XII Конференция молодых ученых, Сочи

Outline

- Motivation
- Physical properties of SmB_6
- Experiment – NMR under pressure
- Results
- Conclusions

Short history

- 2004 - graduated at University of P. J. Šafárik, Košice, Slovakia
- 2008 - PhD. study at Institute of Experimental Physics, SAS, Košice – NFL system $YbCu_{5-x}Al_x$
- 2009 – 2 years postdoc at University of Hyogo, Japan – *Japan Society for the Promotion of Science* (**JSPS**)

Main amis:

- study of **sample SmB_6** (suitable due to high intensity of signal form ^{11}B nuclei)
- utilizing NMR spectroscopy
- high pressure technique (piston-cylinder pressure cell up to 30 kbar)
- apply NMR spectroscopy using **new** high pressure apparatus (modified Bridgman anvil cell)

(12) **United States Patent**
Takeshita et al.

(10) **Patent No.: US 7,487,710 B2**
(45) **Date of Patent: Feb. 10, 2009**

(54) **HIGH-PRESSURE GENERATION APPARATUS**

3,790,322	A *	2/1974	Sirota et al.	.....	425/77
4,021,171	A *	5/1977	Shulzhenko et al.	.....	425/77
4,196,181	A *	4/1980	Vereschagin et al.	.....	425/77

Motivation

- Rare-earth borides (REB_2, REB_4, REB_6, REB_{12} etc. RE=rare-earth metal)
  - High melting point, high hardness, usually metallic behavior
- Hexaborides – various physical phenomenon in one crystallographic structure
  - Simple non-magnetic metal LaB_6
  - Ferromagnetic semiconductor EuB_6
  - Metals with RKKY interaction PrB_6, NdB_6, GdB_6, DyB_6
  - YB_6 supeconductor
  - Heavy-Fermion antiferromagnet CeB_6
  - Valence-fluctuation systems SmB_6
- Lanthanoids – hexaborides REB_6

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Metals

Semiconductors

Number of conduction electrons in SmB_6 should be equal to number of Sm^{3+}
=> metallic behavior, magnetic order **Intermediate-valence system, nonmagnetic !?**

Kondo insulator SmB_6

PROC. PHYS. SOC., 1962, VOL. 80

Boron Nuclear Magnetic Resonance in Rare Earth Intermetallic Compounds

By A. C. GOSSARD and V. JACCARINO

Bell Telephone Laboratories, Murray Hill, New Jersey

MS. received 25th June 1962

Abstract. ^{11}B nuclear magnetic resonance has been observed in a series of rare earth hexaboride intermetallic compounds (LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, GdB_6, DyB_6, HoB_6 as well as ScB_6 and YtB_6) above their magnetic transition temperatures. Shifts in the field for resonance of the ^{11}B nuclei were found which depended in sign and magnitude on the magnetic properties of the rare earth atoms. The shifts are qualitatively similar to, but smaller than, the ^{27}Al shifts previously observed in rare earth aluminium compounds. The results in both series of intermetallic compounds can be explained by the exchange interaction between localized rare earth ion core moments and conduction electrons, which results in a magnetic polarization of the conduction electrons and thus in a shift in the field for resonance.

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Physical Properties of SmB_6 †

J. C. Nickerson* and R. M. White ‡
Department of Physics, Stanford University, Stanford, California 94305

and

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Hansen Laboratories of Physics, Stanford University, Stanford, California 94305

and

T. H. Geballe|| and G. W. Hull, Jr.
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 2 November 1970)

We propose a model for the electronic structure of SmB_6 suggested by new transport measurements in combination with analyses of the magnetic susceptibility and lattice energetics. Our model successfully describes the resistivity, Hall effect, magnetic susceptibility, and Mössbauer isomer shift in this material. In addition, it predicts an anomaly in the low-temperature specific heat. Analysis of the lattice energetics shows that the rigidity of the boron lattice is responsible for the fact that Sm ions on equivalent sites can occur with the 4f shell in either the $4f^5$ or the $4f^6$ configuration. A relationship among the compressibilities of the rare-earth hexaborides is predicted on the basis of this analysis.

PRL 109, 096601 (2012) PHYSICAL REVIEW LETTERS week ending 31 AUGUST 2012

Limit Cycle and Anomalous Capacitance in the Kondo Insulator SmB_6

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Department of Physics and Astronomy, University of California, Irvine, California 92697, USA

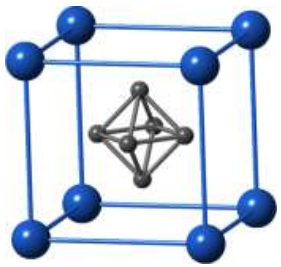
(Received 19 April 2012; published 29 August 2012)

We report a frequency coding limit cycle and anomalous capacitance in the Kondo insulator SmB_6 at low temperatures where the insulating gap becomes fully opened. The limit cycle appears to be associated with local activity and autocatalytic temporal pattern formation, as occurs in biological systems. The measured anomalous capacitance may indicate surface and bulk separation, suggesting the formation of a surface conducting state. The biological analogy suggests lossless information transport and complex information coding, and the surface state with a superconductor would provide a possible venue for quantum computing resources without decoherence.

DOI: 10.1103/PhysRevLett.109.096601 PACS numbers: 72.15.Qm, 71.20.Eh, 72.20.Ht

- ~50 years ~150 papers related to SmB_6
- Still open questions:
  - origin of gap $\mathbf{E_g}$
  - origin of in-gap states
  - mechanism of low temperature conductivity
  - ground state: metallic or non-metallic?

Physical properties of SmB_6



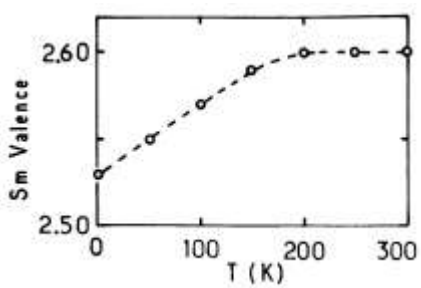
Sm: [Xe] $4f^6\,5d^0\,6s^2$

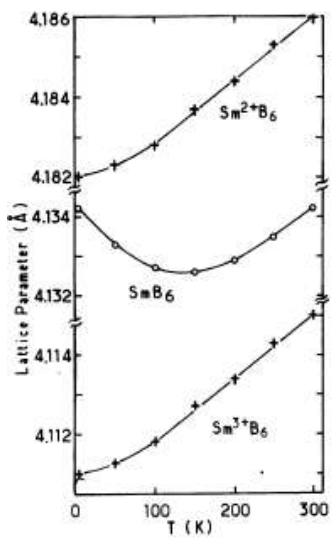
$4f^6$ (Sm^{2+}) J=0 ⇄ $4f^5\,5d^1$ (Sm^{3+}) J=5/2

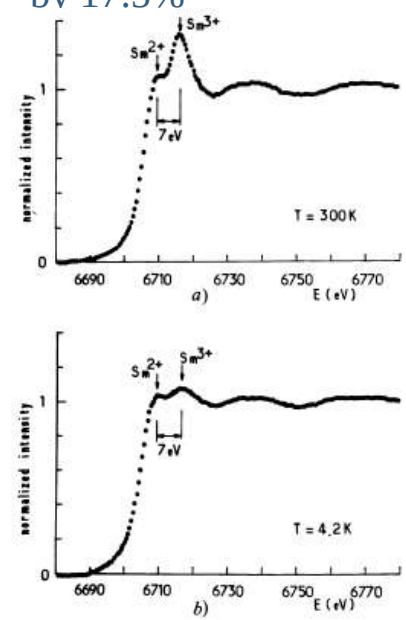
INTERMEDIATE VALENCE SYSTEM

$Sm^{2+} : Sm^{3+} \approx 4 : 6$ ($\nu \approx 2.6$)

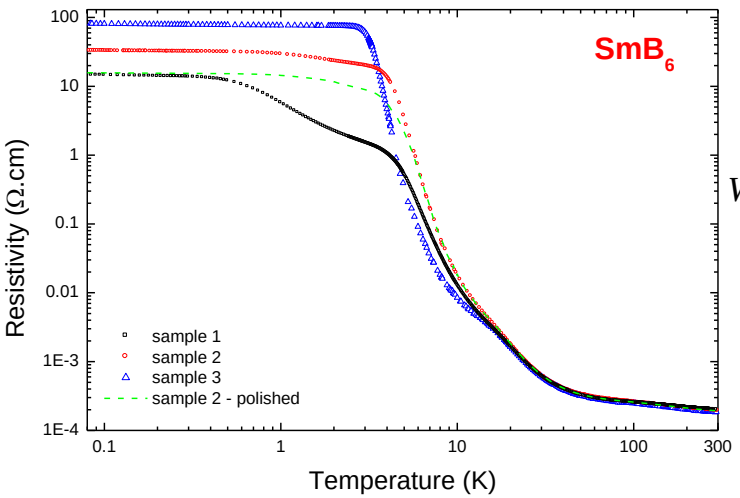
- Cubic structure CsCl type
- X-ray absorption at the L_{III} from 300 K down to 4.2 K [Tarascon et al., JP41, 1141 (1980)]
- Valence change from 2.60 (at 300 K) to 2.53 (at 4.2 K) -> increase of Sm^{2+} by 17.5%
- Fluctuation between Sm^{2+} and Sm^{3+} approximately 10^{12}- 10^{13} s^{-1}
- Homogeneously mixed-valence system



