Measurements of NMR Parameters for Actinide Nuclei in Solids

R. E. Walstedt

Department of Physics, University of Michigan, Ann Arbor, MI, USA

- I. Direct spin echo excitation: $^{235}UO_2$, $^{235}USb_2$
- II. Detection via T_2 cross relaxation: $^{235}URh_3$
- III. T_1 cross relaxation: $^{237}NpO_2$, $^{237}NpPd_5Al_2$

Acknowledgements: Y. Tokunaga, S.Kambe, H. Chudo, H. Sakai, H.Kato, K. Ikushima, H. Yasuoka of the ***Uranium NMR Group*** at the Advanced Science Research Center, J.A.E.A., Tokai-mura, Japan.

Measurements of NMR Parameters for Actinide Nuclei in Solids

R. E. Walstedt

Department of Physics, University of Michigan, Ann Arbor, MI, USA

- I. Direct spin echo excitation: $^{235}UO_2$, $^{235}USb_2$
- II. Detection via T_2 cross relaxation: $^{235}URh_3$
- III. T_1 cross relaxation: $^{237}NpO_2$, $^{237}NpPd_5Al_2$

Acknowledgements: Y. Tokunaga, S.Kambe, H. Chudo, H. Sakai, H.Kato, K. Ikushima, H. Yasuoka of the ***Uranium NMR Group*** at the Advanced Science Research Center, J.A.E.A., Tokai-mura, Japan.

Nuclear Moment Parameters for Selected Actinide Nuclei

Isotope	Spin I	γ(MHz/T)	Q(barns)	Abundance	Half-life	Signal*
^{235}U	7/2	0.76	4.55	0.72%	7.04×10^{8}y	0.00064
^{237}Np	5/2	9.57	3.89	100.0%	2.14×10^{6}y	0.95
^{239}Pu	1/2	3.05	----	-----	24110y	0.0079
^{243}Am	5/2	4.58	4.3	-----	7370y	0.10
^{63}Cu	3/2	11.29	0.21	70.9%	------	1.00

*Signal ~ $\gamma^3 H^2 I(I+1)/(I+1/2)$, normalized to 1 for ^{63}Cu.

$^{235}UO_2$: The Forerunner[*]

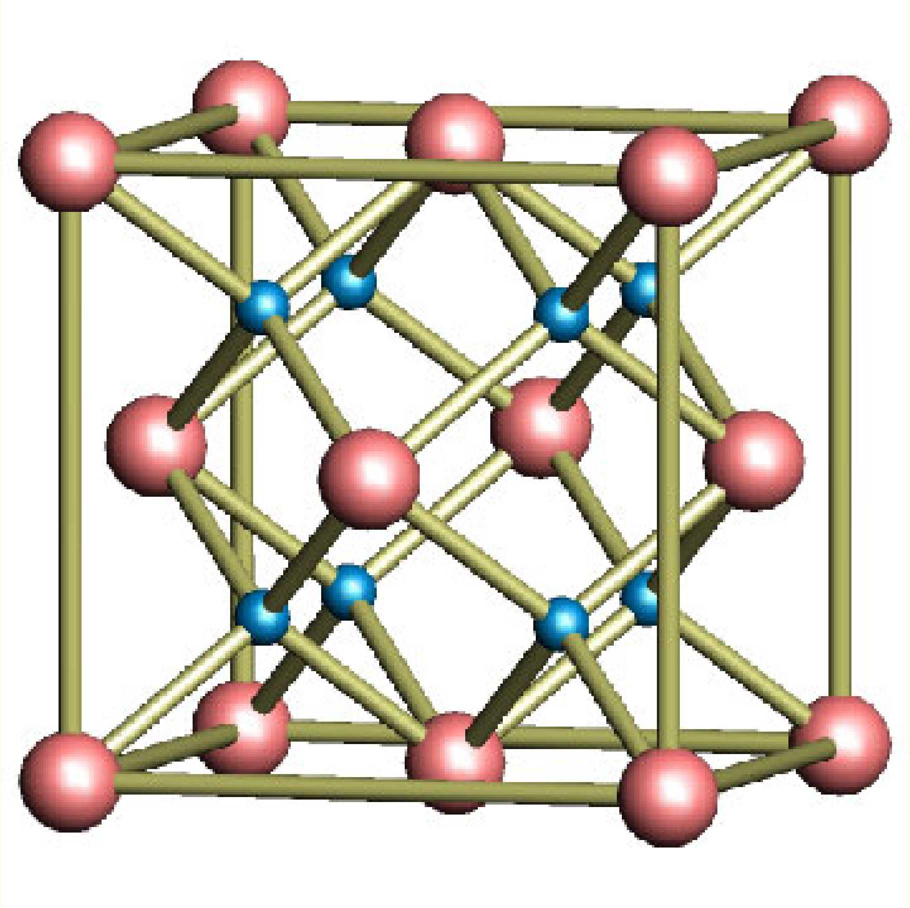
- Fluorite (CaF_2) structure.
- Cubic insulator, AFM at T =31K (1st Order).
- Triple-q AFM structure.
- ^{235}U enriched to 93%.
- ^{235}U ‘AFNMR’ (spin echo) observed only for $T< 15K$.
- $1/T_1 = aT^7$: Phonon Rahman process with magnetoelastic coupling.

[*] K, Ikushima, *et al.,* Phys. Rev. B**63**, 104404 (2001).

Transverse Triple-q AFM Order in UO$_2$

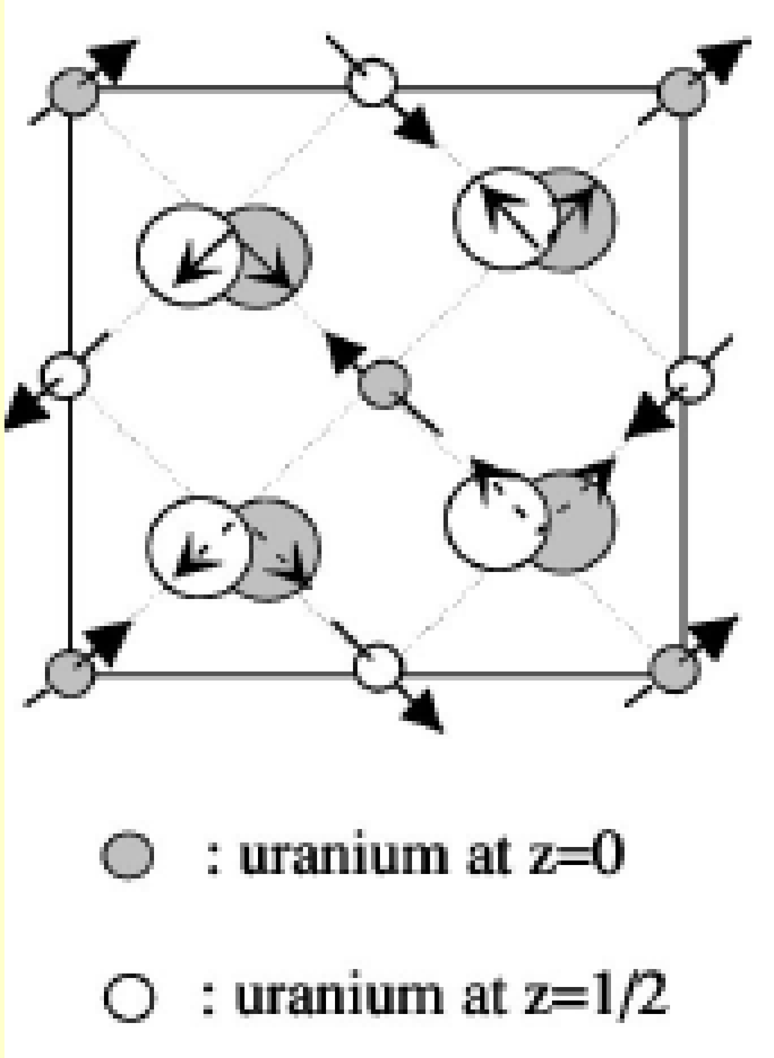
fcc Lattice of U^{4+} in UO$_2$

12 nn – High Level of Frustration

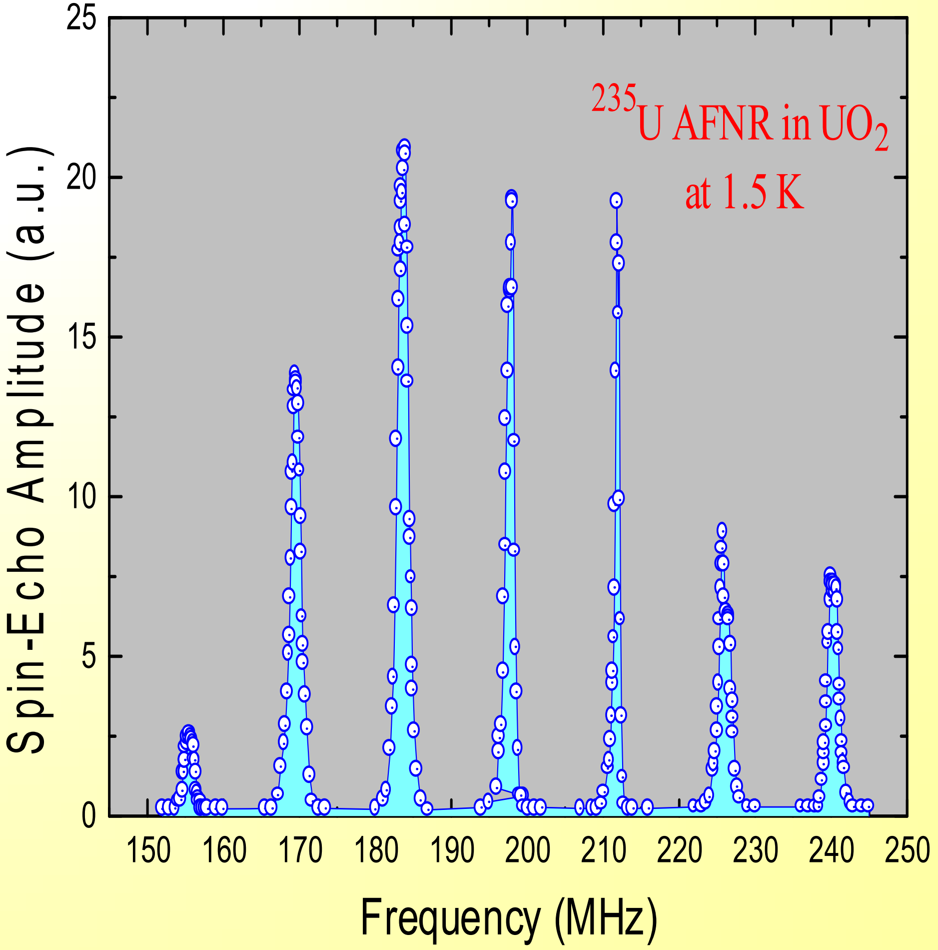


Triple-q AFM in UO$_2$

K. Ikushima et al., PRB **63**,104404 (2001)



^{235}U NMR in UO_2



The ^{235}U AFNMR spectrum in UO_2 is shown. The ordered-state HF field is found to be

$$H_n = 252.3 \pm 1 \text{ T}$$

The AFNMR spectrum is split into 7 lines (I = 7/2) by an electric field gradient:

