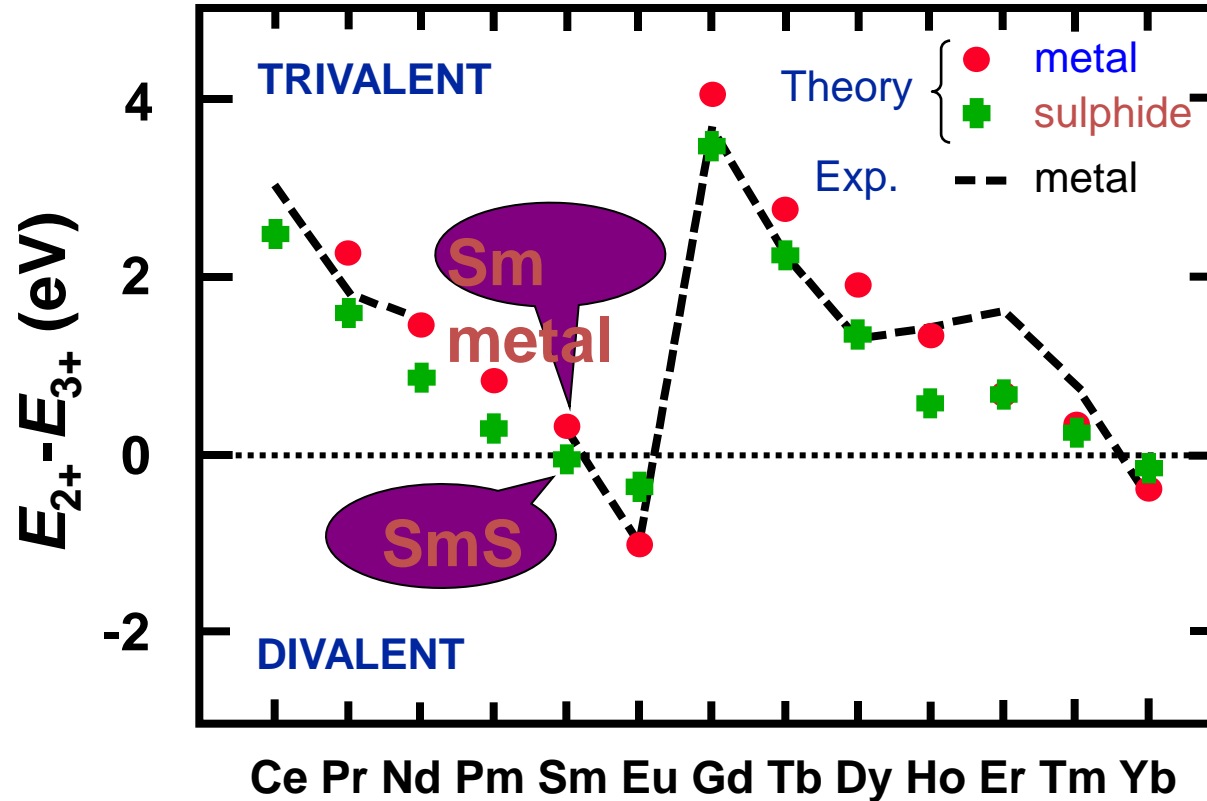


magnetic

SmS: Pressure-induced magnetic ordering in the vicinity of metal insulator transition

Why SmS?

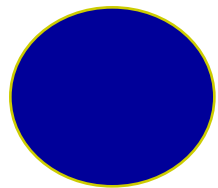
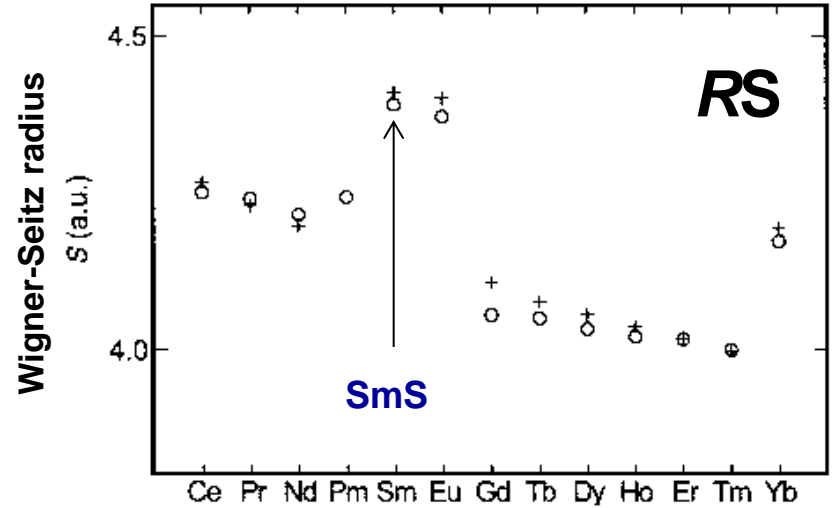
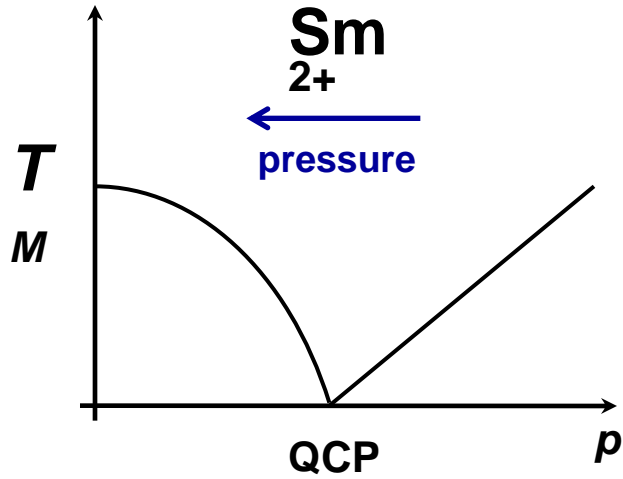
Rare earth valence in elemental R and in the monosulphides RS



P. Strange et al., Nature
399, 756 (1999)



Effect of pressure on Sm^{2+} - Systems



delocalization

$\text{Sm}^{2+} : 4f^6 (J = 0)$
nonmagnetic

$\text{Sm}^{3+} : 4f^5 (J = 5/2)$
magnetic

nonmagnetic
(?)

SmS

ambient pressure

- NaCl-type structure
- Nonmagnetic ground state (Sm^{2+} , $4f^6:7F_0$)
- semiconductor (black phase)

At $p = 0.65\text{GPa}$ (room temperature)

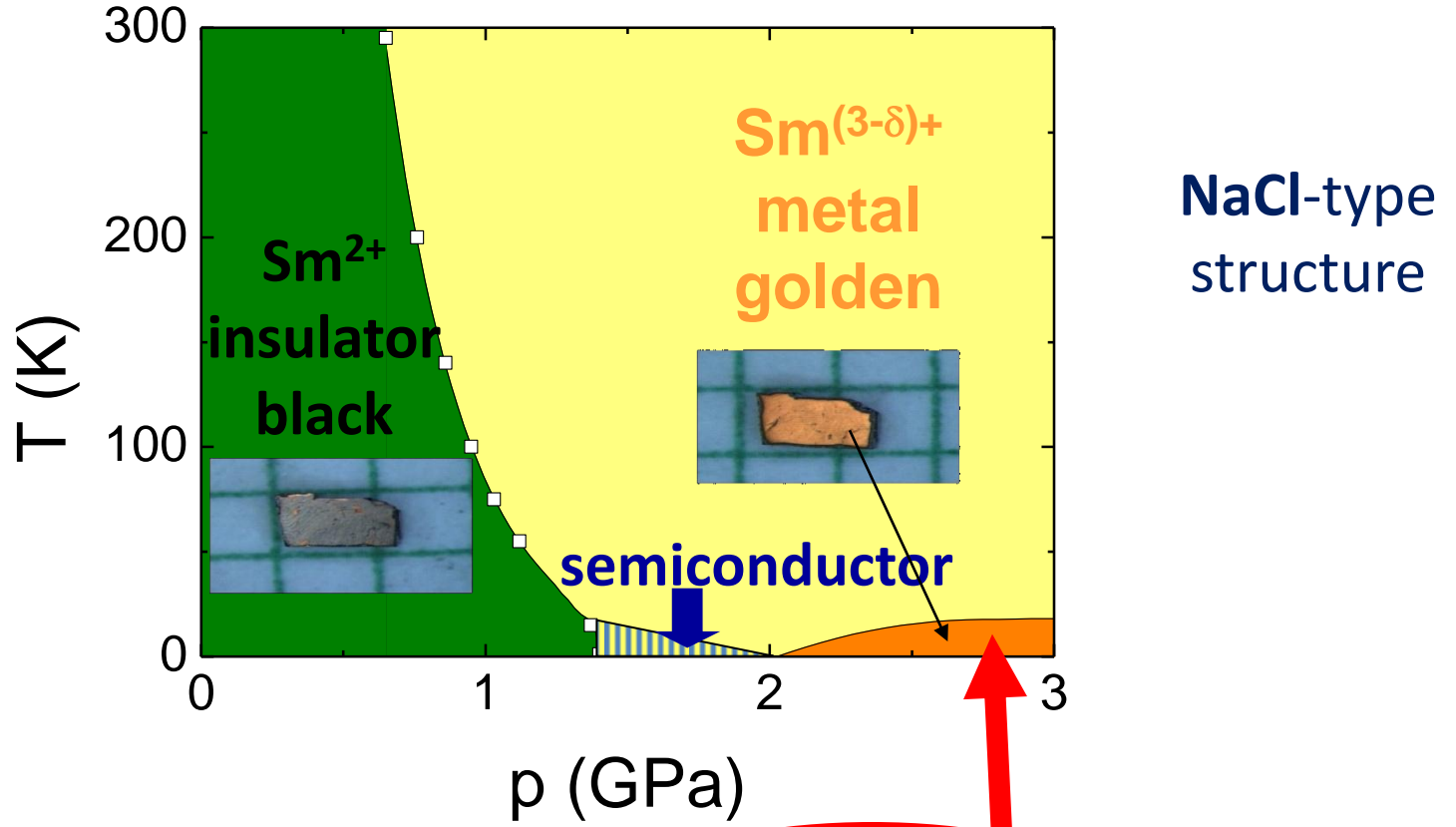
- first order isostructural phase transition
- metallic (golden phase)
- intermediate valence state ($n \sim 2.7$)