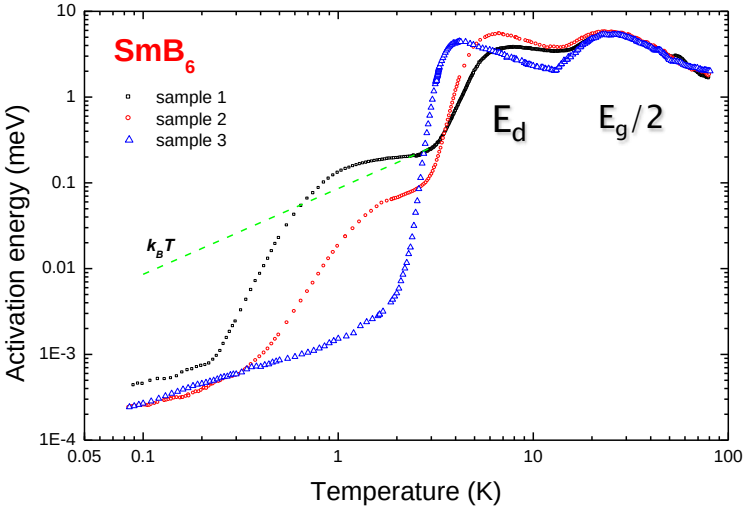




Electrical resitivity

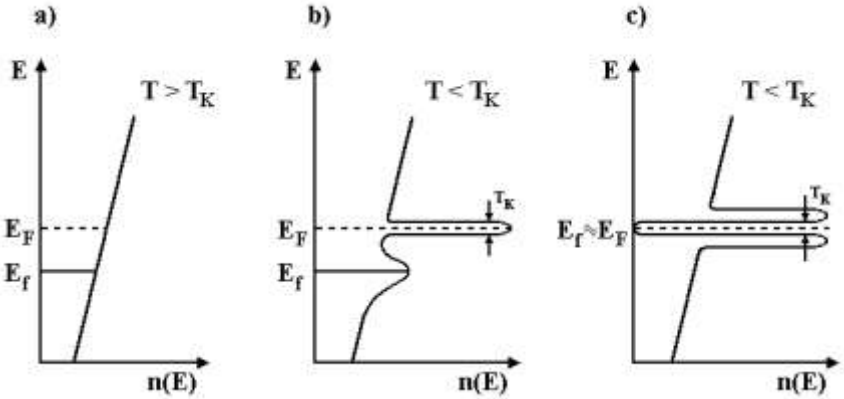


$$W(T) = \frac{d \ln \rho(T)}{d\left(\frac{1}{k_B T}\right)}$$



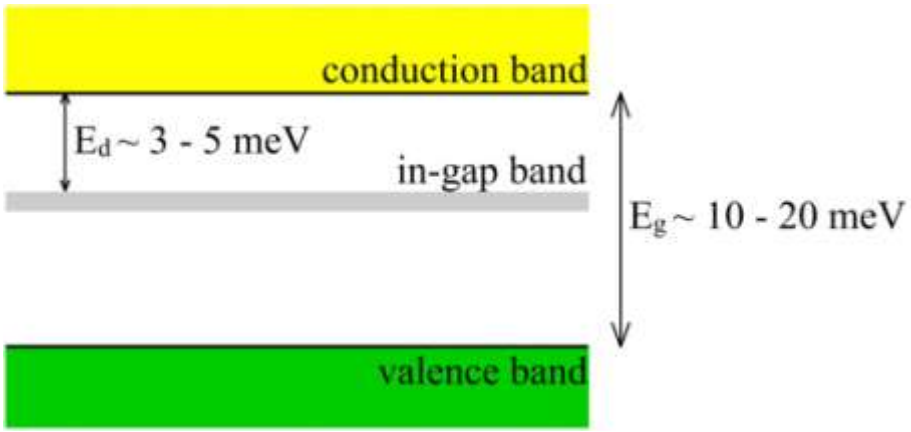
- **SmB_6** is strongly correlated 4*f* system exhibiting gap **E_g** few meV
- **Kondo insulator** with narrow (10meV) transport and spin gap
- <u>**E_g** is stable at high magnetic field and with substitution</u>
  - Suppresed with applied pressure
- Theoretical models of **E_g**:
  - Hybridization of ***d-f*** states; Mott
  - Falicov-Kimball
  - Wigner lattice; Kasuya
  - Kondo lattice

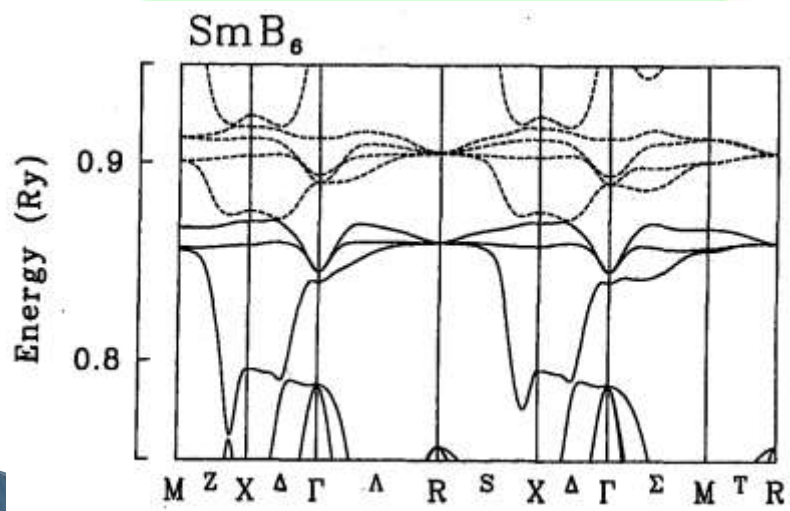
[Flachbart *et al.*, Physica B (2001)]
[Gabáni, PhD. Thesis 2001]



Simple metal HF metal Kondo insulator

Band structure



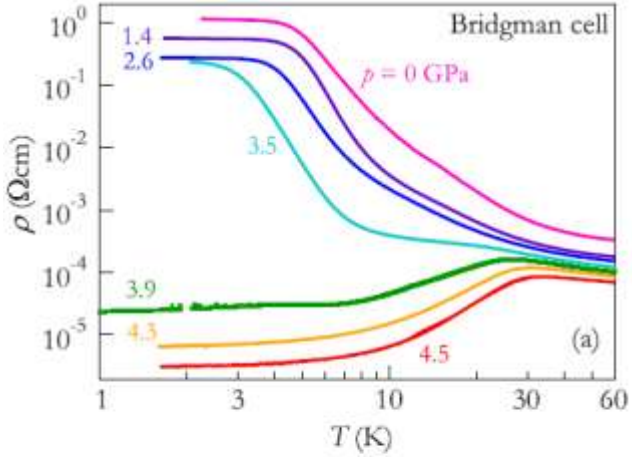


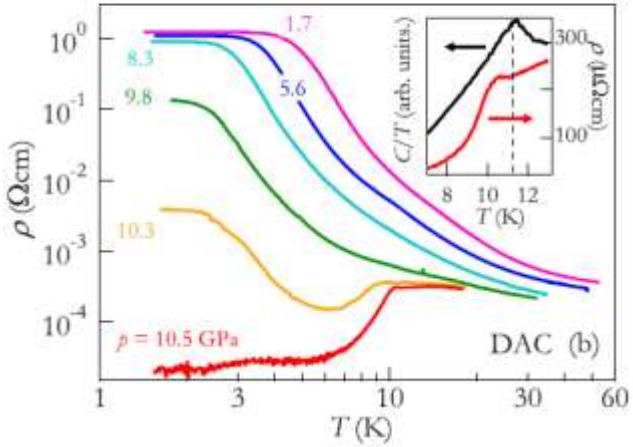
[Yanase and Harima, PTP108 (1992)]

- Hybridization gap $\mathbf{E_g} \sim 10 – 20$ meV
- Below around 15 K another in-gap **band** with $\mathbf{E_d} \sim 3$-5 meV
- Theoretical models:
  - Mott's minimum of conductivity
  - Wigner's liquid
  - Exciton-polaron complexies
  - Bose-Einstein condensation of excitons
  - Anisotropic hybridization – pseudo gap
  - Strongly interacted Kondo holes
  - Etc.

- Open questions:
  - origin of gap $\mathbf{E_g}$
  - origin of in-gap states
  - mechanism of low temperature conductivity
  - ground state: metallic or non-metallic?