$$\frac{e^2qQ}{h} = \left|3cos^2\theta - 1\right| = 392 \pm 14 \text{ MHz}$$

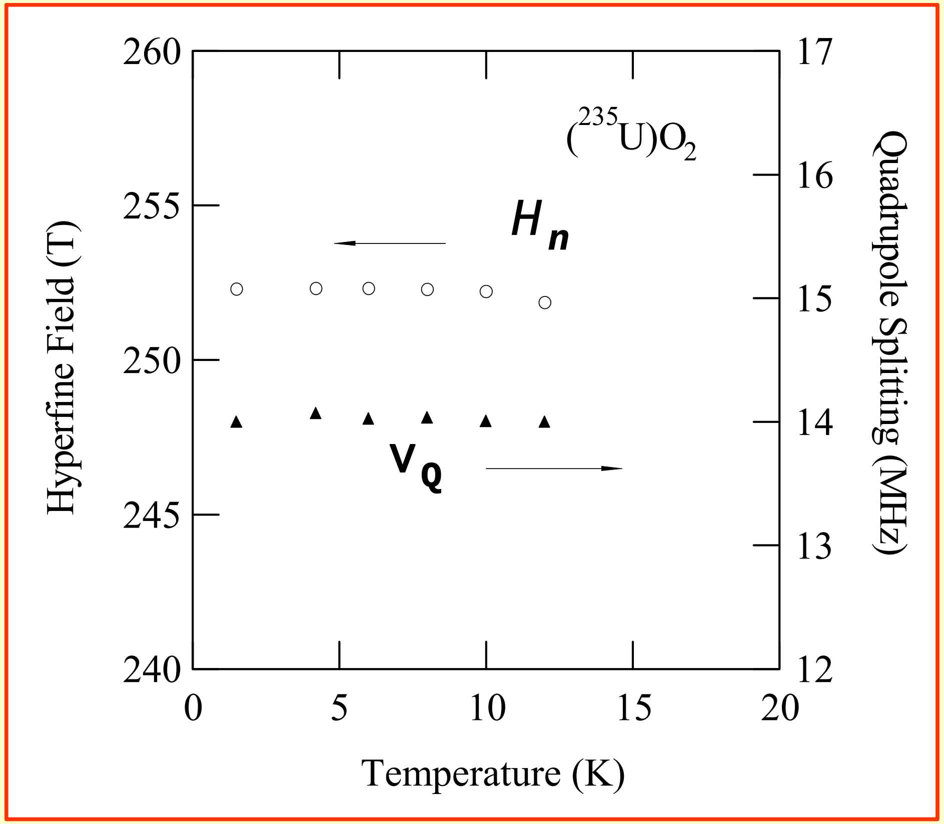
Nuclear Moment Parameters for Selected Actinide Nuclei

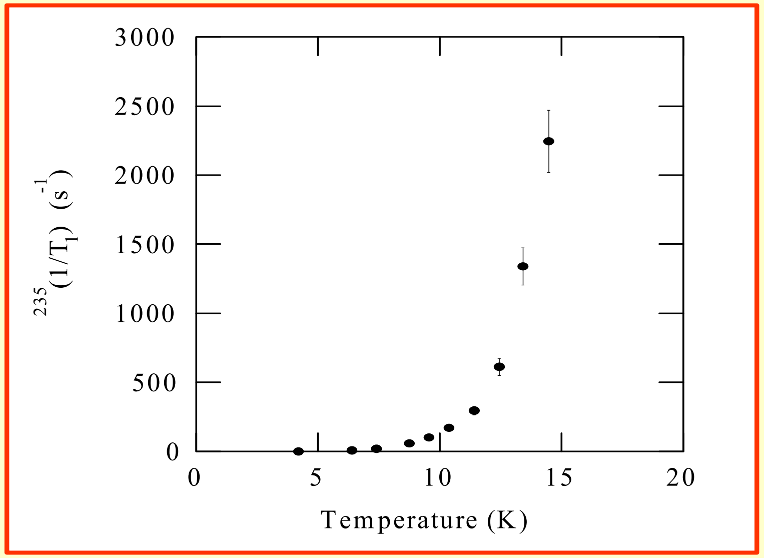
Isotope	Spin I	γ(MHz/T)	Q(barns)	Abundance	Half-life	Signal*
^{235}U	7/2	0.76	4.55	0.72%	7.04×10^{8}y	0.00064
^{237}Np	5/2	9.57	3.89	100.0%	2.14×10^{6}y	0.95
^{239}Pu	1/2	3.05	----	-----	24110y	0.0079
^{243}Am	5/2	4.58	4.3	-----	7370y	0.10
^{63}Cu	3/2	11.29	0.21	70.9%	------	1.00

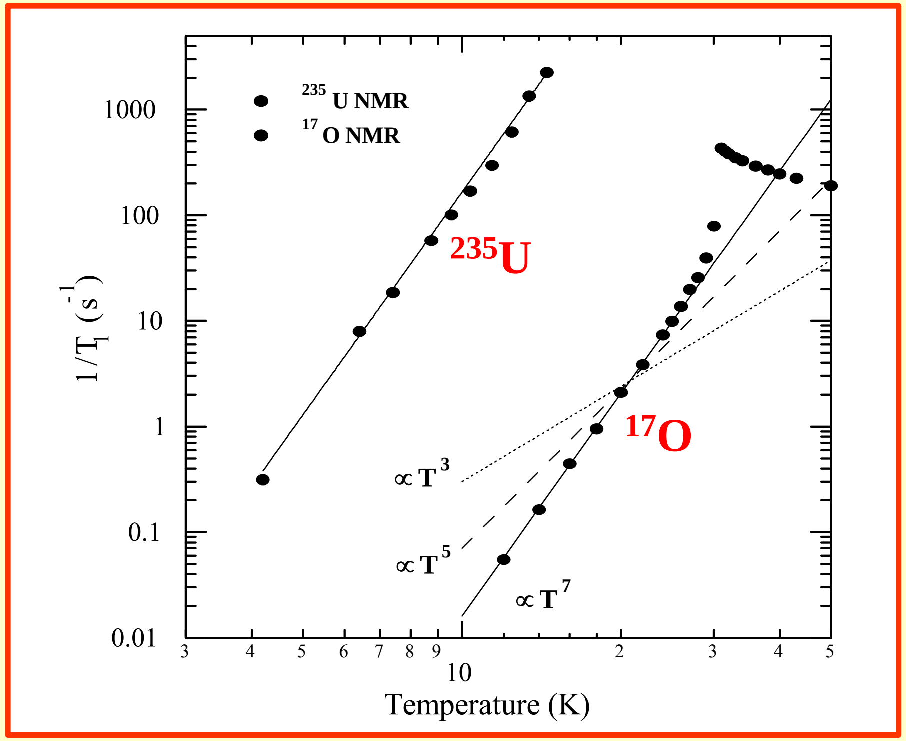
*Signal ~ $\gamma^3 H^2 I(I+1)/(I+1/2)$, normalized to 1 for ^{63}Cu.

^{235}U NMR in UO_2

反強磁性状態におけるH_n, ν_Q and $1/T_1$ の温度依存性

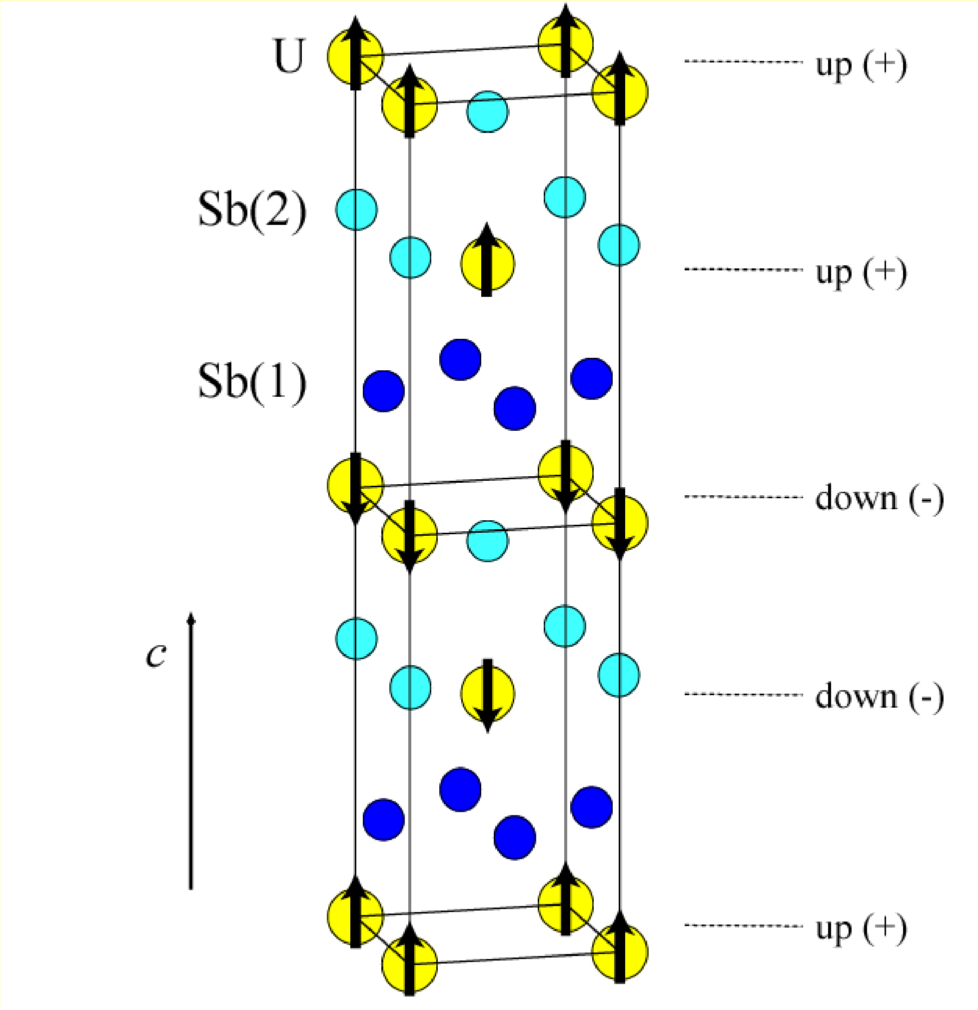






Physical properties of USb_2

USb_2 structure



- 5f itinerant antiferromagnet.
  $T_N = 203$ K, $\langle\mu\rangle = 1.88\ \mu_B$
  Magnetic unit cell is doubled along c-axis.
  (uudd-structure)