A. Jayaraman et al.,
PRL 25, 1430 (1970),

J.M. Coey et al., PRB 14,
3744 (1976)

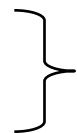
- Metallic behavior down to low temperatures only above 2GPa

(T, p) phase diagram of SmS



High pressure techniques:

- ^{149}Sm Nuclear Forward Scattering
- Specific Heat



$\text{Sm}^{3+?}$
Magnetic order ?

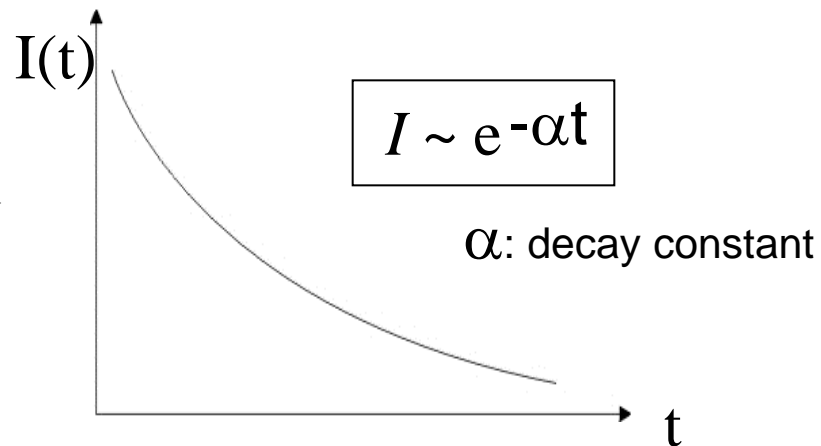
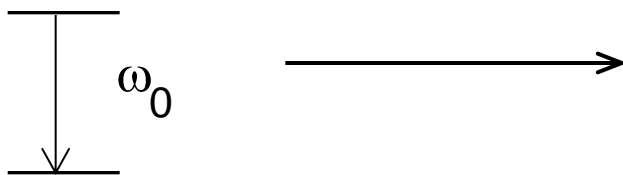
SmS

Experimental results

(a)

excited state

ground state



no hyperfine interactions

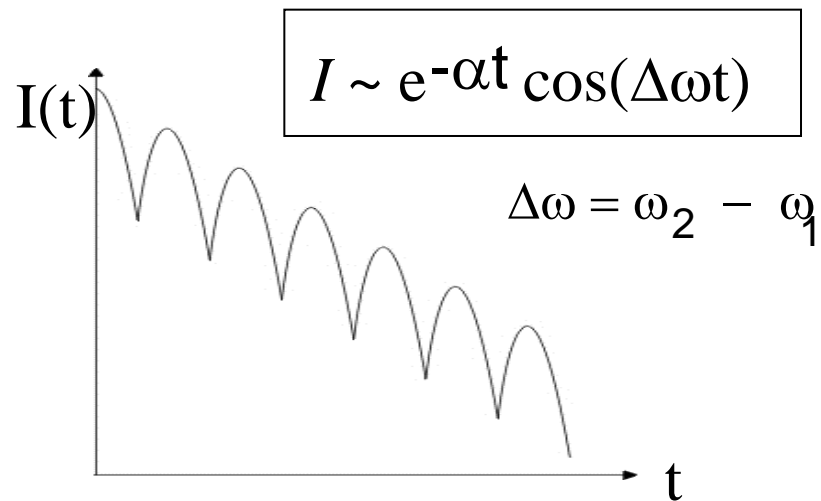
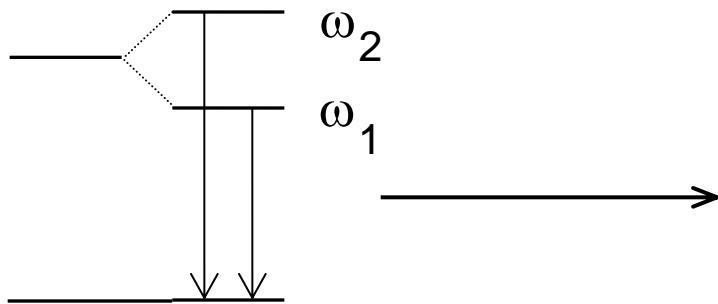


radiative decay

(b)