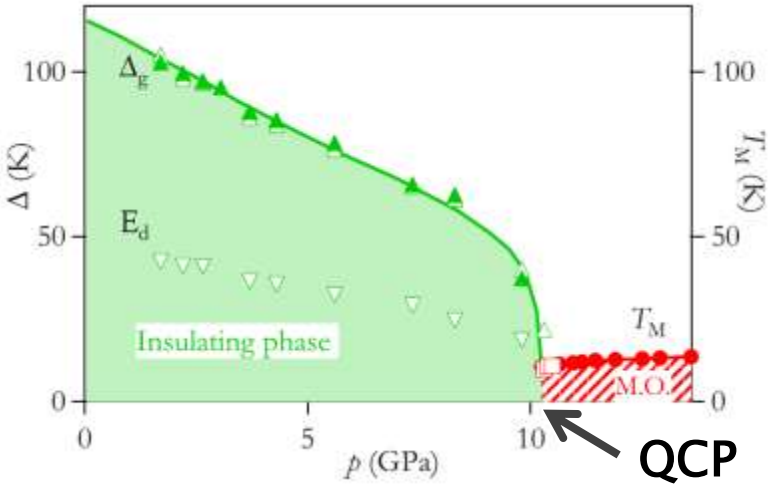
Electrical resitivity under pressure





[Derr *et al.*, PRB77 (2008)]

- Resistivity under excellent hydrostatic conditions
- Pressure medium:
  - ➢Bridgman cell – steatite
  - ➢DAC – liquid argon
- At critical pressure about 10 GPa gap closes
- Transition metal-insulator and magnetic-nonmagnetic phase are intimately liked
- Sensitivity to pressure inhomogeneity – anisotropy of gap

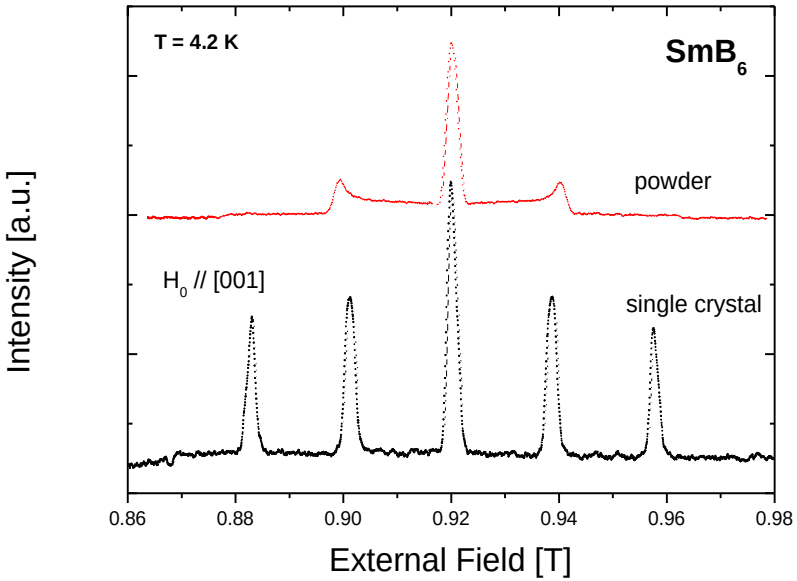


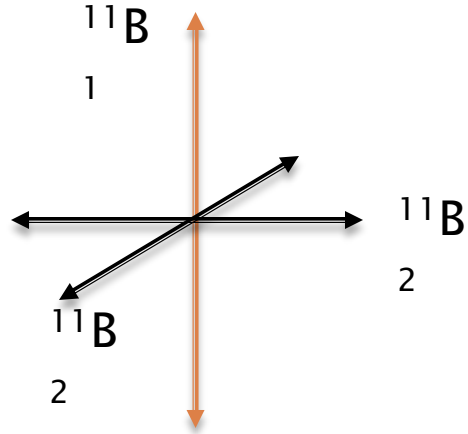
QCP

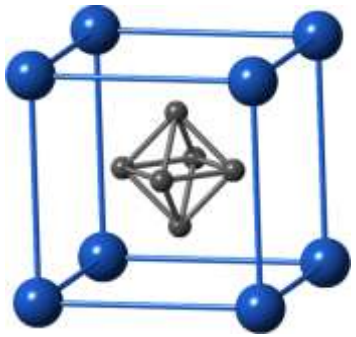
ρ~T

[Gabáni *et al.*, PRB67 (2003)]

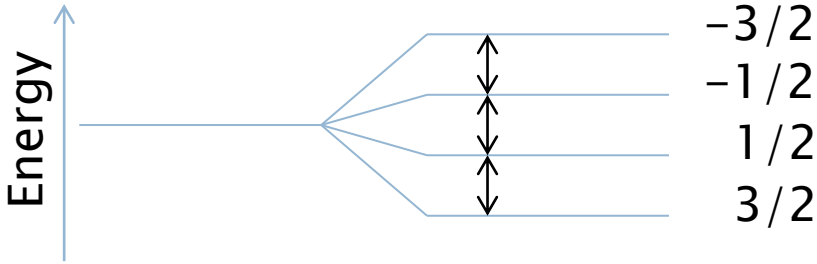
NMR of SmB_6







^{11}B uniaxial local symmetry
I=3/2, γ=13.66 MHz/T



^{11}B nuclear spin system → Sm^{3+} spin fluctuations

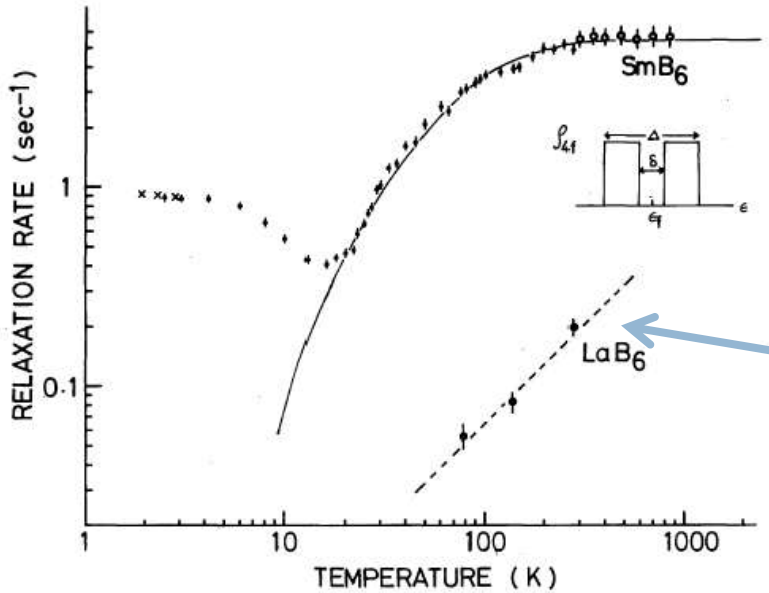
$$\Delta H = -\nu_Q \frac{\pi}{2\gamma_N}\left(3\cos^2\theta - 1\right)\left(2m-1\right)$$

$\theta=0°$: 0, $\pm 2\pi\nu_Q/\gamma_N$ ….. $^{11}B_1$

$\theta=90°$: 0, $\pm \pi\nu_Q/\gamma_N$ ….. $^{11}B_2$

Electric quadrupole interaction – shift of the field for resonance

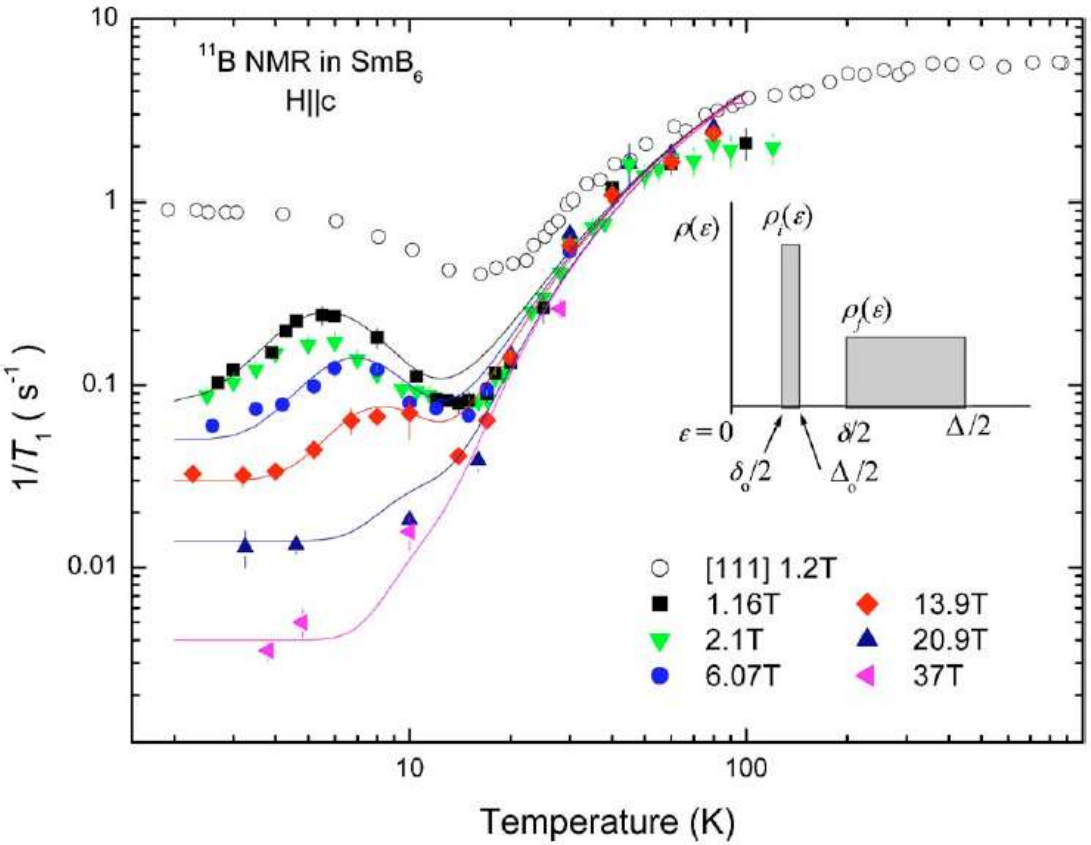
Nuclear Magnetic Resonance of SmB_6



[Takigawa *et al.*, JPSJ50 (1981)]

- NMR of SmB_6 from 2.5 K to 850 K
- Unusual temperature dependence of $\mathbf{1/T_1}$
- Not like in case of other semiconductors
- Above 20 K <u>activation type</u> temperature dependence
- <u>Relaxation process</u> – dominant hyperfine interaction of the ^{11}B with 4*f* electrons of the $\mathbf{Sm^{3+}}$ ions
- LaB_6 – non-magnetic, relaxation only with conduction electrons
- Qualitatively can be explained by simple model of DOS of 4*f* states with gap of 50 K
- Below 15 K **another relaxation process**
- Low energy magnetic excitations which cannot be attributed to the magnetic impurities => **intrinsic** properties of SmB_6