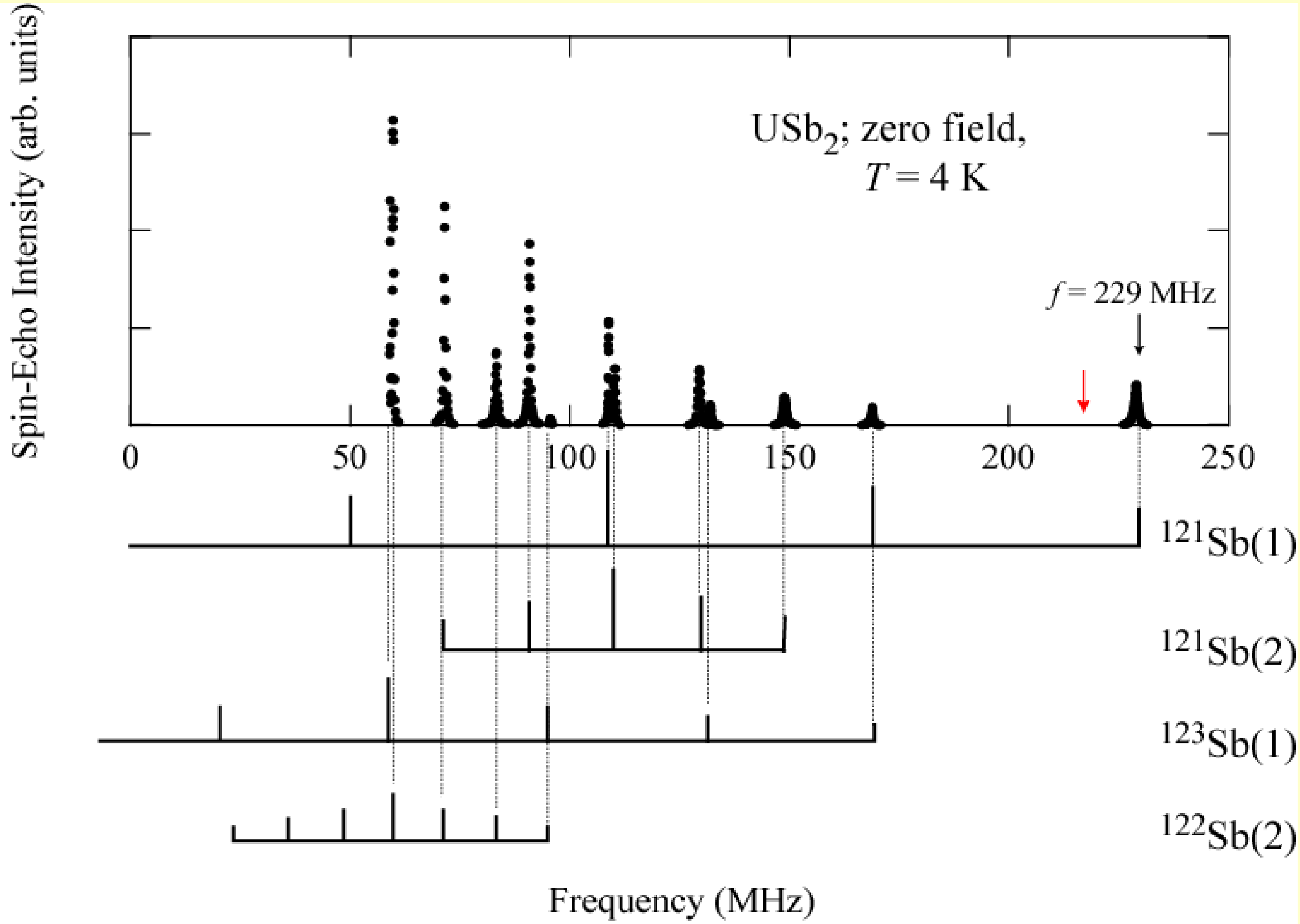
Mössbauer study (Tsutsui, et. al.)

$H_{int} = 270$ T
$e^2qQ = -35$ mm/s,

corresponding to:

$\nu_z \sim 205$ MHz
$\nu_Q \sim 140$ MHz

^{121,123}Sb AFNMR: USb$_2$ with H = 0



^{121}Sb; I = 5/2

γ = 10.189 MHz/T

^{123}Sb; I = 7/2

γ = 5.5176 MHz/T

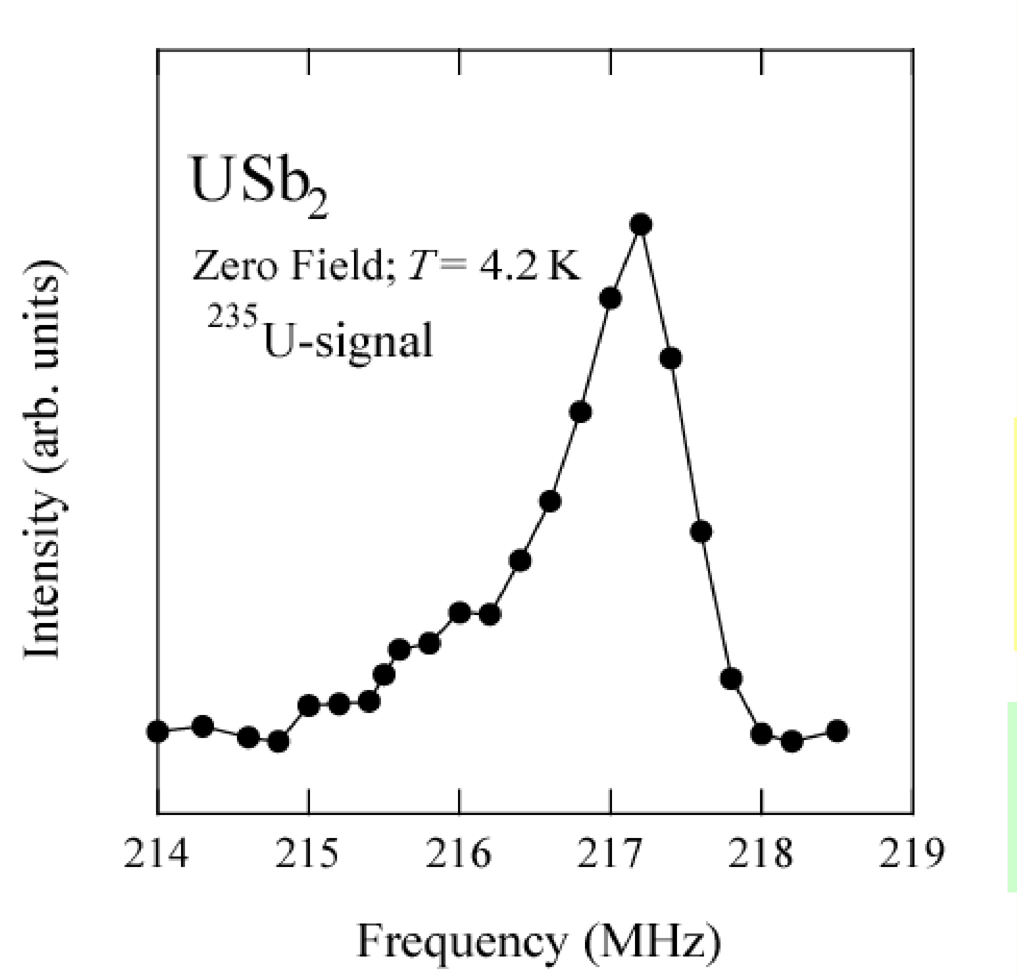
H_{tr} = 10.7 T (Sb(1))

10.8 T (Sb(2))

K. Ikushima, *et. al.*

Zero-field Spectrum: ^{235}U Spin Echo Amplitude

20 % enriched sample; randomly oriented powder.



H. Kato: Weak signal observed at f = 217 MHz

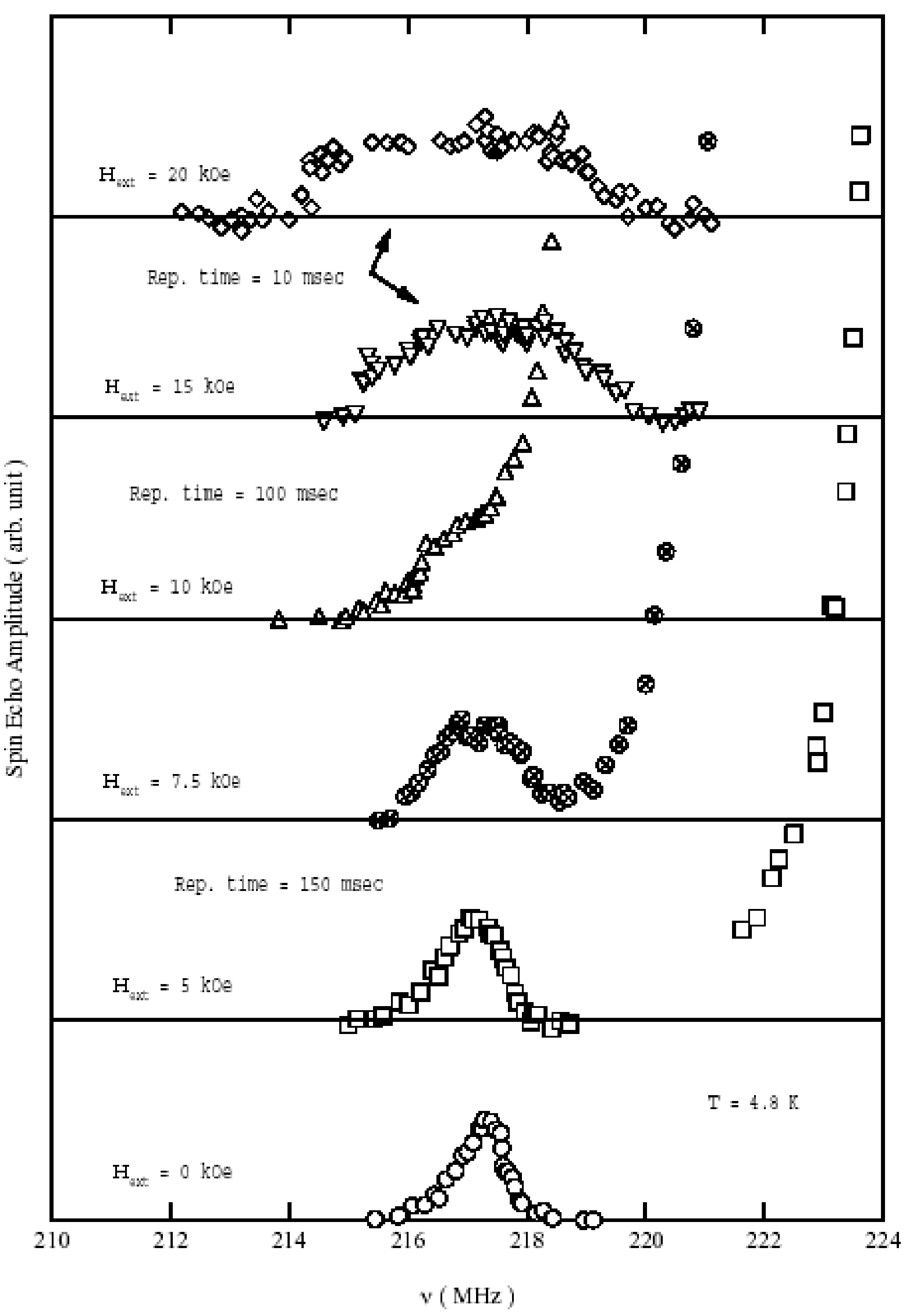
Consistent with the Mössbauer study.

* Appropriate Pulse conditions for this signal are quite different from those for Sb signal.

First observation of a ^{235}U NMR signal in a metallic system.