excited state

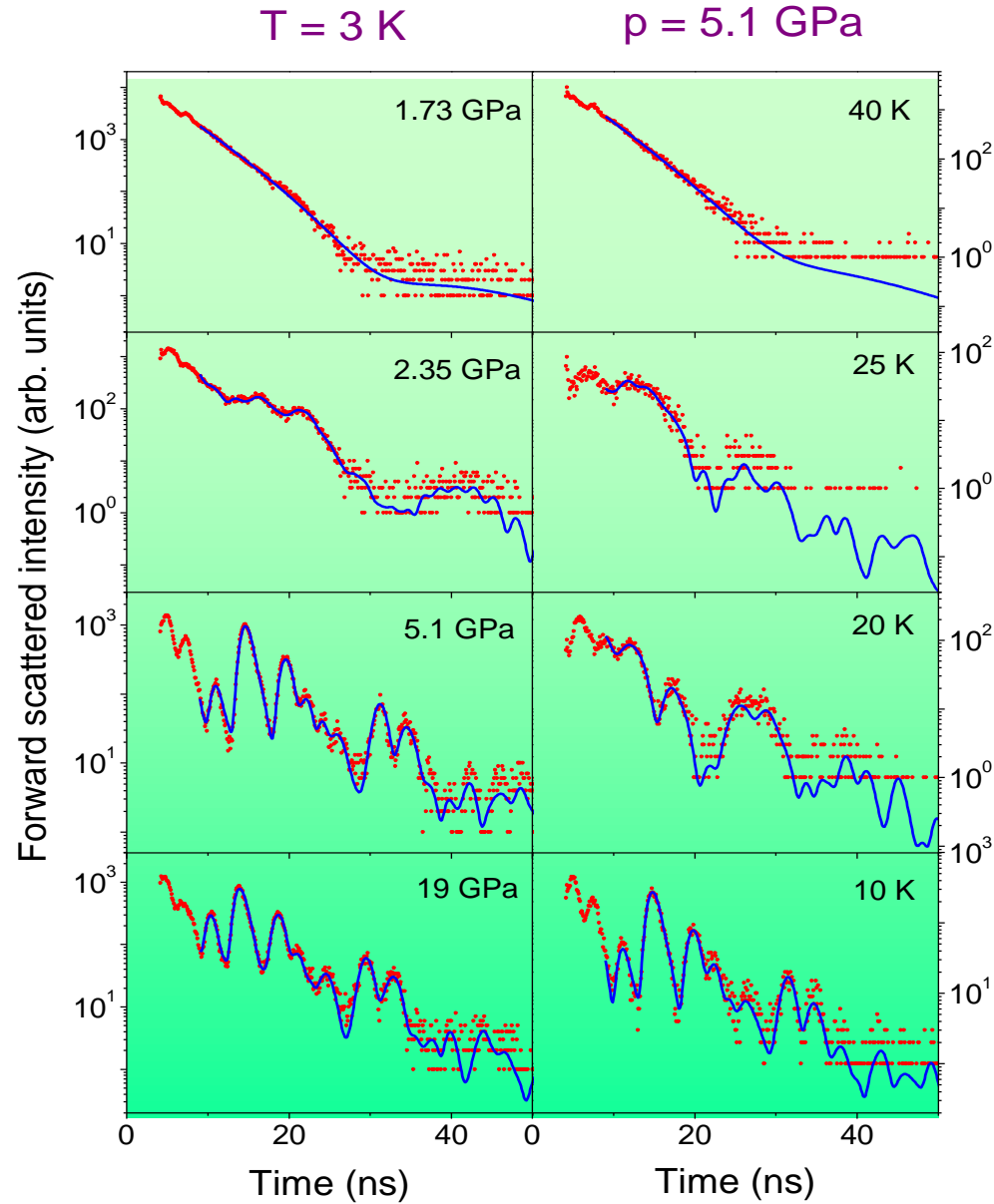
ground state

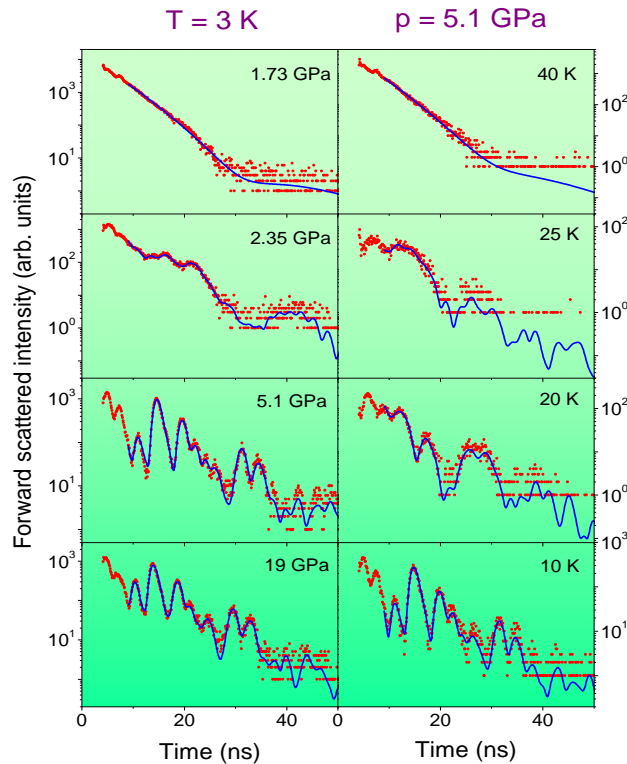


hyperfine interactions



quantum beats

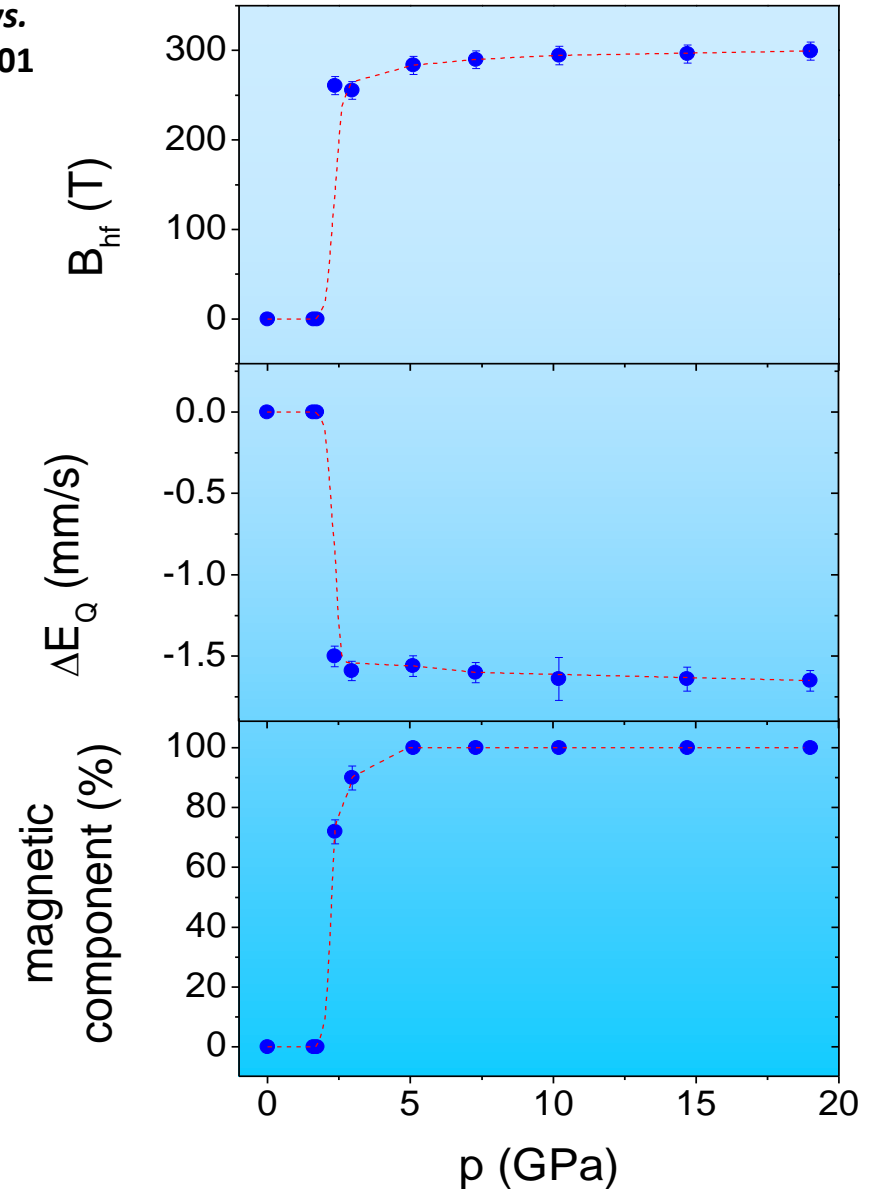




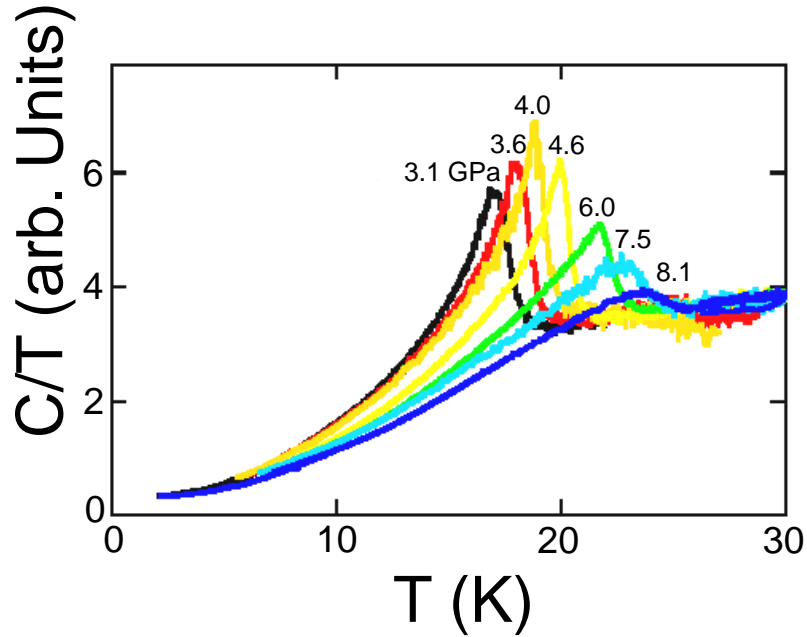
A. Barla et al., *Phys. Rev. Lett.* 92, 066401 (2004)