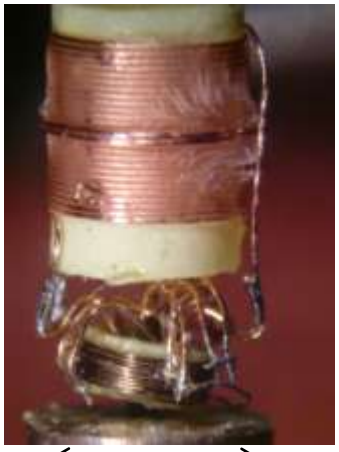
NMR at high magnetic fields



[Caldwell *et al.*, PRB75 (2007)]

- Above 20 K the $1/T_1$ is **not sensitive** on mag. field up to 37 T – hybridization gap remains open
- Magnetic field suppress $1/T_1$ below 20 K
- Intrinsic origin rather than from impurity

Experimental details



4 mm

NMR

•No report about NMR under pressure

•Single crystal samples prepared by floating zone melting crushed into powder

- ➢Higher penetration of RF signal
- ➢Demagnetization effect

•RRR = R(300 K)/R(4.2 K) = 1.2×10^4

•^{11}B-NMR - standard spin-echo technique with a phase-coherent pulsed spectrometer

Presssure

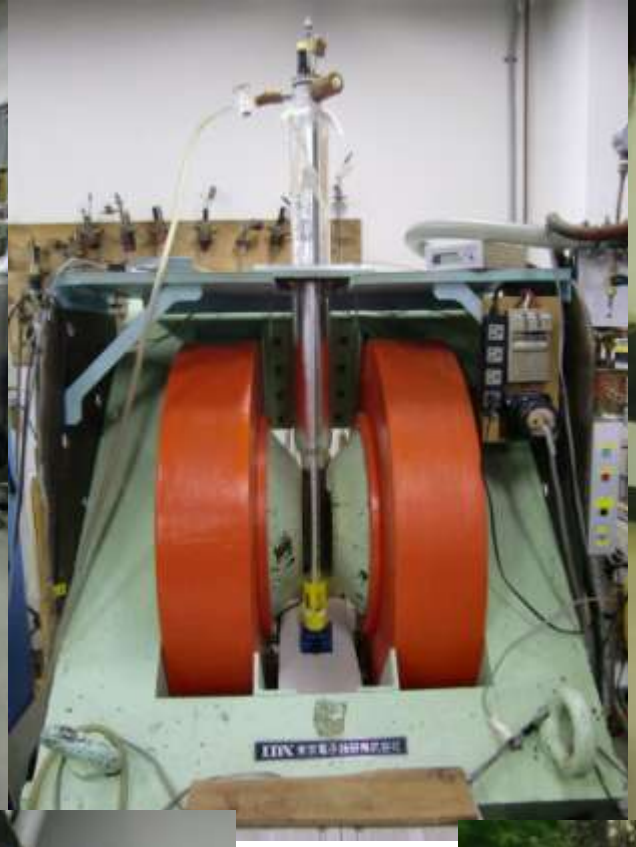
•Piston-cylinder type pressure cell (NiCrAl/ BeCu alloy)

•Maximum pressure up to 30 kbar

•Manganin (room temperature) and tin (low temeprature, T_c) wire manometers

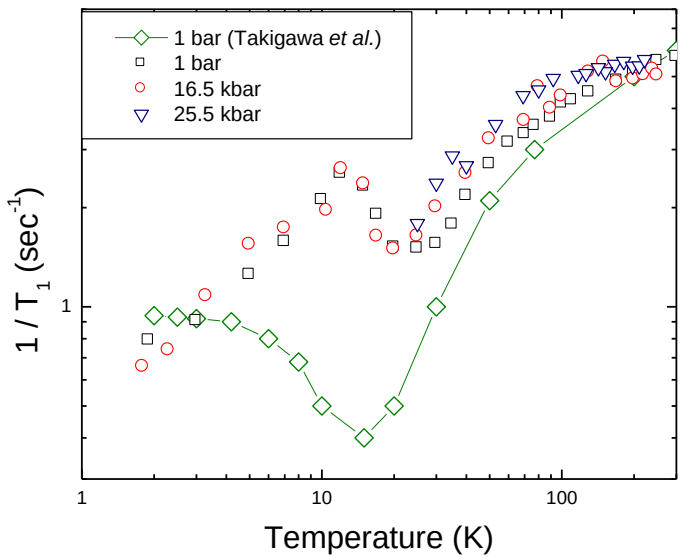
•Pressure medium:

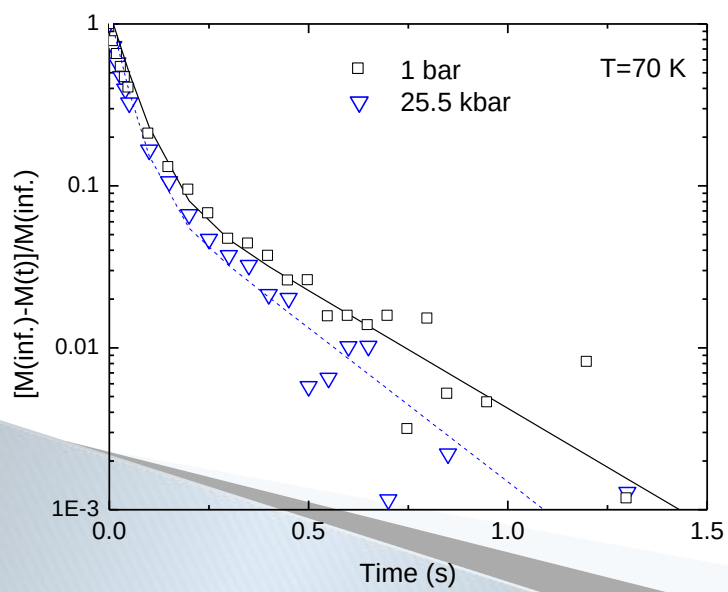
- – Daphne oil 7373 (16.5 kbar)
- – polyethylsiloxane (25.5 kbar)




BNC

Spin-lattice relaxation time



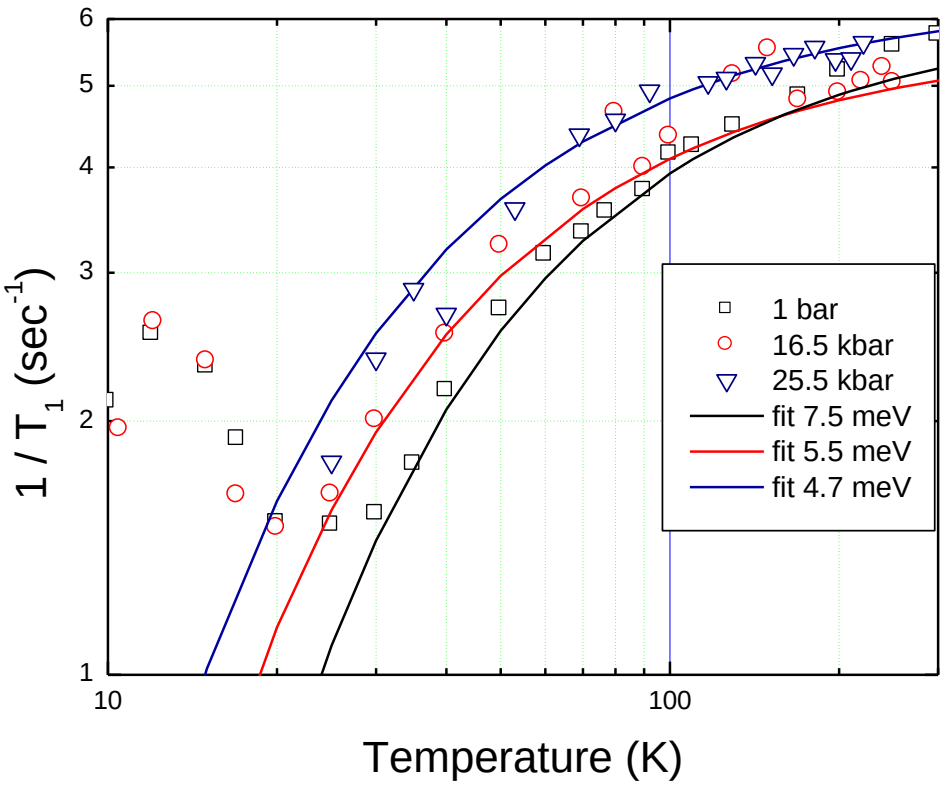


- T_1 was measured at the central line (+1/2 =>1/2), and determined by fitting the data to the relaxation function

$$\frac{M(\infty)-M(t)}{M(\infty)} = A\left(\frac{1}{10}\exp\left(\frac{-t}{T_1}\right)+\frac{9}{10}\exp\left(\frac{-6t}{T_1}\right)\right)$$

- Above 20 K in good agreement with Takigawa *et al.*
- **$1/T_1$ increases with increasing pressure**
- $1/T_1$ at 25.5 kbar is enhanced by 30.7% (at 70 K) compared to the value at ambient pressure, fitting error is less than 3%.
- Pressure-induced increase in $1/T_1$ is expected from the reduction of the gap upon pressure as indicated by the transport measurements under pressure