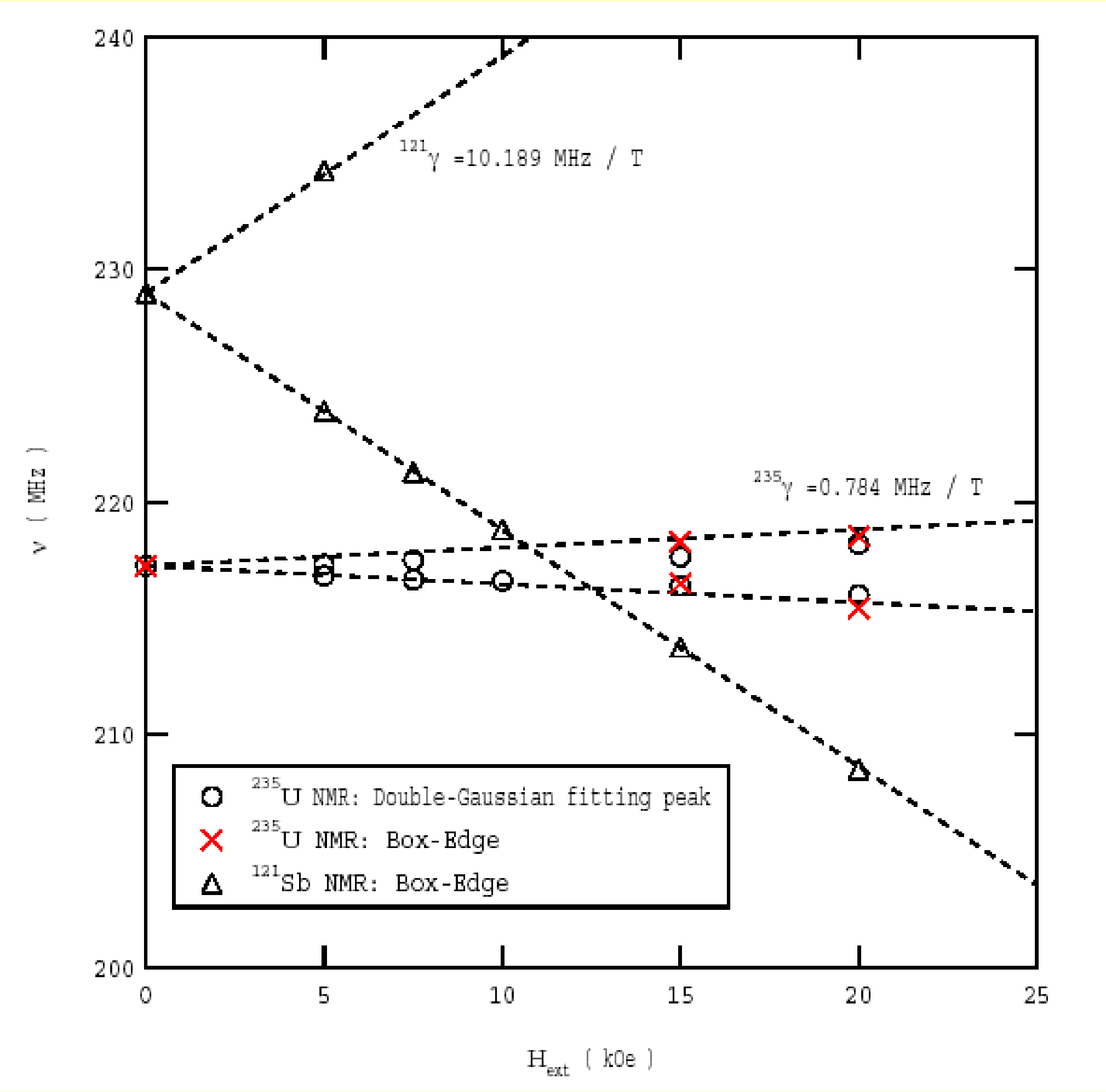
^{235}U AFNMR in USb_2

Broadening effect in applied magnetic field. T=4.2K.



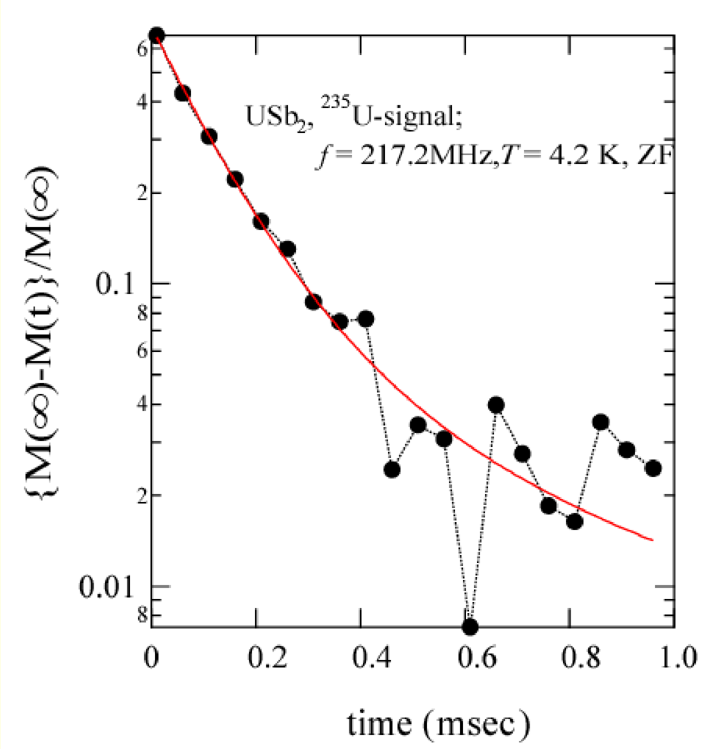
USb$_2$: f$_{NMR}$ vs. H

Magnetic field broadening of ^{121}Sb and ^{235}U at T=4.2K.



^{235}U Relaxation Times at 4.2 K

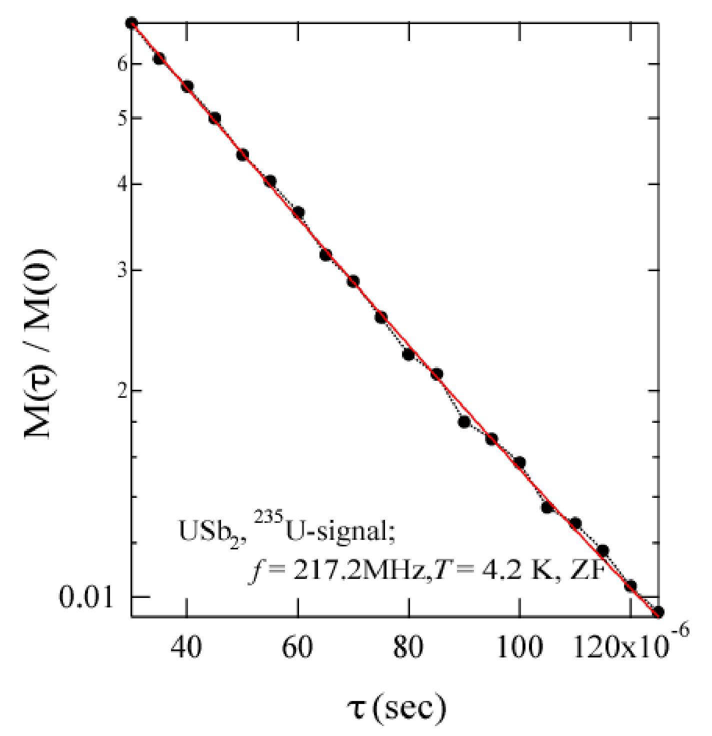
T_1 measurement



$$M(t) \propto \frac{1}{84} e^{(-\frac{t}{T_1})} + \frac{1}{44} e^{(-\frac{6t}{T_1})} + \frac{75}{364} e^{(-\frac{15t}{T_1})} + \frac{1225}{1716} e^{(-\frac{28t}{T_1})}$$

T_1 ~ 14.5 msec

T_2 measurement



$$M(\tau) \propto e^{(-\frac{t}{T_2})}$$

T_2 ~ 80 μsec. ($T_1/16$ = 90 μsec).

Indirect Measurement of $^{235}T_1$ in URh_3

(Y. Tokunaga)

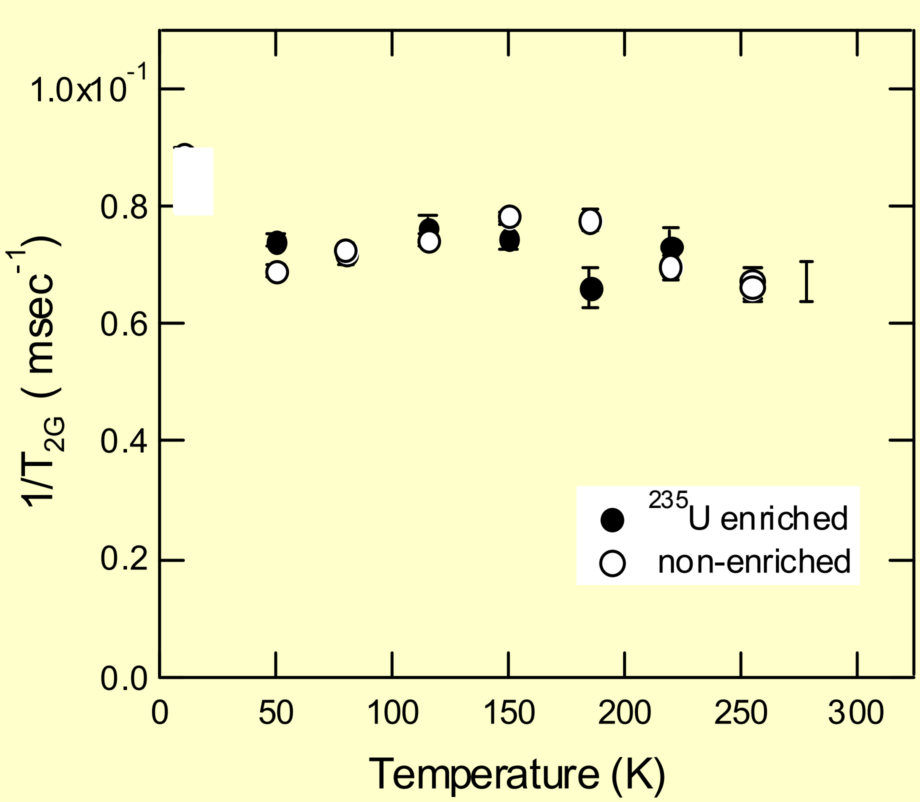
- URh_3: Pauli paramagnet.
- $H_{AB} = \Sigma_{ij}\, D_{ij} I_{Azi} I_{Bzj}(t) \Rightarrow$ Transverse Cross Relaxation.
- ^{103}Rh NMR *observed.*
- $\Rightarrow SE(t) \approx S_0 \exp(-t/T_{2G})^2 \exp(-t/T_{2CR})$,
- where $1/T_{2CR} = \langle \Delta\omega^2 \rangle_{AB}\, {}^{235}T_1$.

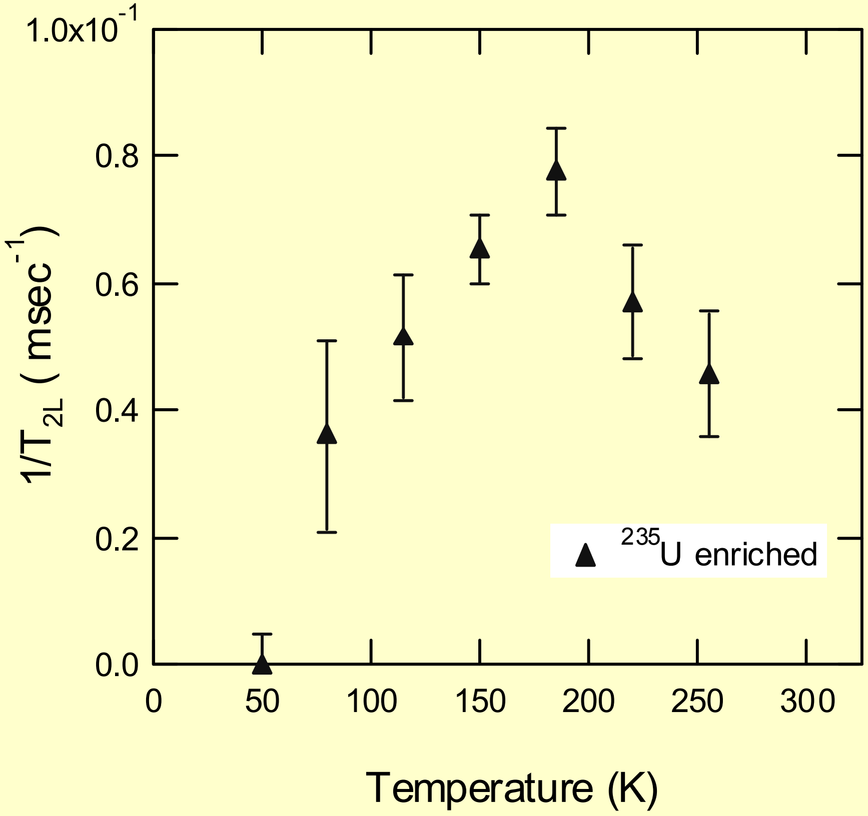
I_{Azi}: ^{103}Rh

$I_{Bzj}(t)$: ^{235}U

- **Results:** 20% enriched vs. unenriched ^{235}U.
- Gaussian (like-spin) process same in both samples.
- 20% enriched sample has $1/T_{2CR}$ *in addition.*
- $1/T_{2CR}(T)$ gives: $^{235}T_1 T \sim\ \ 2$ sec K.
- First measurement of $^{235}T_1$ in I-M compound.