ESRF – ID22N

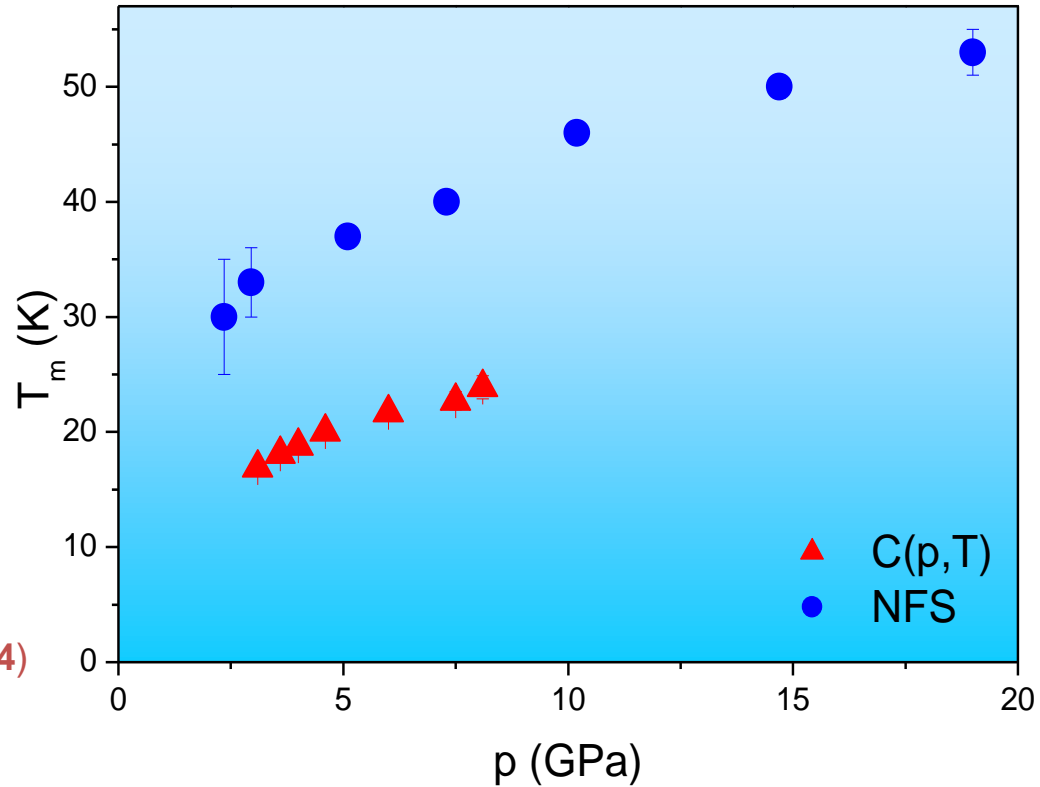
- first order magnetic phase transition at $p \sim 2$ GPa
- Γ_8 crystal field ground state ($B_{\text{hf}} = 250$ T, $\Delta E_{\text{Q}} = -1.7$ mm/s)
- $\mu_{\text{Sm}} \approx 0.5\mu_{\text{B}}$ ($0.7\mu_{\text{B}}$ Sm^{3+} free ion)



SmS – specific heat



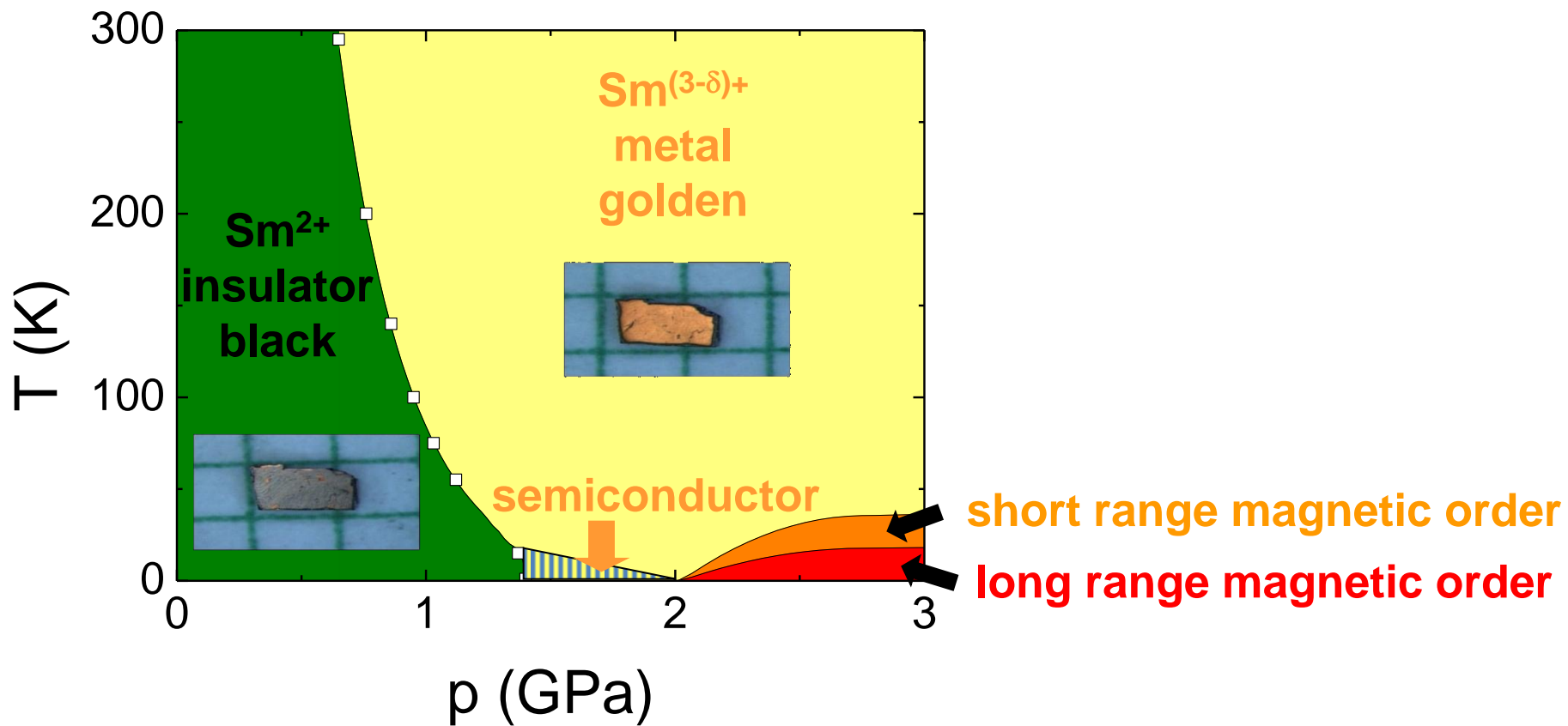
Y. Haga et al., *Phys. Rev. B* 70, 220406(R) (2004)



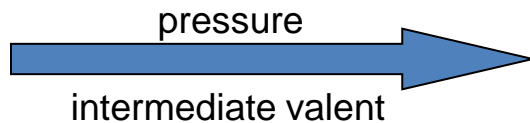
Specific heat anomaly \longrightarrow onset of long range magnetic order

Magnetic short range order above T_m deduced from $C(p, T)$

SmS



**Sm²⁺
insulator**



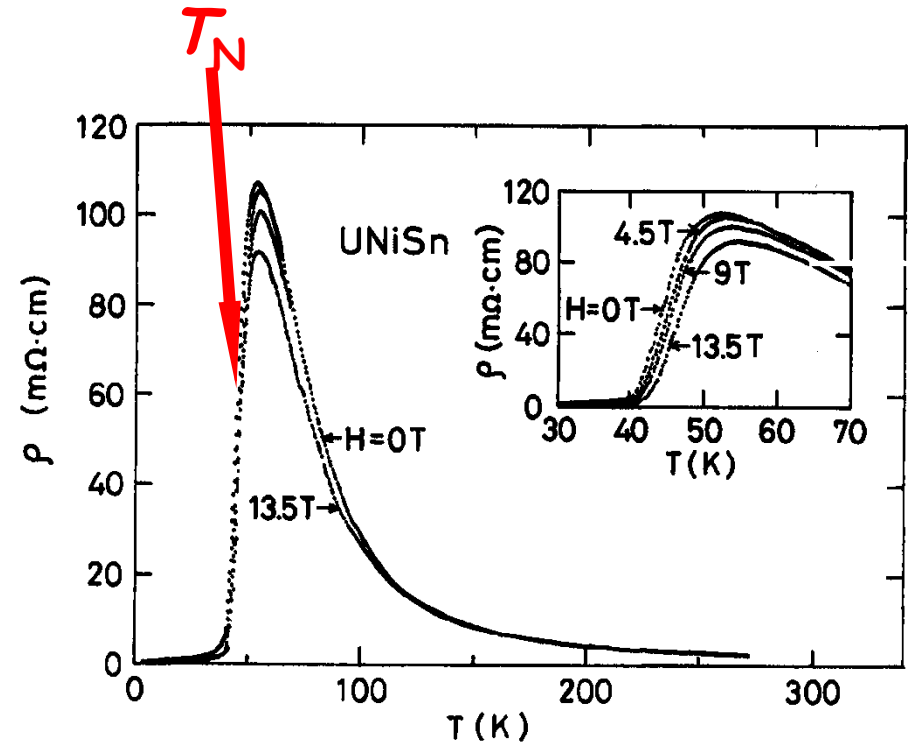
**~ Sm³⁺
metallic and magnetic**

UNiSn: pressure-induced collapse of magnetism

UNiSn: Why Interesting?