Hybridization gap



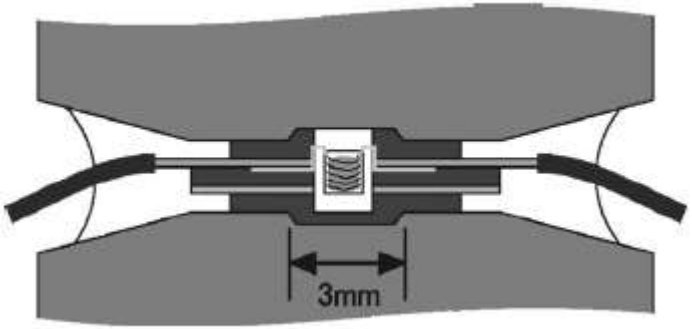
- The number of electrons excited above the energy gap E_g increases with temperature and $1/T_1$ will show an activation type temperature dependence
- To extract pressure dependence of E_g we can fit the data with simple exponential function:

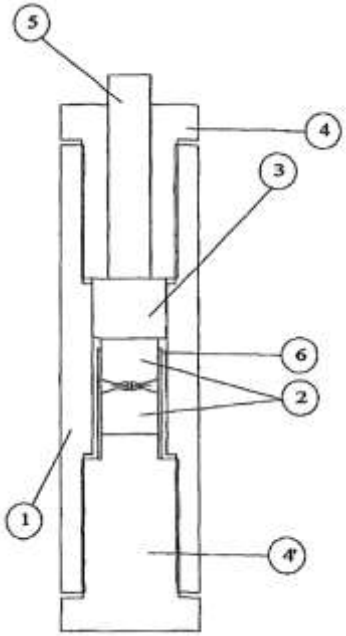
$$\frac{1}{T_1} \approx \exp\left(\frac{-E_g}{2k_B T}\right)$$

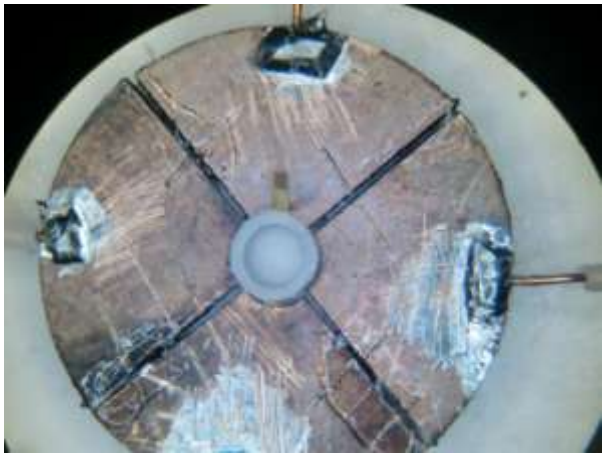
- Gap energy: **7.5** meV at 1 bar,
  5.5 meV at 16.5 kbar
  4.7 meV at 25.5 kbar
- At critical pressure is expected MO at 12 K => divergence of $1/T_1$

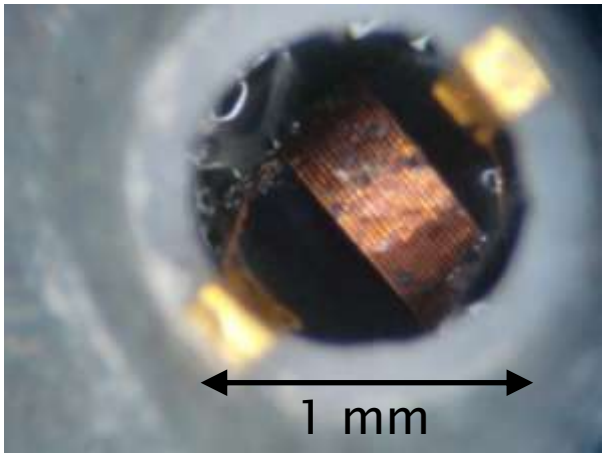
Modified Bridgman anvil cell

N. Takeshita, NIAIST, Tsukuba
Y. Kohori, H. Fukazawa – Chiba Univ.
Pressure up to 10 GPa
1.5 x 1.5 mm, glycerine – press. medium

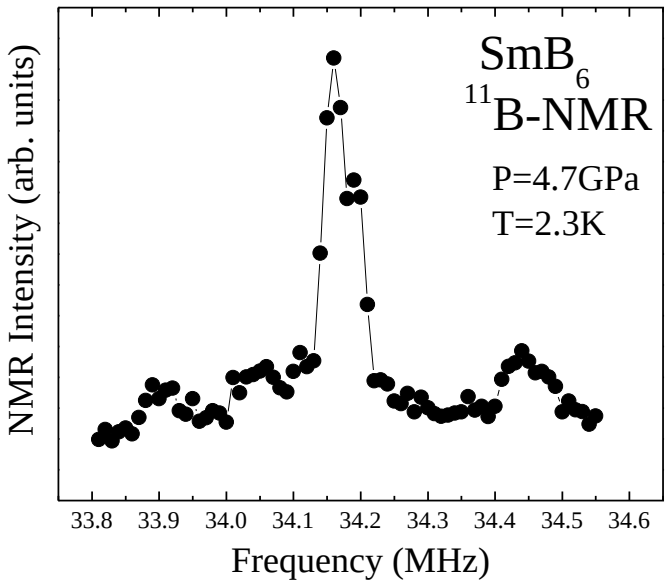






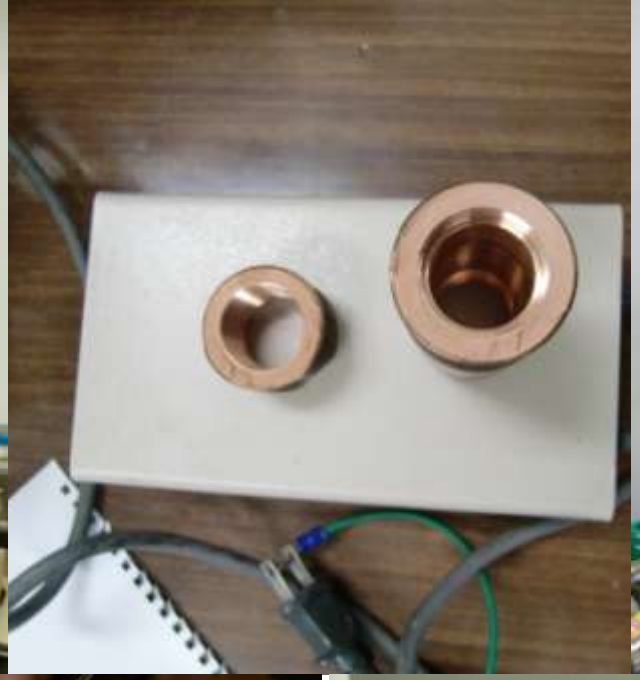


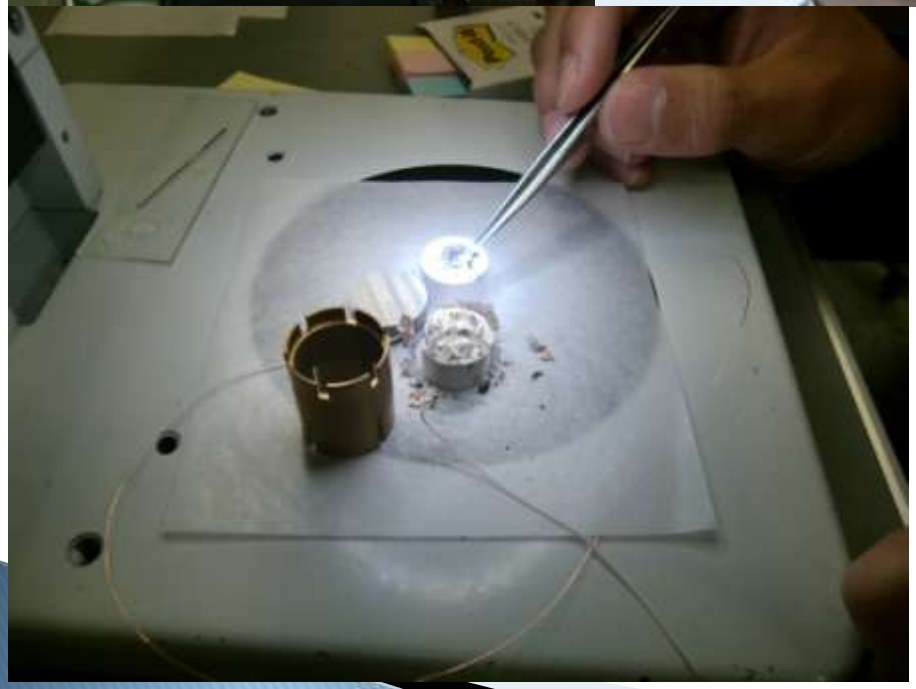
NMR under very high pressure



- Measurements under very high pressure
- Very few NMR measurements above 3 GPa
  - ➢Limitation of piston-cylinder pressure cell
  - ➢Very small experimental volume in case of diamond anvil cell and Bridgman anvil cell
  - ➢Boron – strong signal
  - ➢Actually more than 6 GPa