$^{235}U - ^{103}Rh$ Cross Relaxation Study of ^{235}U T_1 Process in URh_3





Cross-Relaxation in NpO_2

Specific-heat anomaly at $T \sim 26K$ (1953)

Absence of dipole moment

Neutron, Mössbauer:

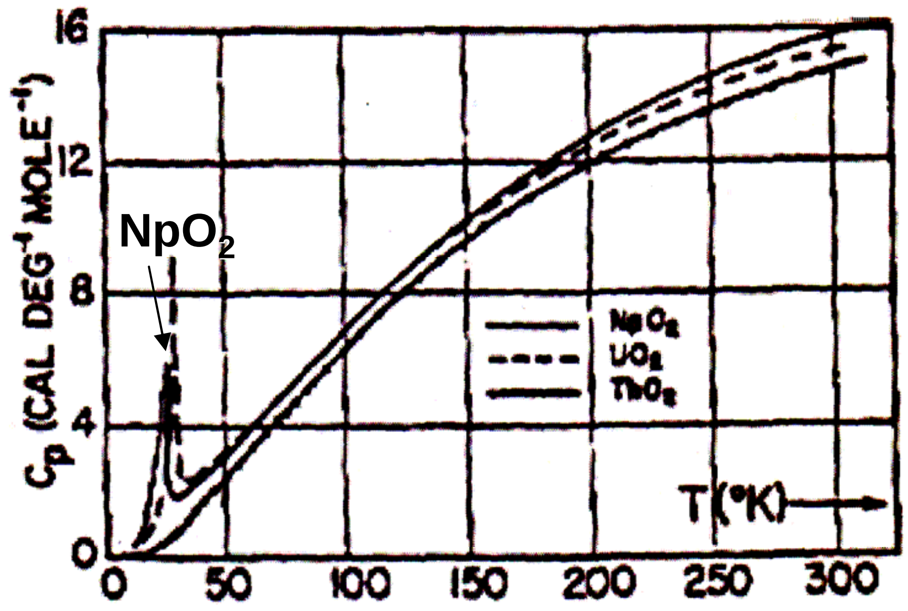
$\mu_0 < 0.01\mu_B$/Np.

Not purely Quadrupolar!

Breaking of time reversal invariance

Susceptibility, μSR

No lattice distortion through T_0



Molar heat capacities C_p of NpO_2, UO_2, and ThO_2 as functions of the temperature *T*. Experiments by Osborne and Westrum [1].

D.W. Osborne and E.F.Westrum (1953)

NpO_2: Triple-q Octupolar-Quadrupolar Ordering

Resonant X-ray Scattering Study

J. A. Paixao et al, PRL89 (2002) 187202-1

longitudinal Triple-*q* antiferro quadrupolar (AFQ) ordering of Γ_5 -quadrupole.

Secondary OP

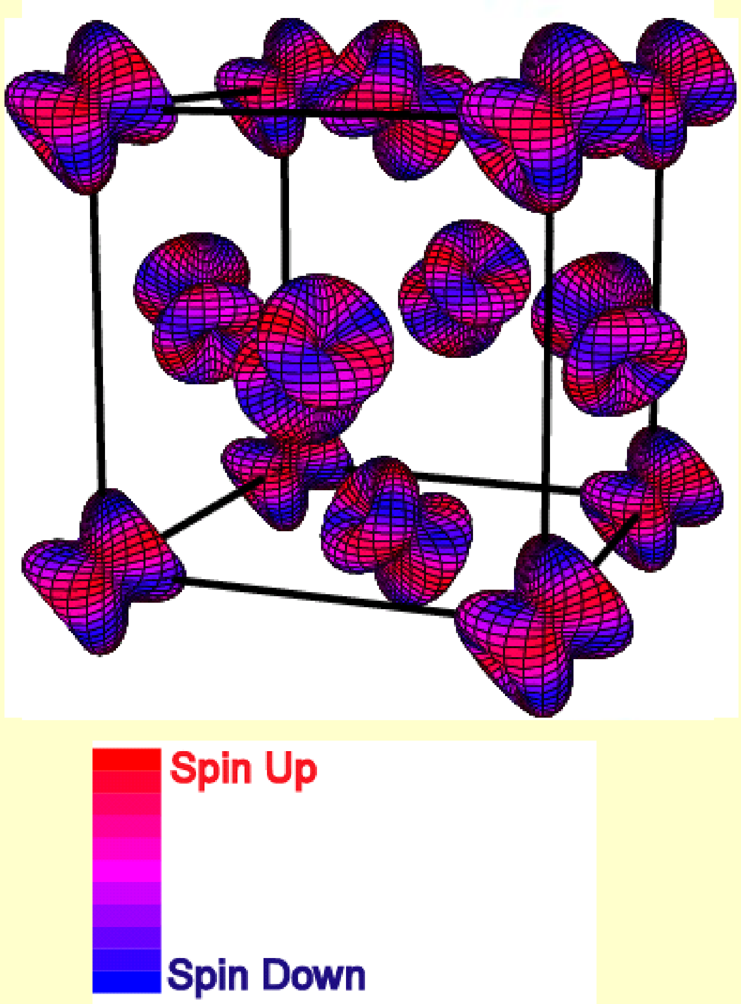
↑

Driven by the ordering of **magnetic octupoles (AFO) of Γ_5 symmetry**- Proposal.