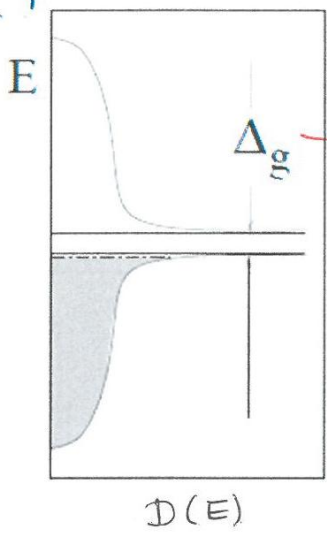
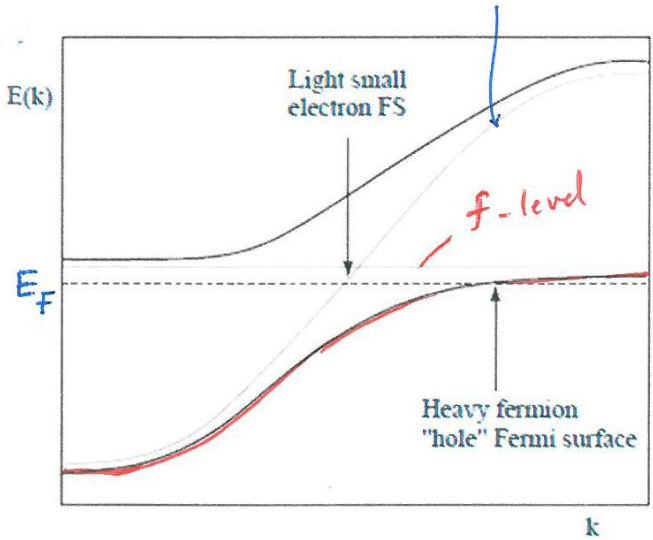
metal-insulator transition
associated with the AF
transition

→ Inverse Mott-Hubbard type
metal-insulator transition



→ UNiSn belongs to the class of the so-called **Kondo insulator** or **narrow gap semiconductor** (like SmB_6 , golden SmS)

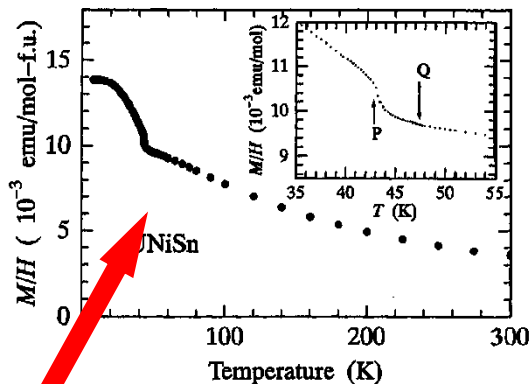
conduction electrons



Hybridization gap
 \Rightarrow Kondo insulator

UNiSn: Properties at ambient pressure

MAGNETIC SUSCEPTIBILITY



Curie-Weiss law

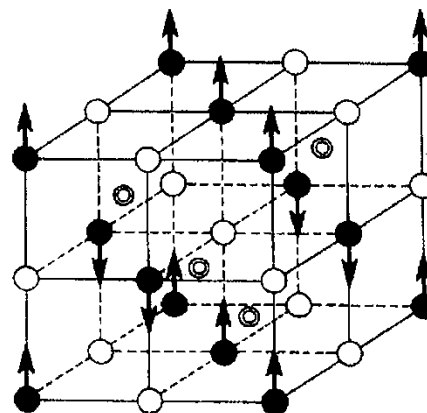
$$\mu_{\text{eff}} = 3.08 \mu_B$$

$$\theta_p = -75 \text{ K}$$

$$T_N \sim 43 \text{ K}$$

H. Fujii et al., *J. Phys. Soc. Jpn.* 58, 2495 (1989)
 Y. Aoki et al., *Phys. Rev. B* 47, 15060 (1993)
 H. Kawanaka et al., *J. Phys. Soc. Jpn.* 58, 3481 (1989)

CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE



Cubic (MgAgAs-type)

$$a(\text{U-U}) = 4.53 \text{ \AA}$$

AF – type I

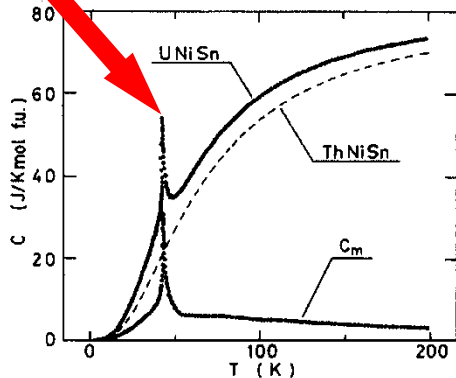
$$m \parallel [001]$$

$$T_N \sim 46 \text{ K}$$

$$m = 1.55(10)\mu_B$$

● U ○ Sn ⊙ Ni

SPECIFIC HEAT

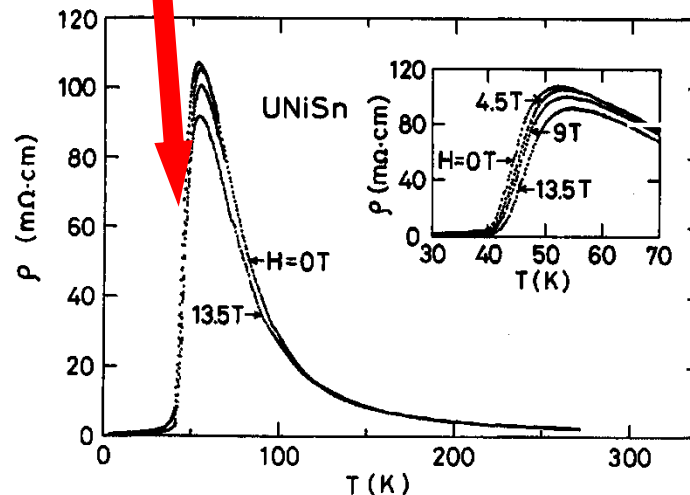


anomaly at 43 K

$$S_m(43\text{K}) \sim R \ln 2$$

$$\gamma = 18.2 \text{ mJ}/(\text{mol K}^2)$$

RESISTIVITY

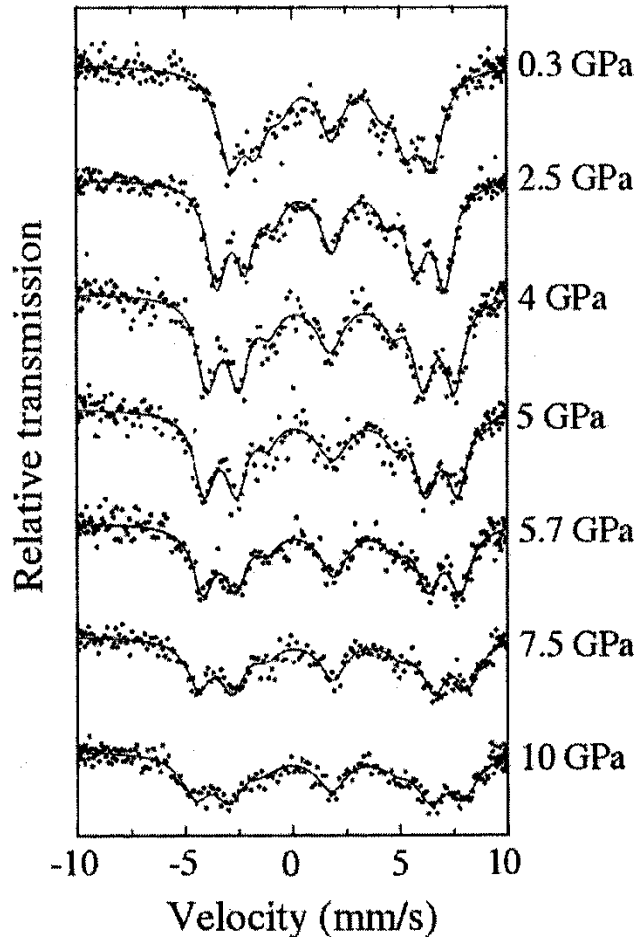


High pressure results:

- **x-ray diffraction**
- **Mössbauer and NFS of synchrotron radiation**
- **Electrical resistance**

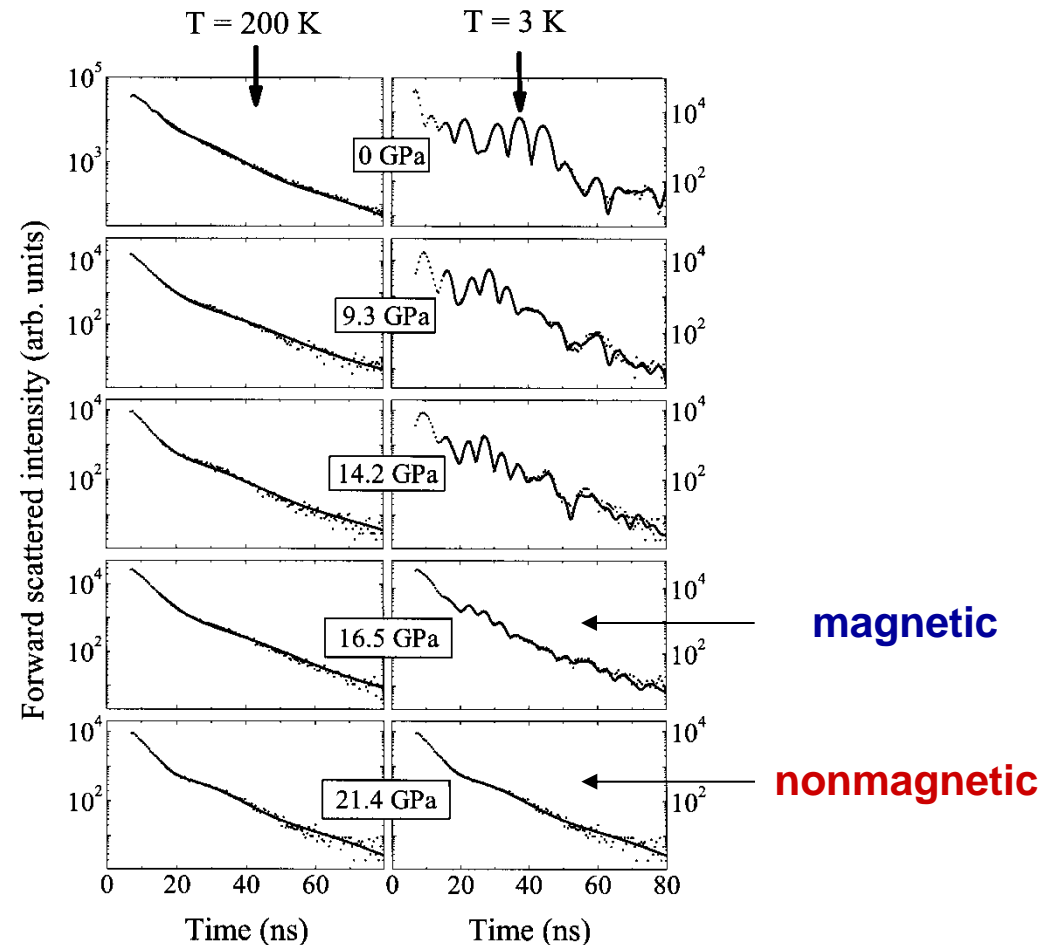
UNiSn : High pressure ^{119}Sn Mössbauer and NFS