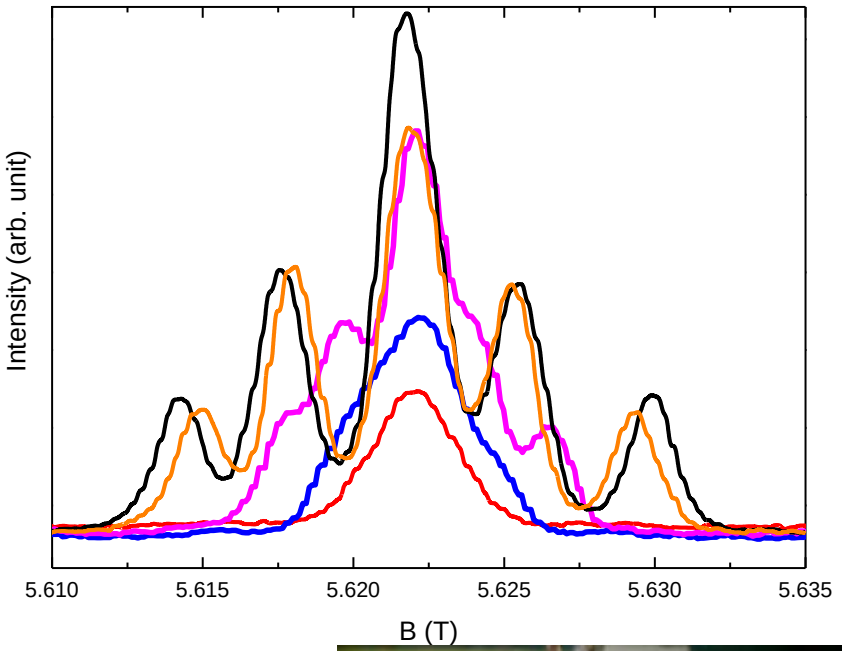
Pristas et al. , unpublished



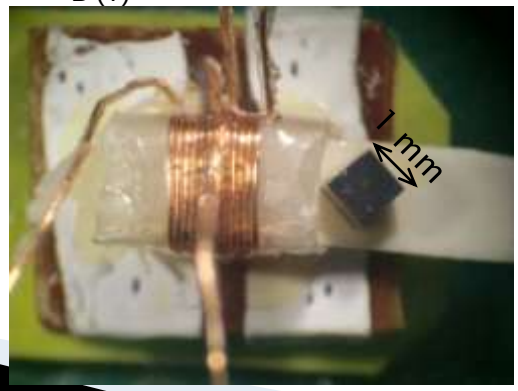



KFe2As2 #101021

Single crystal NMR



- ^{11}B-NMR of single crystal sample of SmB_6
- In <111> direction signal is weaker
- Anisotropy of relaxation times



Conclusions

- Measurement of ^{11}B-NMR of powder sample of SmB_6 under pressure up to **25.5 kbar** at different magnetic fields
  - Above 20 K the spin-lattice relaxation rate is not sensitive on change of magnetic field
- With increasing pressure – **enhancement of value of $1/T_1$ => closing of hybridization gap**:
  - From **7.5 meV** at ambient pressure down to **4.7 meV** at 25.5 kbar
- **Possibility** of measurement ^{11}B-NMR spectra using modified Bridgman anvil cell
- **Anisotropy** of relaxation times in different directions for single crystal

Publications

- G. PRISTÁŠ, T. Mito, T. Kohara, S. Gabáni, M. Reiffers, K. Flachbart, N. Takeshita, N. Shitsevalova: ^{11}B-NMR Study of SmB_6 under Pressure. CSMAG ´10: 14th Czech and Slovak Conference on Magnetism, July 6.-9., 2010, Košice, Slovakia. In *Acta Physica Polonica A*, 2010, vol. 118, no. 5, p. 895-896. (0.433 - IF2009).

- G. PRISTÁŠ, T. Mito, T. Kohara, S. Gabáni, M. Reiffers, K. Flachbart, N. Takeshita, N. Shitsevalova: Pressure-induced suppression of energy gap in the Kondo insulator SmB_6 studied by ^{11}B-NMR. ***J. Phys. Soc. Jpn.*** 80, SA078 (2011), (**2.905** - IF2010).

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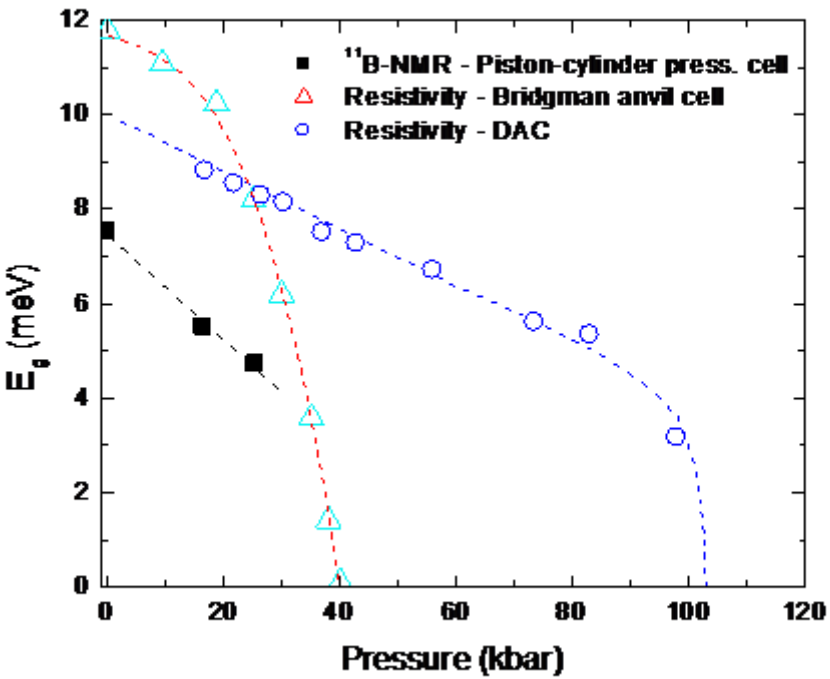
Thank you for your attention!

Comparison with resistivity data



•Difference attributed to 'probe dependence'

➢Estimation from T_1 data - only magnetic 4*f* electronic states are reflected

➢Transport measurement probes basically all components of electrons excited above the gap.

•More rapid decrease of E_g as a function of pressure

➢not only from the suppression of the gap, but also from change of Sm valence (Sm^{2+} => Sm^{3+})

➢Gradual shift of ground state from nonmagnetic to magnetic

Difference in comparison with resistivity – attributed to 'probe dependence'

Different mechanism of measurement; resistivity 'see' all electrons in conduction band;
NMR only Sm^{3+} ions
shift of ground state from nonmagnetic to magnetic

Basics of NMR

- **Nuclear magnetic resonance (NMR)** is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation.

Nucleus posses a total magnetic moment $\boldsymbol{\mu}$ and total angular momentum $\mathbf{J}$

$\boldsymbol{\mu} = \gamma \mathbf{J}$,

two parallel vectors, γ gyromagnetic ratio

Aplication of magnetic field produces an interaction energy:

$E = -\boldsymbol{\mu}\mathbf{B}$

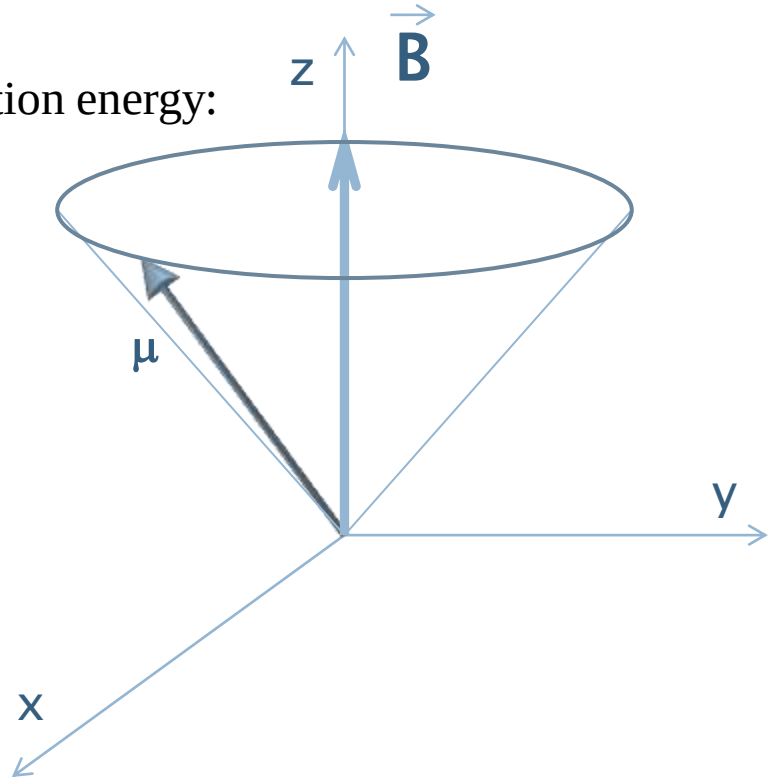
if B is along the z-direction:

$E = -\gamma\hbar B_0 m$, $m = I, I-1, \ldots, -I$

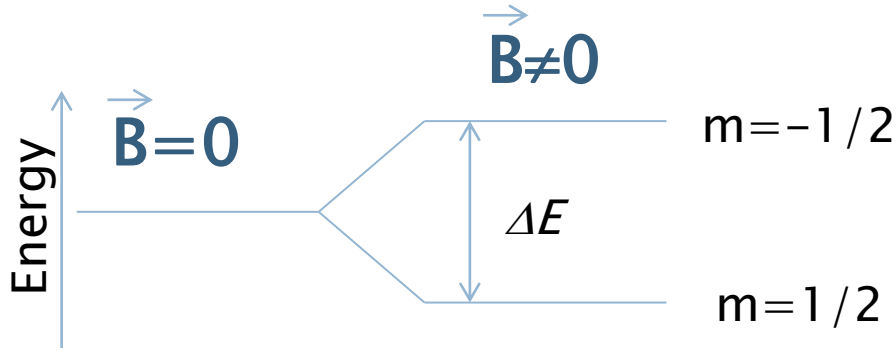
Angular momentum operator $\mathbf{I}$,

$\mathbf{J} = \hbar\mathbf{I}$

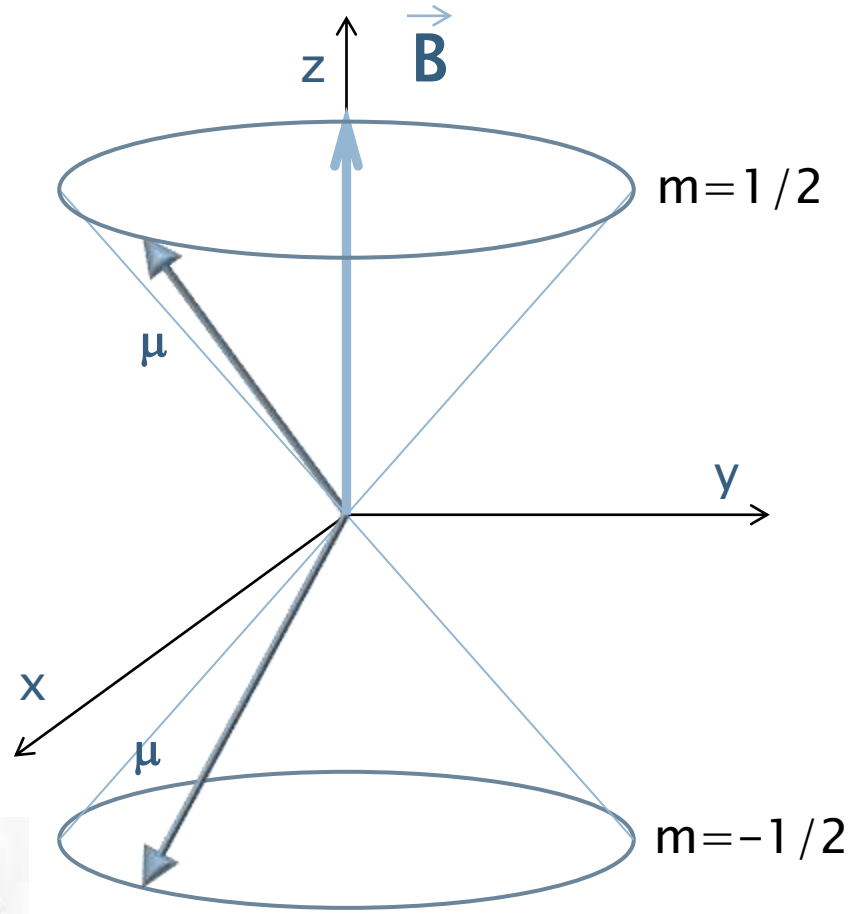
2I+1 values



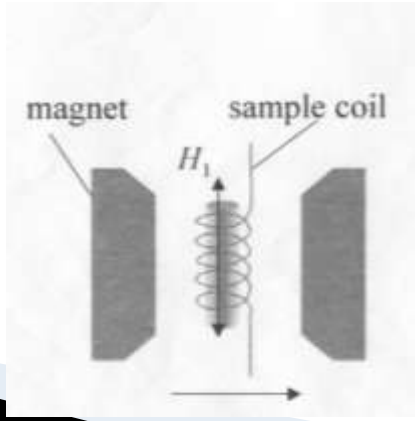
- Nucleus with I=1/2



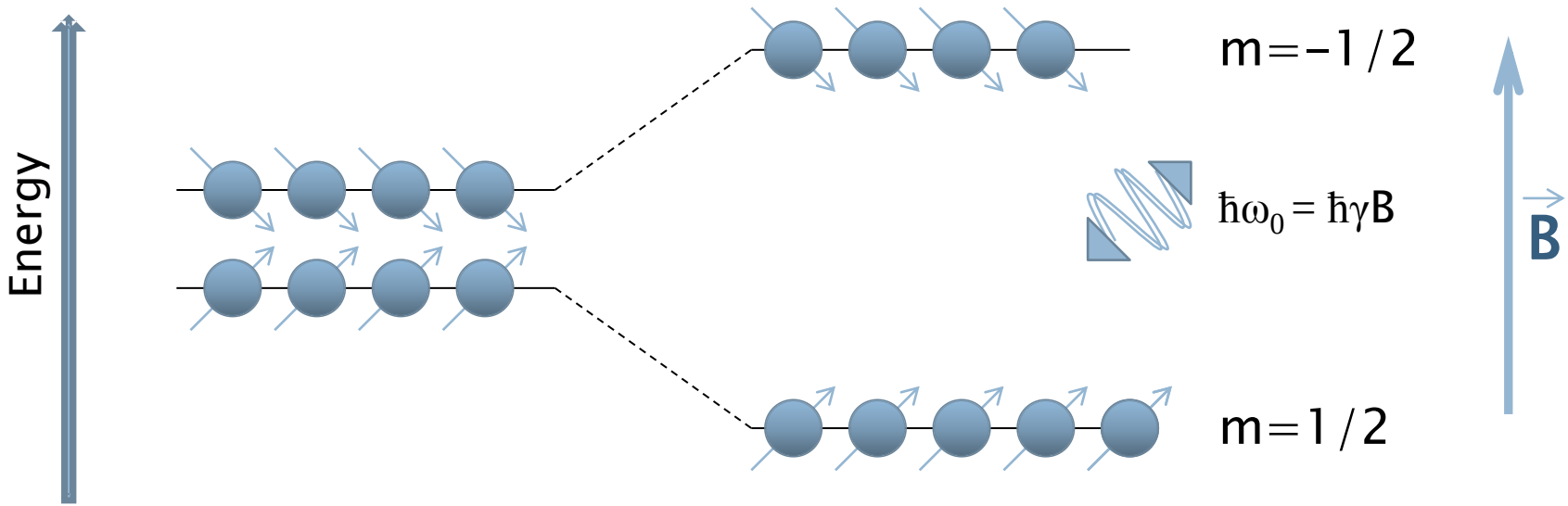
$$\hbar\omega = \Delta E = \gamma\hbar H_0$$



To detect such transition we have to employed resonant technique.
We can excite system by applying radio frequency (RF) signal.



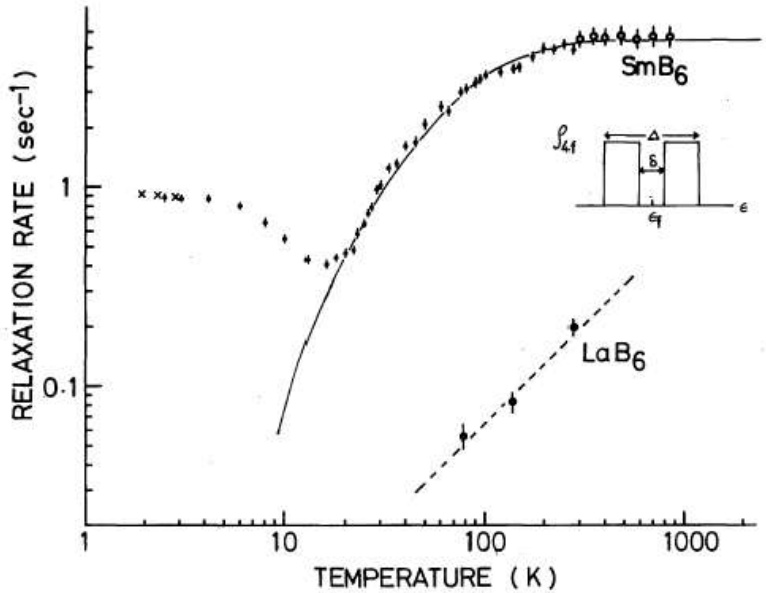
Absorption and radiation of nuclei (I=1/2) in magnetic field **B**.



Population distribution: $\frac{N_-}{N_+} = \exp^{-\gamma\hbar B/k_B T}$

$\mathbf{T_1}$ is the mean time for an individual nucleus to return to its thermal equilibrium state with lattice. ***Spin-lattice relaxation time.***

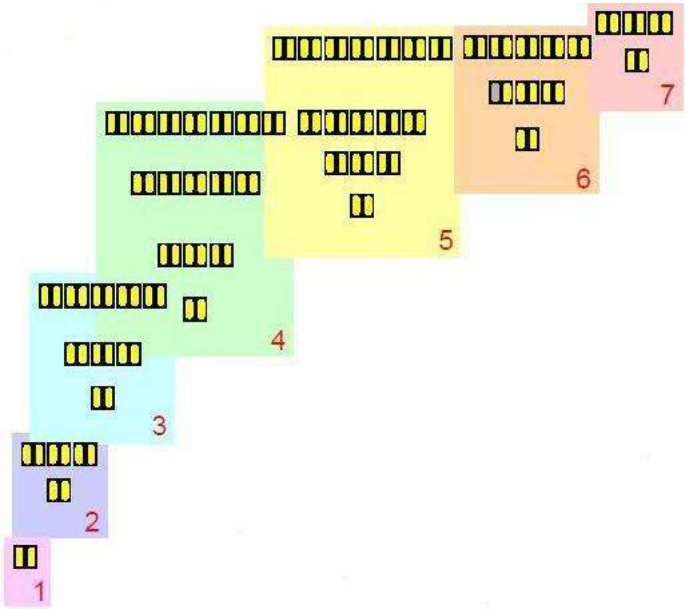
Nuclear Magnetic Resonance of SmB_6

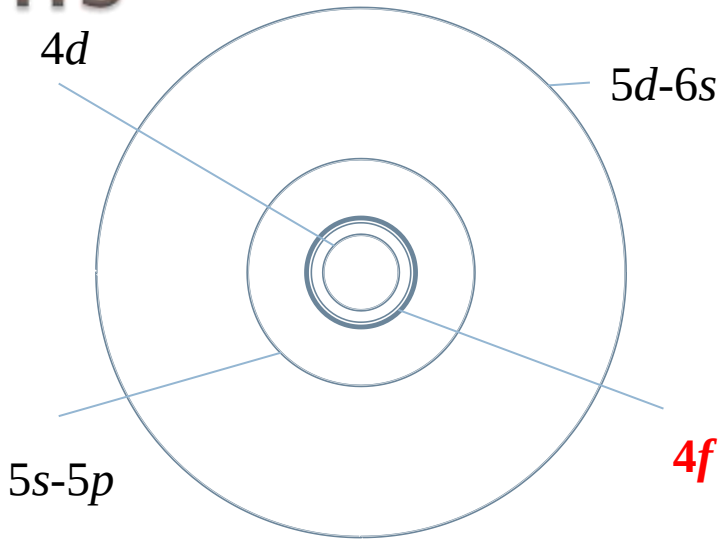


[Takigawa *et al.*, JPSJ50 (1981)]