Primary OP

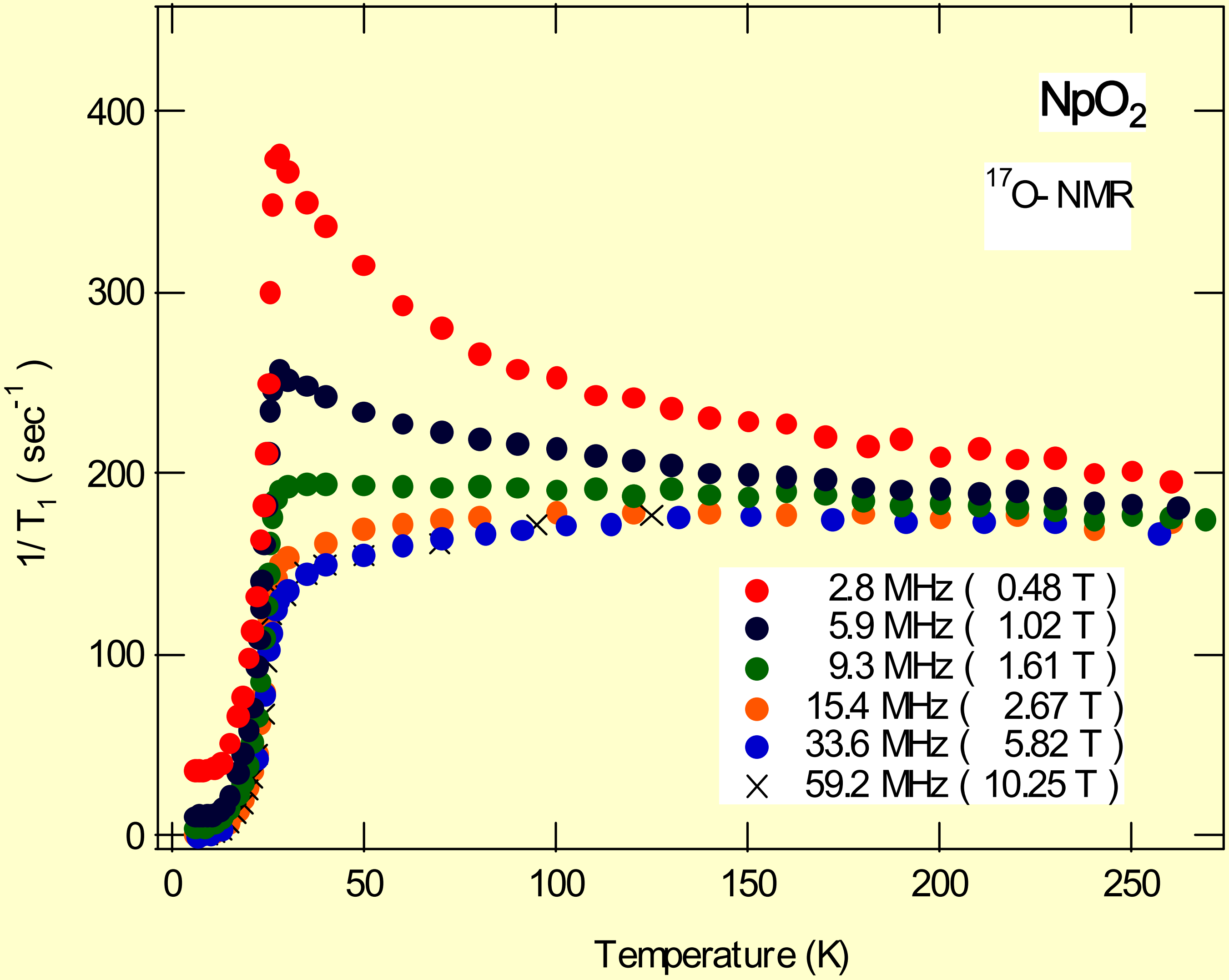
Mean-field model of Γ_5 octupolar order

K. Kubo and T. Hotta, PRB 71, 140404(R) (2005).

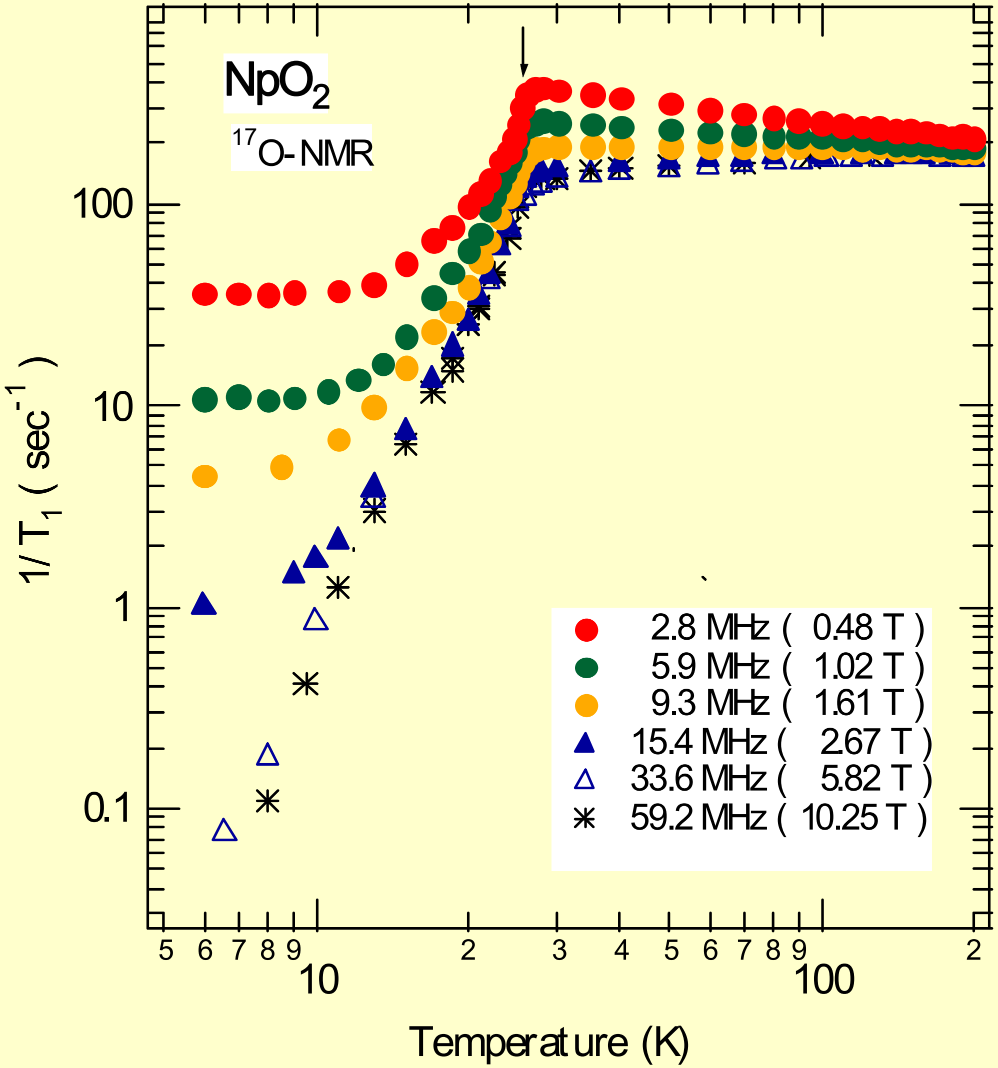


Ref: Kubo and Hotta (JAERI)

Spin-Lattice Relaxation: ^{17}O



^{17}O Spin-Lattice Relaxation – Low T

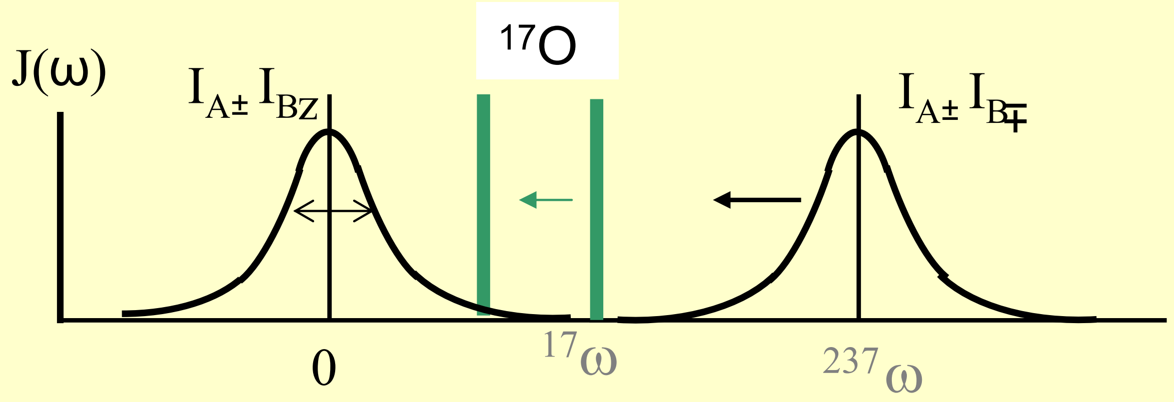


^{237}Np – ^{17}O Cross Relaxation $^{17}T_1$ Process

^{237}Np Nuclear Spin

Fluctuation Spectra:

I_A : ^{17}O I_B : ^{237}Np



$J^{(q)}(\omega)$: spectral densities

ANALYSIS: $1/T_{1A} = \langle \Delta\omega^2 \rangle_{AB} T_{1B} / (1 + \omega_A^2 T_{1B}^2)$,

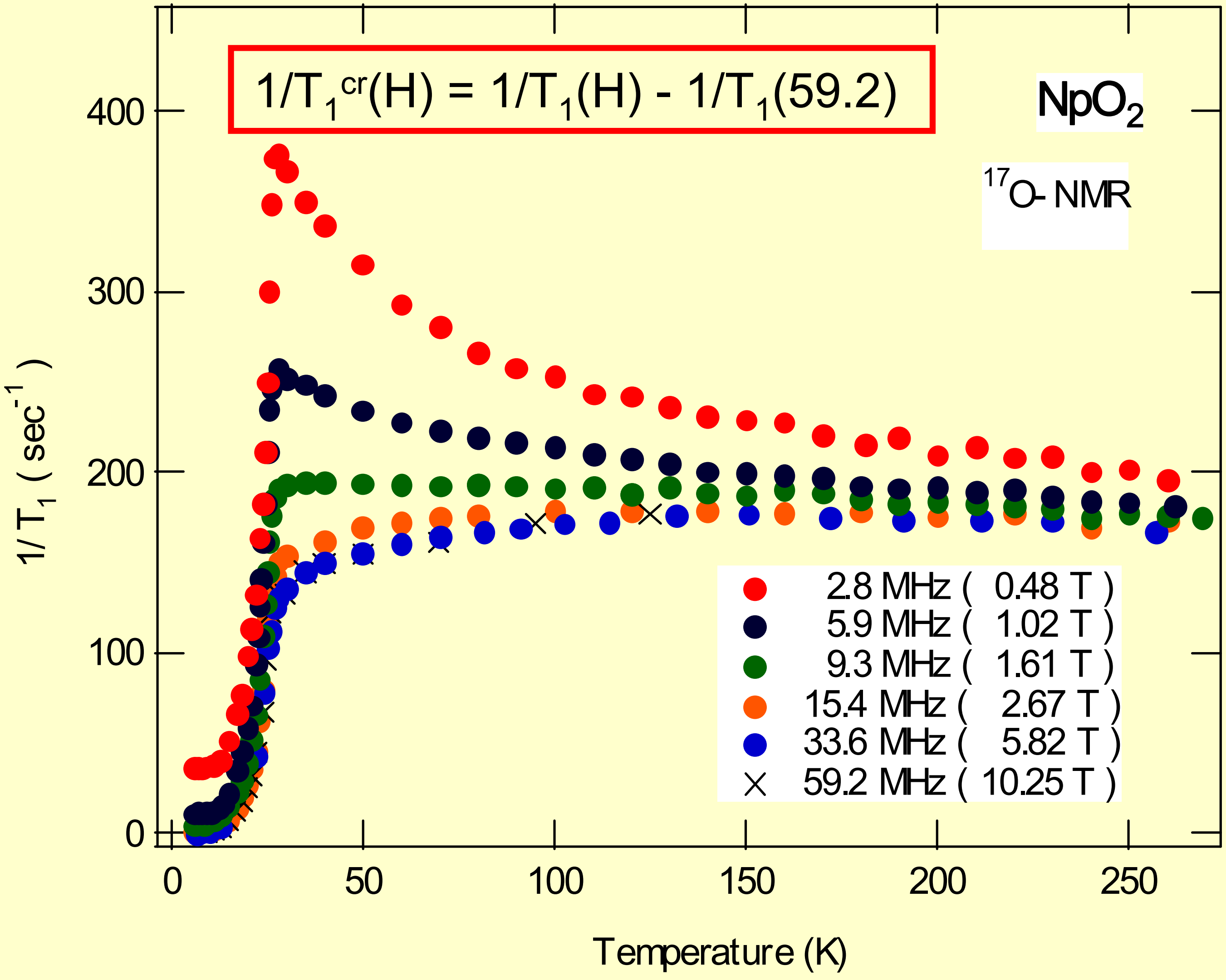
OR: $T_{1A} = \omega_A^2 T_{1B} / \langle \Delta\omega^2 \rangle_{AB} + [\langle \Delta\omega^2 \rangle_{AB} T_{1B}]^{-1}$

Check:

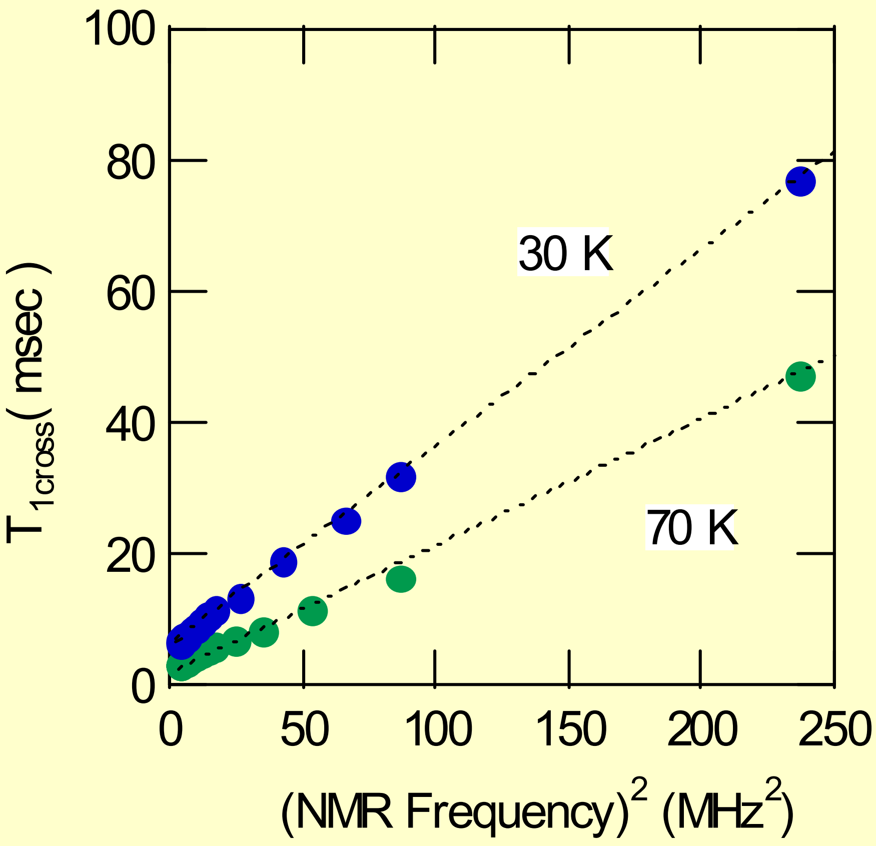
$\langle \Delta\omega^2 \rangle_{AB}^{dip} \sim 2.2 \times 10^7 \text{ s}^{-2} \rightarrow \langle \Delta\omega^2 \rangle_{AB}^{dip} T_{1B} \sim 0.88 \text{ s}^{-1}$.

$T_{1B} \sim 40 \times 10^{-9}$ s.