- ^{119}Sn Mössbauer spectroscopy at 4.2 K

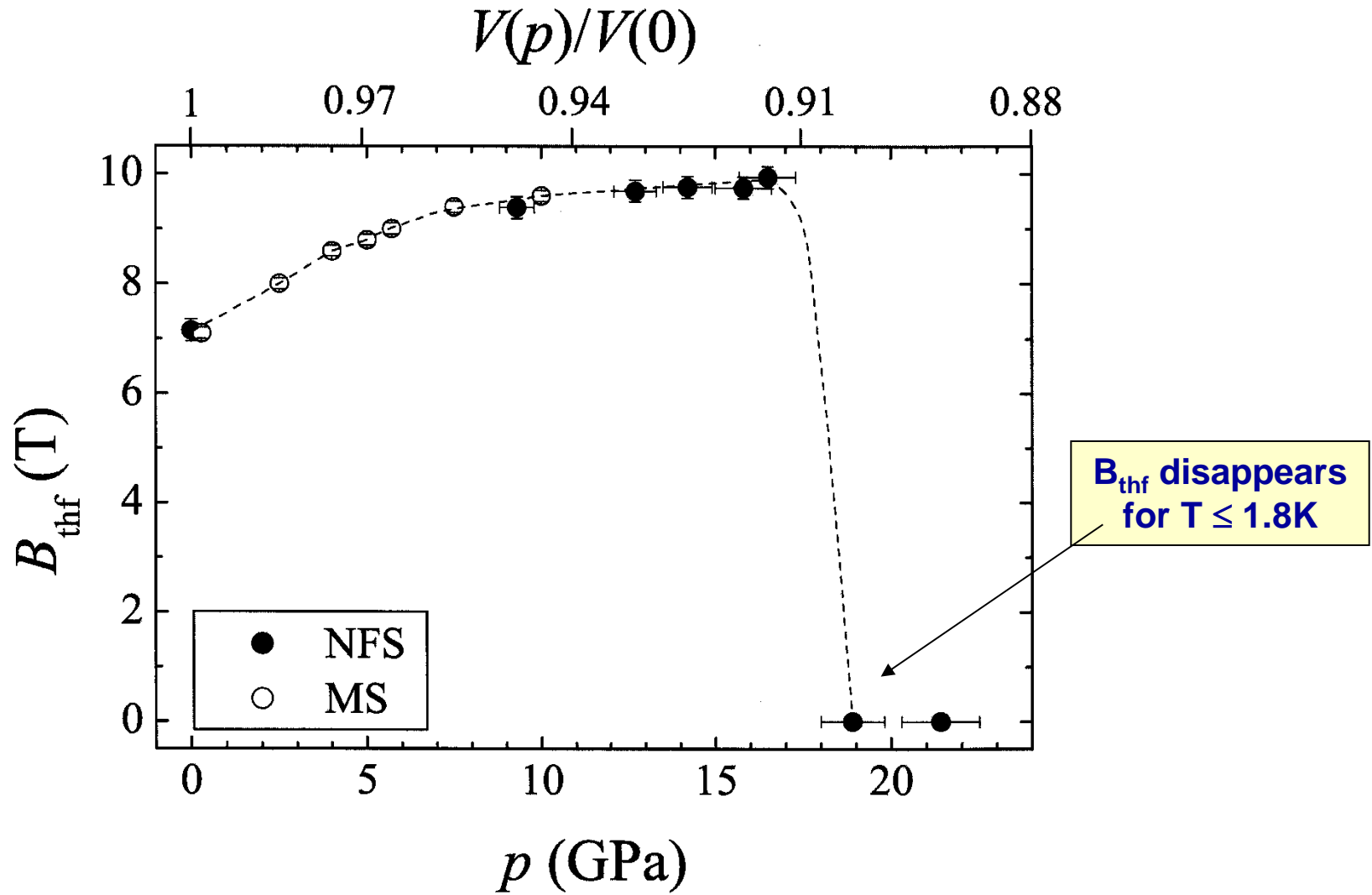


$B_{\text{thf}} = 7.15\text{T}$ at $p = 0$

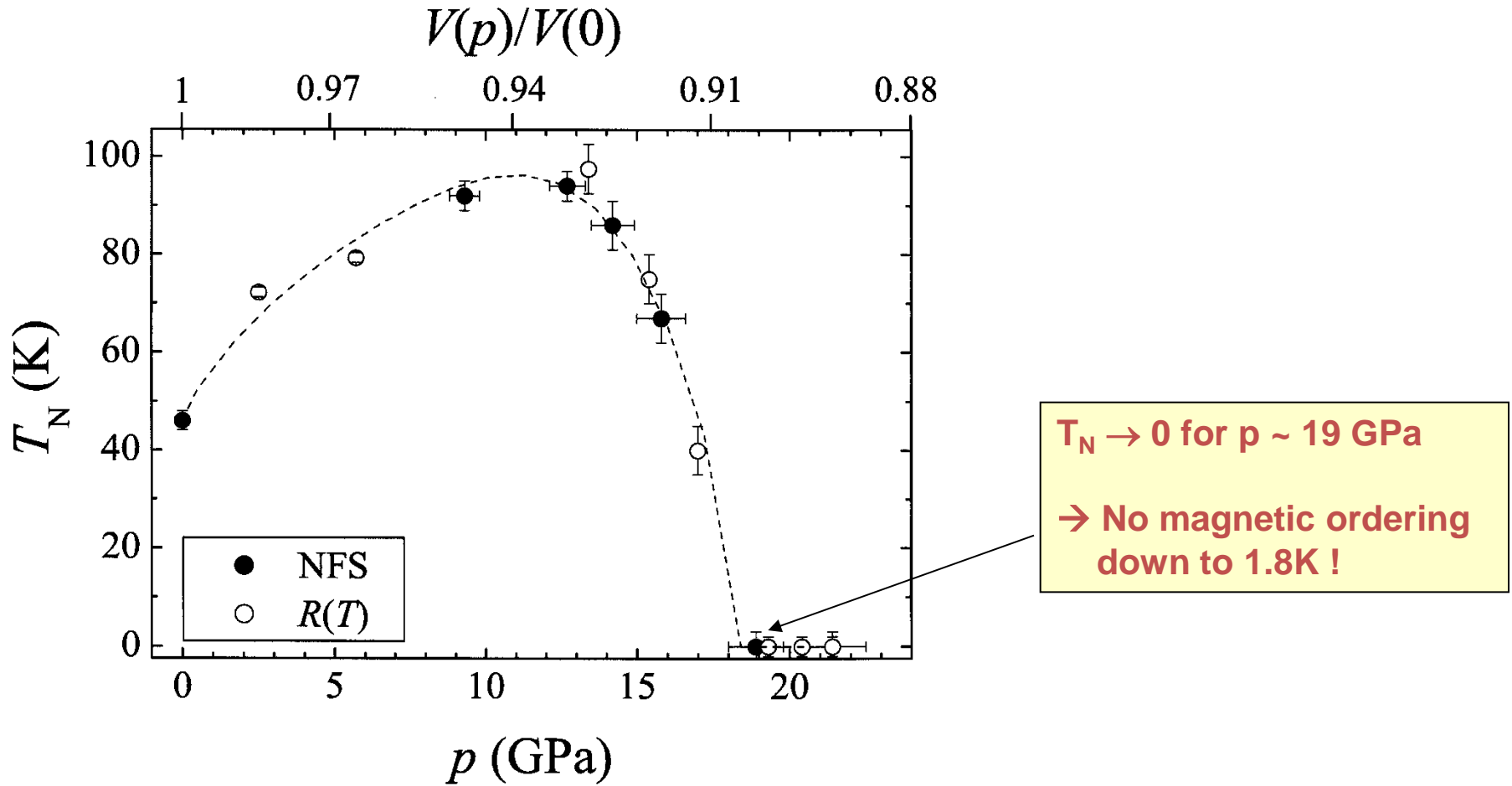
- ^{119}Sn NFS of synchrotron radiation



UNiSn : pressure dependence of B_{thf}

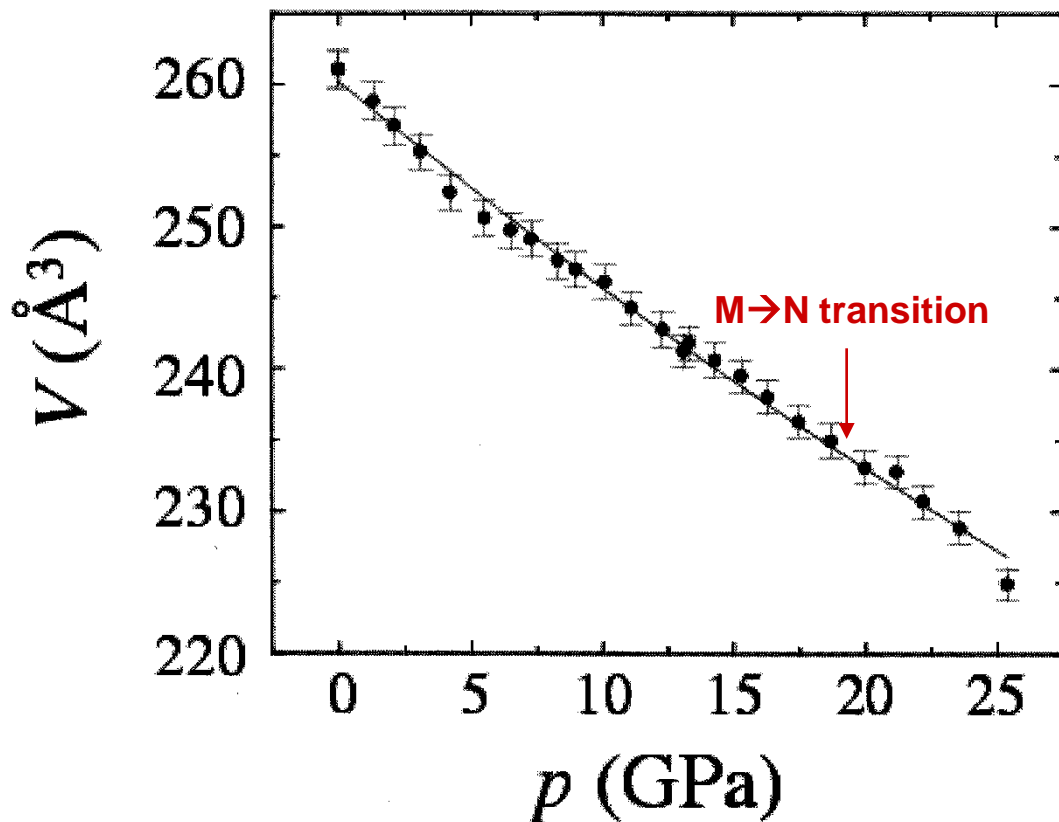


UNiSn : pressure dependence of T_N



UNiSn : High pressure x-ray diffraction

- Energy dispersive method at RT



- Fit with Murnaghan's EOS

$$B_0 = 168(10)\text{GPa}$$

$$B_0' \sim 1.4$$

Comparable to RNiSn compounds

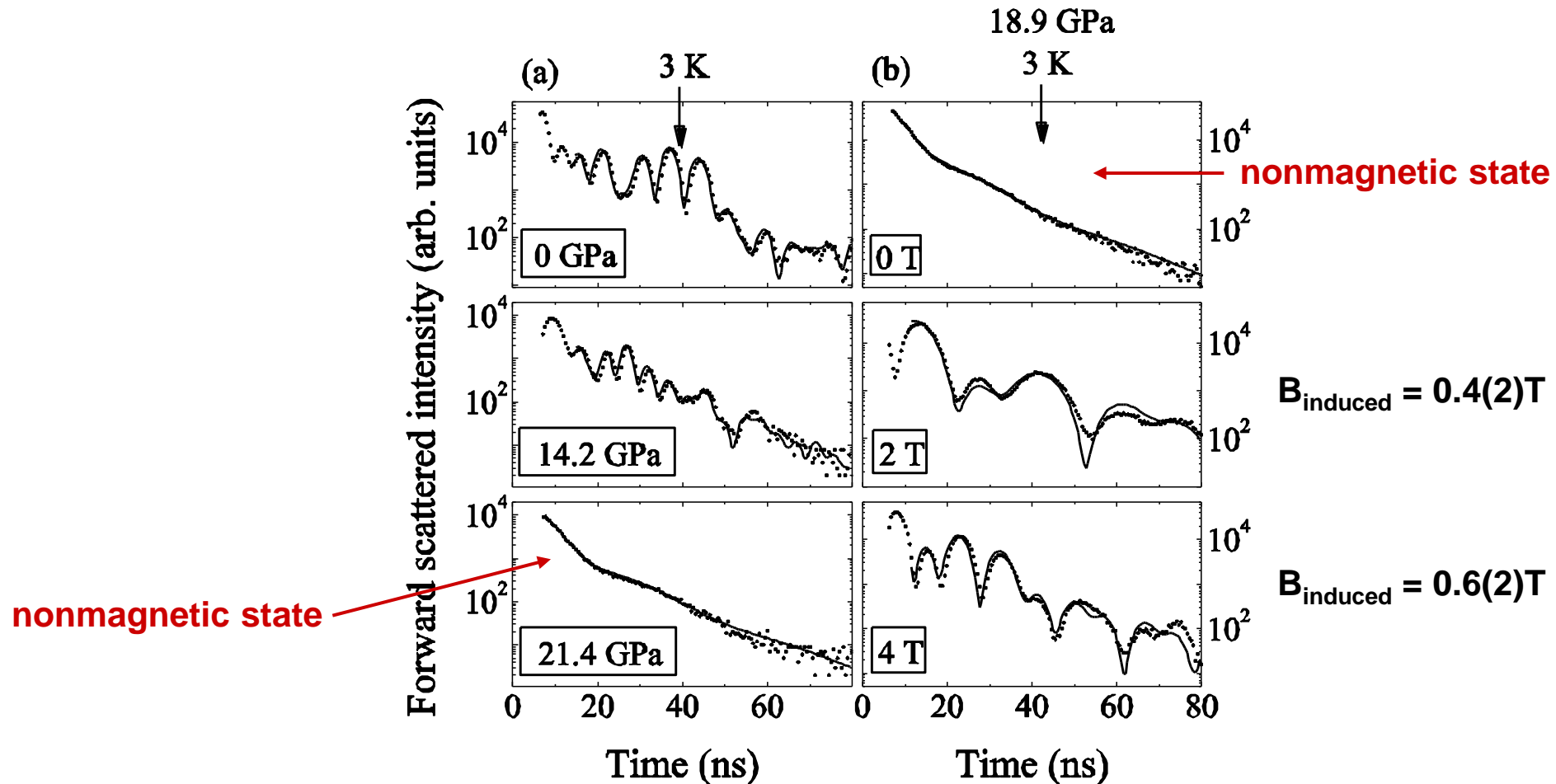
Structure remains stable (cubic)
up to 25 GPa !!