- NMR of SmB_6 from 2.5 K to 850 K
- Unusual temperature dependence of $\mathbf{1/T_1}$
- Not like in case of other semiconductors
- Above 20 K <u>activation type</u> temperature dependence
- <u>Relaxation process</u> – dominant hyperfine interaction of the ^{11}B with 4*f* electrons of the $\mathbf{Sm^{3+}}$ ions
- LaB_6 – non-magnetic, relaxation only with conduction electrons
- Qualitatively can be explained by simple model of DOS of 4*f* states with gap of 50 K
- Below 15 K **another relaxation process**
- Low energy magnetic excitations which cannot be attributed to the magnetic impurities => **intrinsic** properties of SmB_6

4f – electron systems



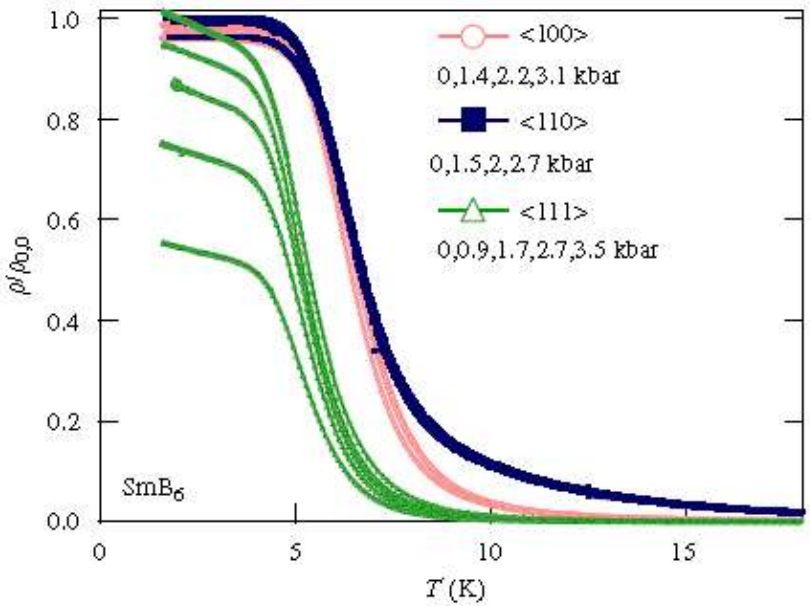


4f shell is very compact:
-Strong on-site interaction between electrons sitting in the same shell
-Almost no overlap between adjacent f-shells -> subsystem of 4f electrons can be modelled by free ion limit.

- 2009–2011 – postdoc., Japonsko
  – NMR under pressure

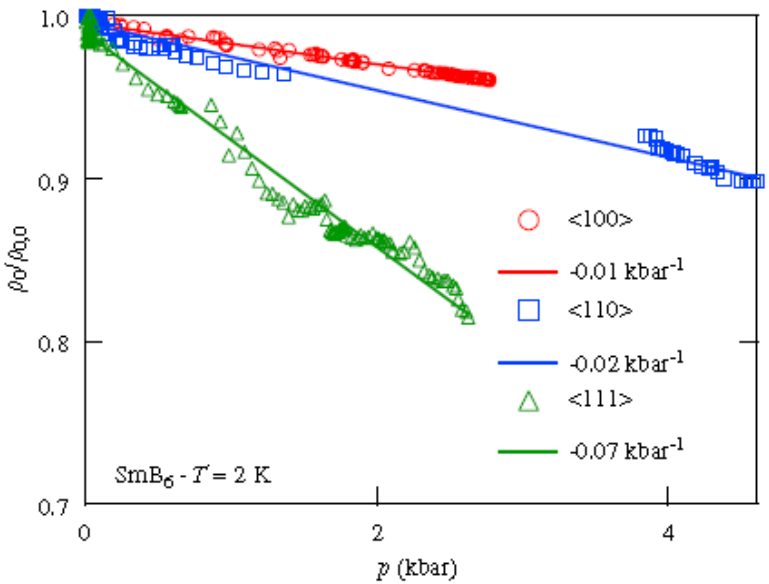
University of Hyogo

Resistivity under uniaxial stress

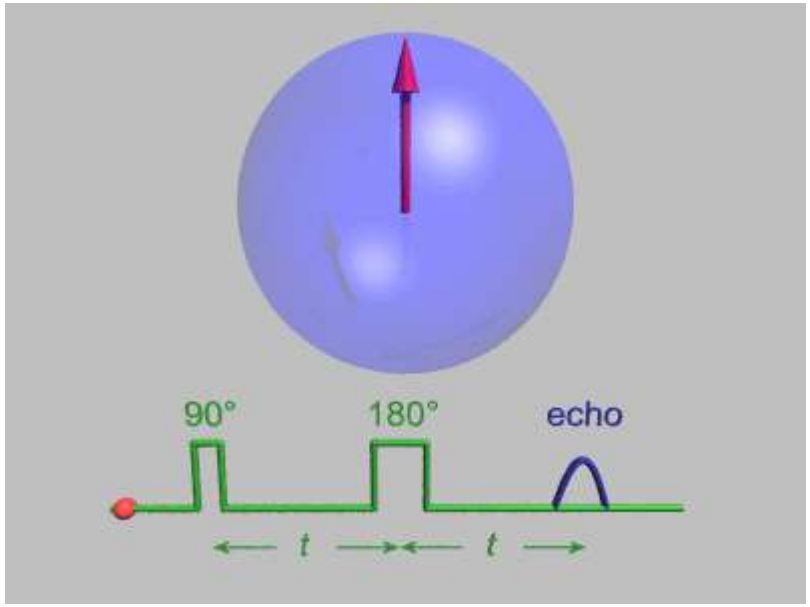


Derr *et al.*, JMMM310 (2007)

- Resistivity under uniaxial stress
- Anisotropy of resistivity
- <111> direction is more sensitive for stress
- Anisotropy of gap



Spin echo technique



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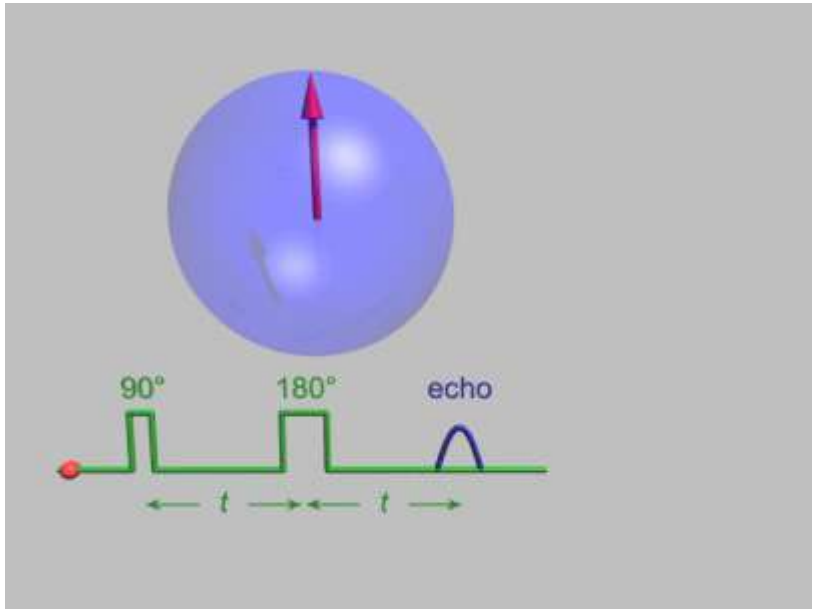

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•In real system, there are additional magnetic fields due to electrons as well as due to other nuclei.

•The nuclear spin Hamiltonian involves interactions that are related to the magnetic and electric properties of the nuclei and the experimental conditions of the experiment:

1. ***External interactions*** - with the static magnetic field **H** (*Zeeman effect)*
   - with the oscillating magnetic RF field applied perpendicular to **H**

Both external interactions dominate the behaviour of the spin system, but in general they **<u>do not</u>** contain the structural and dynamical information.

2. ***Internal interactions*** – chemical shift interaction – orbital motion of electrons in **H**
   - dipolar interaction – with other nucler spins
   - quadrupolar interaction – electric field gradients

Ethyl alcohol (CH_3CH_2OH)
-splitting of the proton resonance