Spin-Lattice Relaxation: ^{17}O



^{17}O Cross – Relaxation Analysis



$$T_{1A} = \omega^2 T_{1B} / \langle \Delta\omega^2 \rangle_{AB} + [\langle \Delta\omega^2 \rangle_{AB} T_{1B}]^{-1}$$

$$S = T_{1\mathrm{Np}} / \langle \Delta\omega^2 \rangle_\beta$$

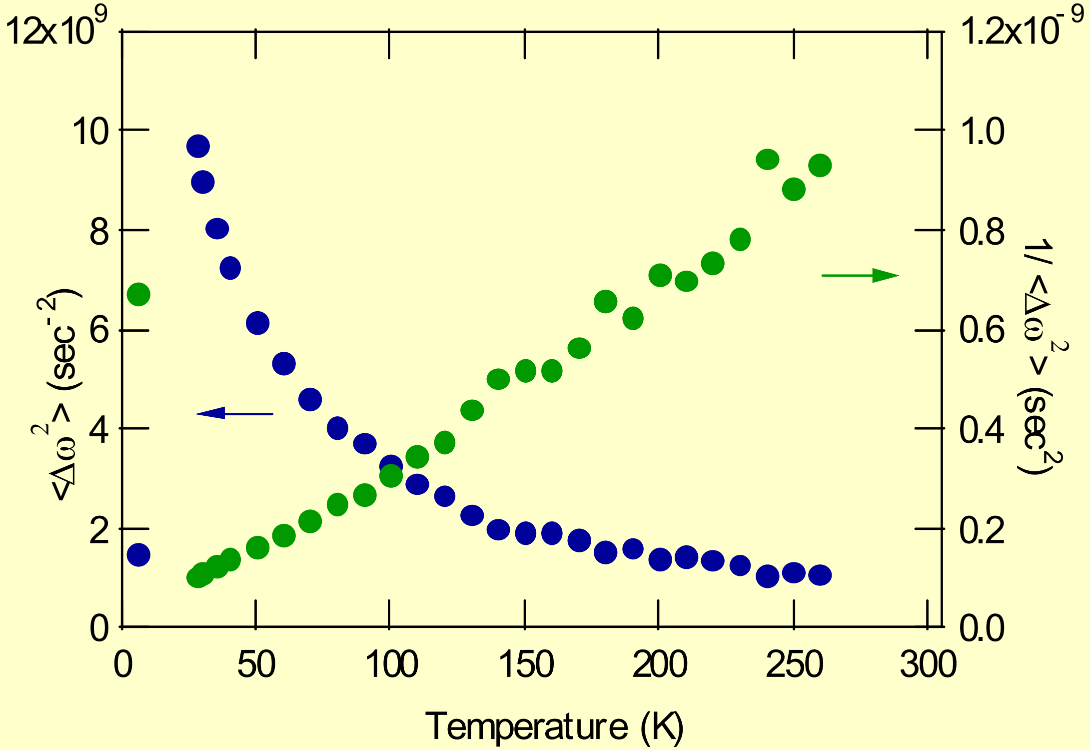
$$I = (T_{1\mathrm{Np}} \langle \Delta\omega^2 \rangle_\beta)^{-1}$$

$$1/T_{1\mathrm{Np}} = (I/S)^{1/2}$$

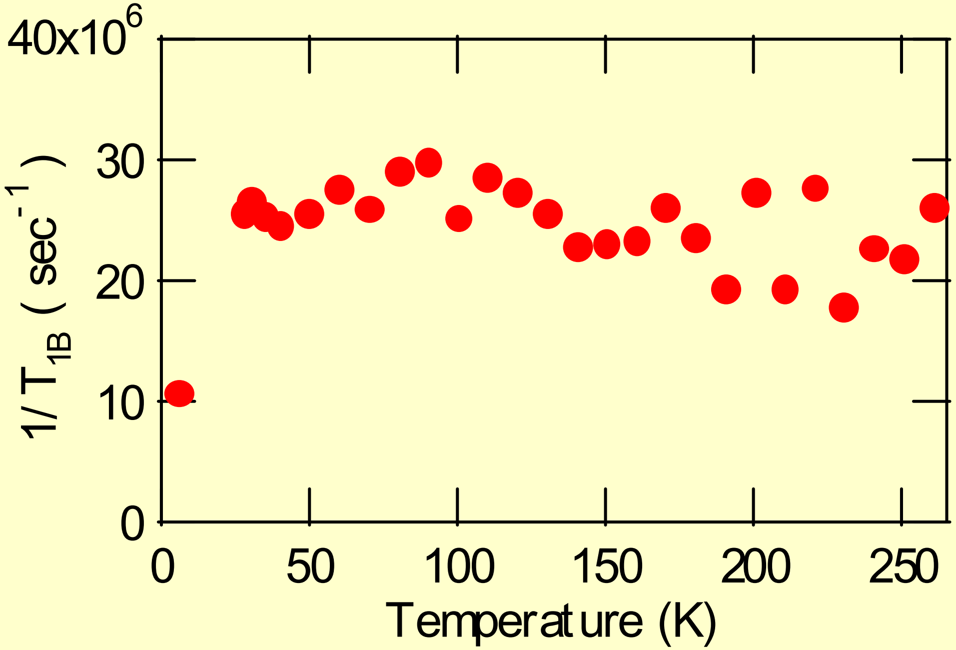
$$\langle \Delta\omega^2 \rangle_\beta = (SI)^{-1/2}$$

Unlike Spin

Second Moment:



^{237}Np T_1 = 40±8 ns



Enhancement of Dipolar Unlike Spin – Spin Coupling

- ^{237}Np Hyperfine Coupling: $A_{Np}\mathbf{I_B}\cdot\mathbf{S} \Rightarrow \quad K = A_{Np}\chi_m/(N_a\hbar\gamma g\mu_B)$

- Moment induced by $\hbar\gamma\mathbf{I_B}$: $\quad g\mu_B\Delta S = I_B A_{Np}\chi_m/(N_a g\mu_B)$

$$\Rightarrow \quad g\mu_B\Delta S = \gamma\hbar I_B K$$

- HF Coupling with ^{17}O: $\hat{H}_{hf} = \hat{H}_{dip}(1+\xi)$, $\quad \xi$ = Hybridization Coef.

- Enhanced ^{237}Np-^{17}O Dipolar Coupling:

$$[1 + K(1+ \xi)]\,\hat{H}_{dAB} \quad \Rightarrow \quad [\langle\Delta\omega^2\rangle_{AB}]^{1/2} \propto K(T) \propto \chi_m(T).$$

Unlike-Spin Second Moment Enhancement

Maximum enhancement of

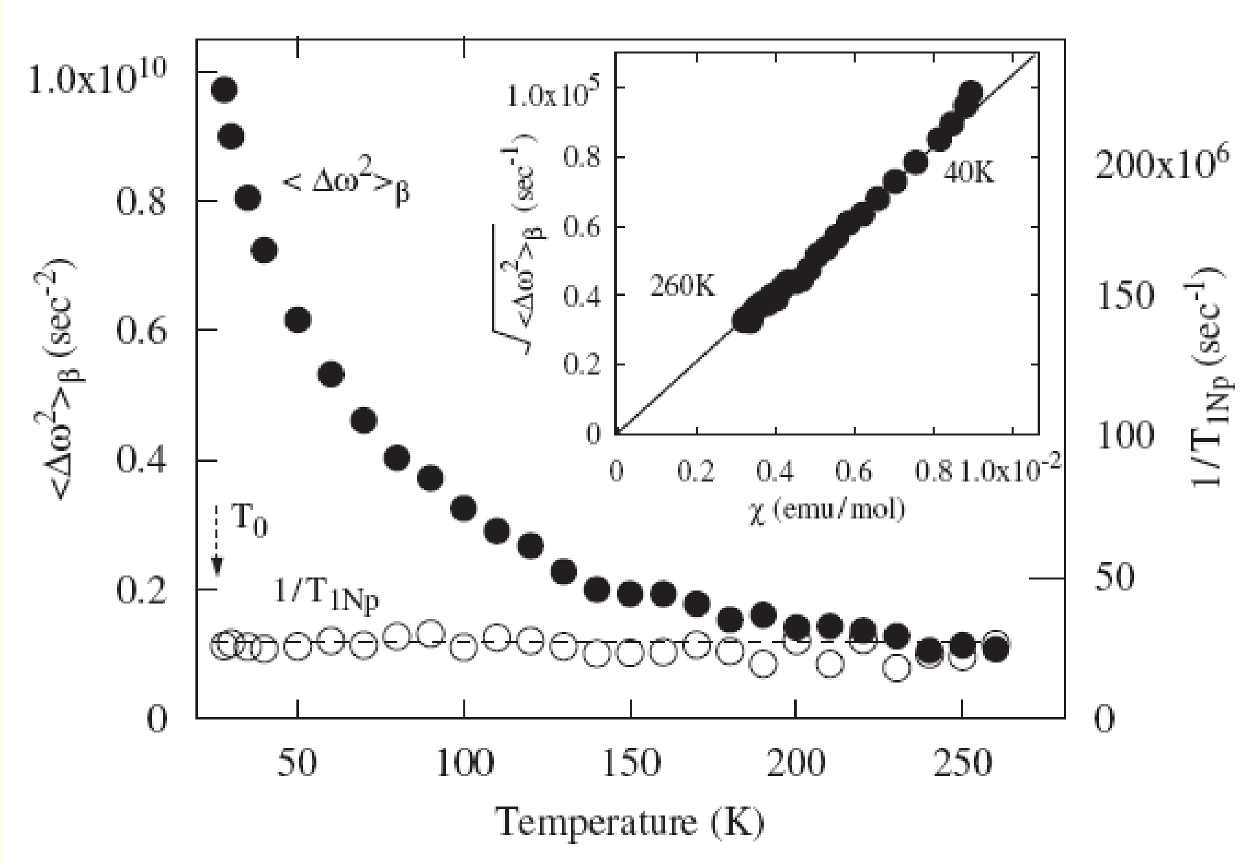
$[\langle\Delta\omega^2\rangle_{AB}]^{1/2} \sim [1+K(1+\xi)] \sim 21$