Pressure-induced magnetic \rightarrow nonmagnetic transition is not connected with structural phase transition

Nature of the high-pressure nonmagnetic state

A.) NFS spectra in external magnetic field



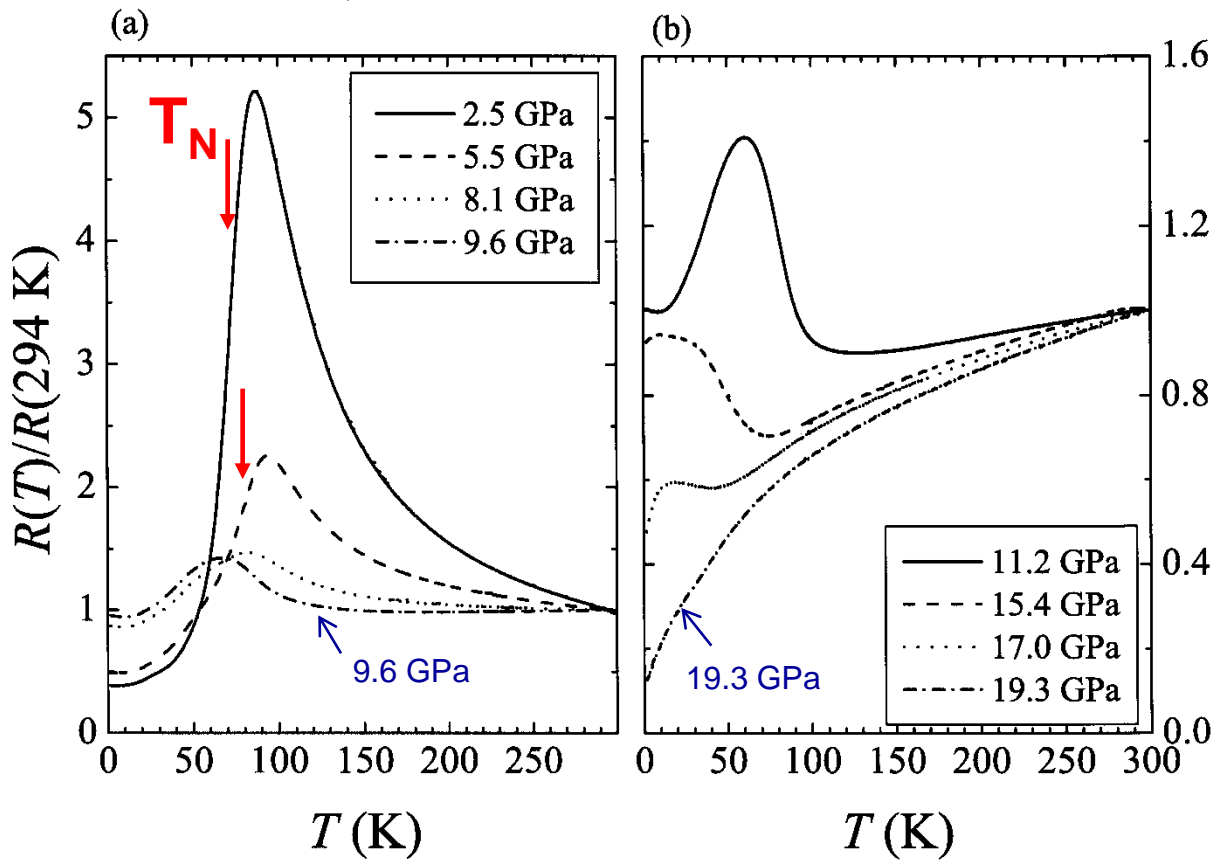
Evidence for rapidly fluctuating U 5f moments in the nonmagnetic state

B.) pressure dependence of the resistance at low temperatures

Semiconducting gap decreases with pressure



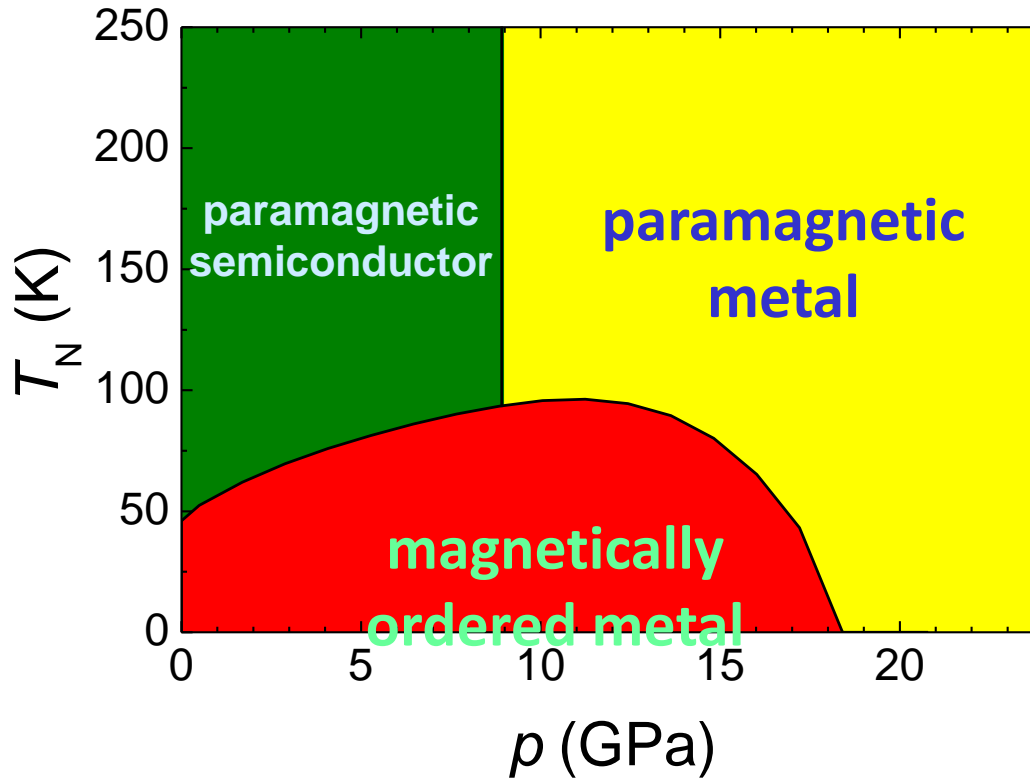
metallic state at $p \sim 9\text{GPa}$



nonmagnetic state at $p > 19\text{GPa}$:

- $R(T)$ at 19.3 GPa typical for nonmagnetic materials close to a magnetic instability
- No evidence for superconductivity down to $\sim 60\text{mK}$.

Conclusions



- **Metallic behavior above $p \sim 9$ GPa**

- **Interplay between RKKY interaction and U(5f)-Sn(5sp) hybridization**

↳ **crossover localized \rightarrow itinerant at $p \sim 12$ GPa**

collapse of magnetism \rightarrow QPT at $p \sim 19$ GPa

no superconductivity in the proximity of QCP