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)

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<th>United States Patent</th>
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<th>HIGH-PRESSURE GENERATION APPARATUS</th>
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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$_6$ superconductor
  - Heavy–Fermion antiferromagnet CeB$_6$
  - Valence-fluctuation systems SmB$_6$
- Lanthanoids – hexaborides REB$_6$

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Number of conduction electrons in SmB$_6$ should be equal to number of Sm$^{3+}$

=> metallic behavior, magnetic order Intermediat–valence system, nonmagnetic !?
Kondo insulator SmB$_6$

- ~50 years ~150 papers related to SmB$_6$
- Still open questions:
  - origin of gap $E_g$
  - origin of in-gap states
  - mechanism of low temperature conductivity
  - ground state: metallic or non-metallic?
Physical properties of SmB$_6$

- 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

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$^{3+}$ $\approx 4 : 6$ ($\nu \approx 2.6$)
Electrical resistivity

- **SmB$_6$** is strongly correlated 4f system exhibiting gap $E_g$ few meV
- **Kondo insulator** with narrow (10meV) transport and spin gap
  - $E_g$ is stable at high magnetic field and with substitution
    - Suppressed with applied pressure
- Theoretical models of $E_g$:
  - Hybridization of $d$-$f$ states; Mott
  - Falicov-Kimball
  - Wigner lattice; Kasuya
  - Kondo lattice

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

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

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

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

[Yanase and Harima, PTP108 (1992)]
Electrical resistivity under pressure

- 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

[Derr et al., PRB77 (2008)]

[Gabáni et al., PRB67 (2003)]
NMR of SmB$_6$

Intensity [a.u.]
External Field [T]

$T = 4.2 \text{ K}$

$H_0 \parallel [001]$

single crystal
powder

$\theta = 0^\circ$: 0, $\pm 2\pi \nu_Q/\gamma_N$ ...... $^{11}\text{B}_1$

$\theta = 90^\circ$: 0, $\pm \pi \nu_Q/\gamma_N$ ...... $^{11}\text{B}_2$

Electric quadrupole interaction – shift of the field for resonance

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

$^{11}\text{B}$ uniaxial local symmetry
$I = 3/2, \gamma = 13.66 \text{ MHz/T}$

$^{11}\text{B}$ nuclear spin system

Sm$^{3+}$ spin fluctuations
NMR of SmB\textsubscript{6} from 2.5 K to 850 K

Unusual temperature dependence of $1/T_1$

Not like in case of other semiconductors

Above 20 K activation type temperature dependence

Relaxation process – dominant hyperfine interaction of the $^{11}$B with $4f$ electrons of the Sm$^{3+}$ ions

LaB\textsubscript{6} – non-magnetic, relaxation only with conduction electrons

Qualitatively can be explained by simple model of DOS of $4f$ 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\textsubscript{6}

[Takigawa et al., JPSJ50 (1981)]
NMR at high magnetic fields

- 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

[Image of NMR graph showing temperature vs. $1/T_1$ for different magnetic fields]

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

**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
- $\text{RRR} = \frac{R(300 \text{ K})}{R(4.2 \text{ K})} = 1.2 \times 10^4$
- $^{11}\text{B-NMR}$ - standard spin-echo technique with a phase-coherent pulsed spectrometer

**Pressure**
- Piston-cylinder type pressure cell (NiCrAl/ BeCu alloy)
- Maximum pressure up to 30 kbar
- Manganin (room temperature) and tin (low temperature, $T_c$) wire manometers
- Pressure medium:
  - Daphne oil 7373 (16.5 kbar)
  - polyethylsiloxane (25.5 kbar)
Spin–lattice relaxation time

- \( T_1 \) was measured at the central line (+1/2 \( \rightarrow \) 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.
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 $\Rightarrow$ 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
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


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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 $4f$ 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 ($\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$)
  - 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 $\text{Sm}^{3+}$ ions

shift of ground state from nonmagnetic to magnetic
Nuclear magnetic resonance (NMR) is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation.

Nucleus possesses a total magnetic moment $\mu$ and total angular momentum $J$

$\mu = \gamma J$

two parallel vectors, $\gamma$ gyromagnetic ratio

Application of magnetic field produces an interaction energy:

$E = -\mu B$

if $B$ is along the $z$-direction:

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

Angular momentum operator $I$,

$J = \hbar I$

$2I+1$ values
Nucleus with I=1/2

\[ \Delta E = \gamma \hbar H_0 \]

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

$T_1$ 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$_6$

- NMR of SmB$_6$ from 2.5 K to 850 K
- Unusual temperature dependence of $1/T_1$
- Not like in case of other semiconductors
- Above 20 K activation type temperature dependence
- Relaxation process – dominant hyperfine interaction of the $^{11}$B with 4$f$ electrons of the Sm$^{3+}$ ions
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- Qualitatively can be explained by simple model of DOS of 4$f$ states with gap of 50 K
- Below 15 K another relaxation process
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[Takigawa et al., JPSJ50 (1981)]
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
Resistivity under uniaxial stress

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

Derr et al., JMMM310 (2007)
Spin echo technique

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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 $\mathbf{H}$ (*Zeeman effect*)
   - with the oscillating magnetic RF field applied perpendicular to $\mathbf{H}$

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

2. **Internal interactions** – chemical shift interaction – orbital motion of electrons in $\mathbf{H}$
   - dipolar interaction – with other nuclei spins
   - quadrupolar interaction – electric field gradients

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Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$)
- splitting of the proton resonance