Mössbauer: $K_{max} \sim 4$

$\Rightarrow \quad \xi \sim 4$

Ratio of spin fluctuation

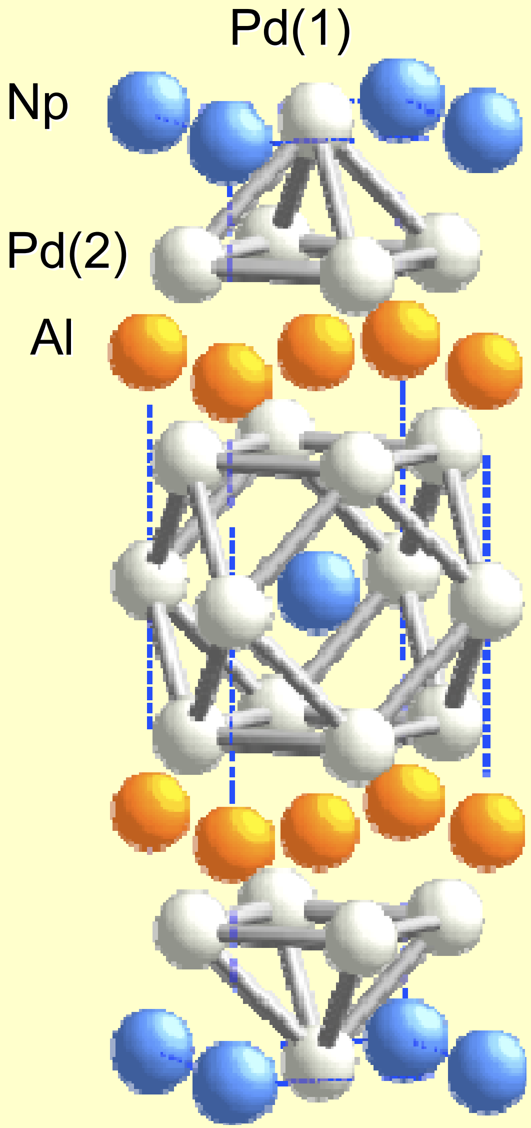
T_1's (Moriya): $\xi \sim 3$



$NpPd_5Al_2$

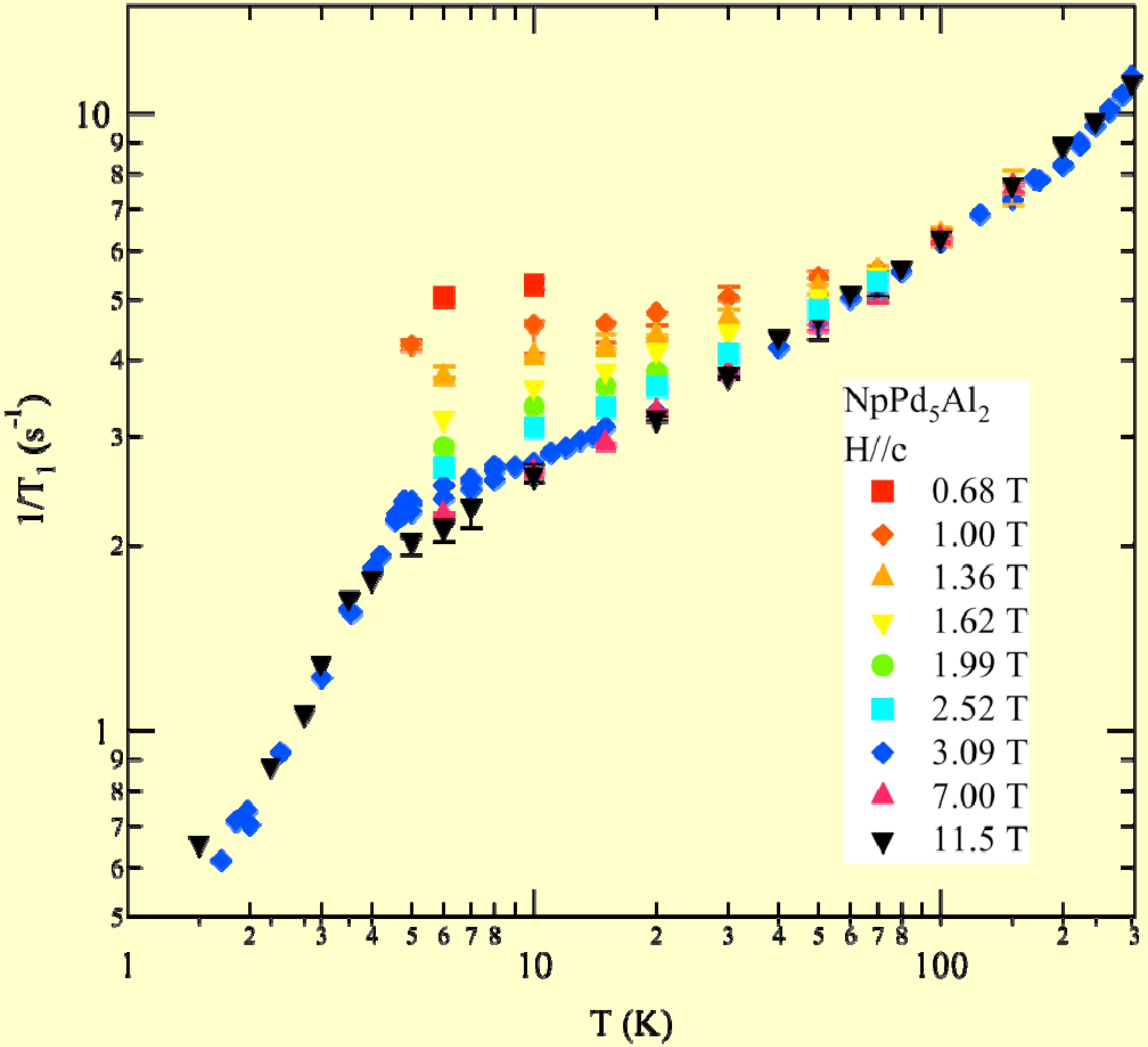
Heavy-Fermion Superconductor:

- γ = 200 mJ/mol K^2
- T_c ~ 4.9 K



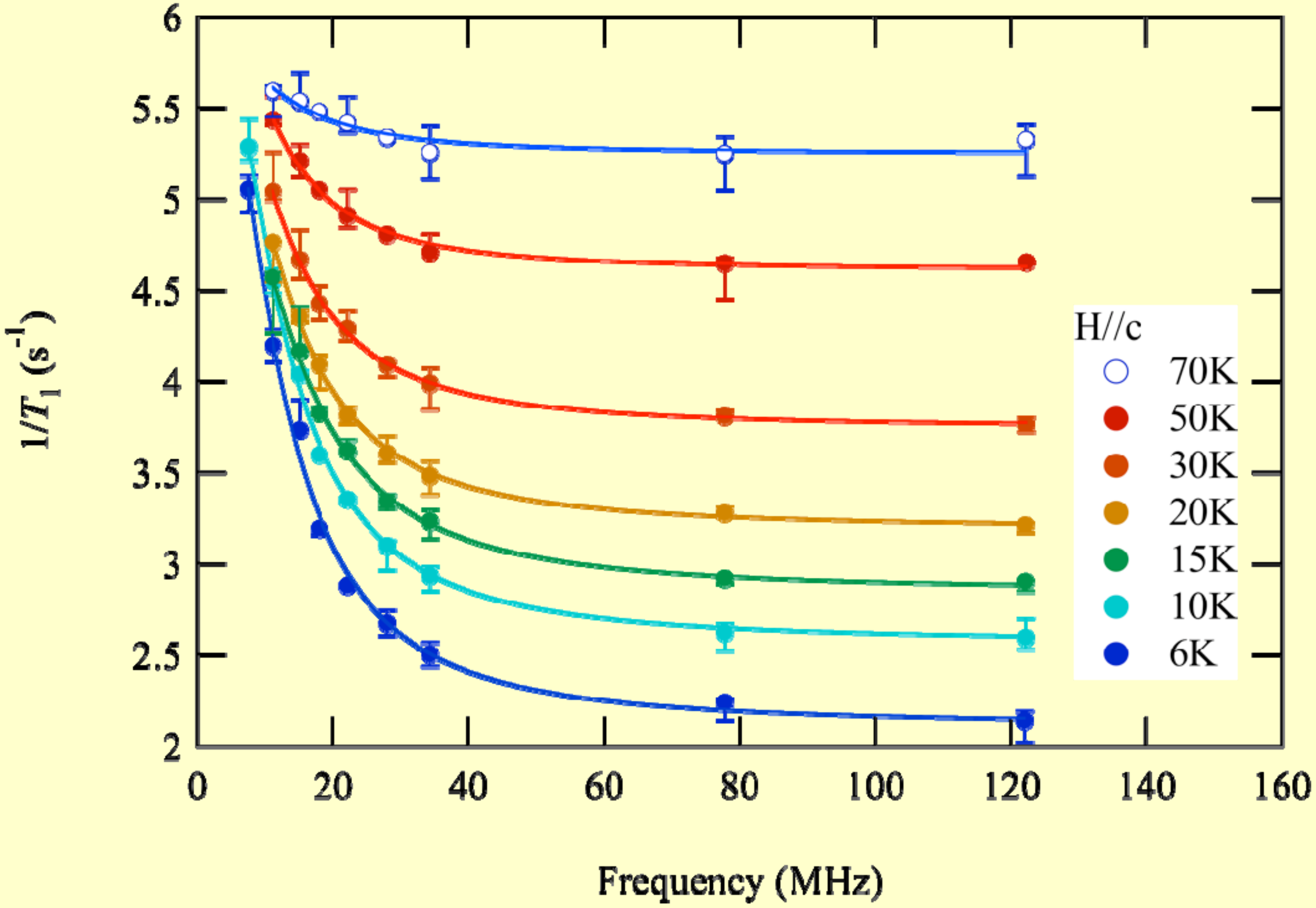
Field Dependence of ^{27}Al T_1 in $NpPd_5Al_2$

(ν_{res}~122MHz, H~11 T)

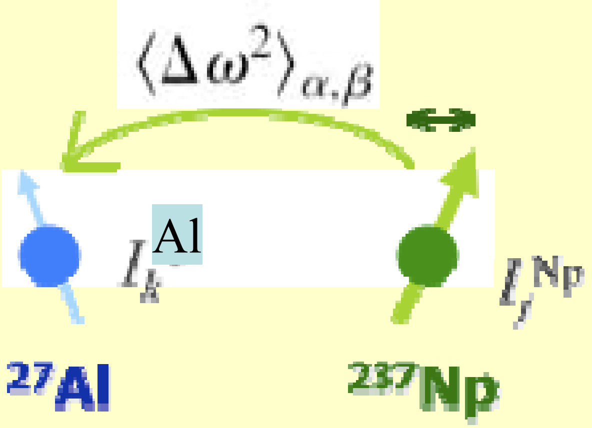


Frequency Dependence of ^{27}Al T_1 Decay Curves in $NpPd_5Al_2$

(H. Chudo and Y. Tokunaga)



Cross-relaxation from fluctuating ^{237}Np nuclear spins



$$\mathcal{H}^{aa}_{\rm NpAl} = \sum_{j,k(NN)} \beta_{jk} I^{\rm Np}_{zj} (I^{\rm Al}_{-k} + I^{\rm Al}_{+k}) + \sum_{j,k(NN)} \alpha_{jk} (I^{\rm Np}_{+j} I^{\rm Al}_{-k} + I^{\rm Np}_{-j} I^{\rm Al}_{+k})$$

N_A=100%
γ_N=11.094 MHz/T

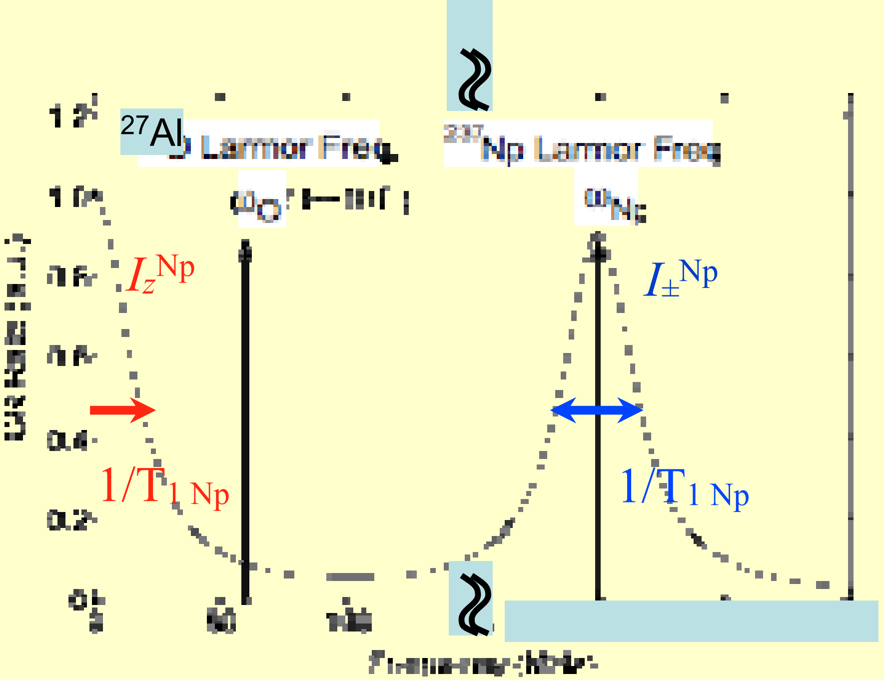
N_A=100%
γ_N=4.78 MHz/T

Cross-relaxation rate

$$\frac{1}{T^{CR}_{1\rm Al}} = \frac{\langle \Delta\omega^2 \rangle_\beta T_{1\rm Np}}{1 + \omega^2_{\rm Al} T^2_{1\rm Np}} + \frac{\langle \Delta\omega^2 \rangle_\alpha T_{1\rm Np}}{1 + (\omega_{\rm Al} - \omega_{\rm Np})^2 T^2_{1\rm Np}}$$

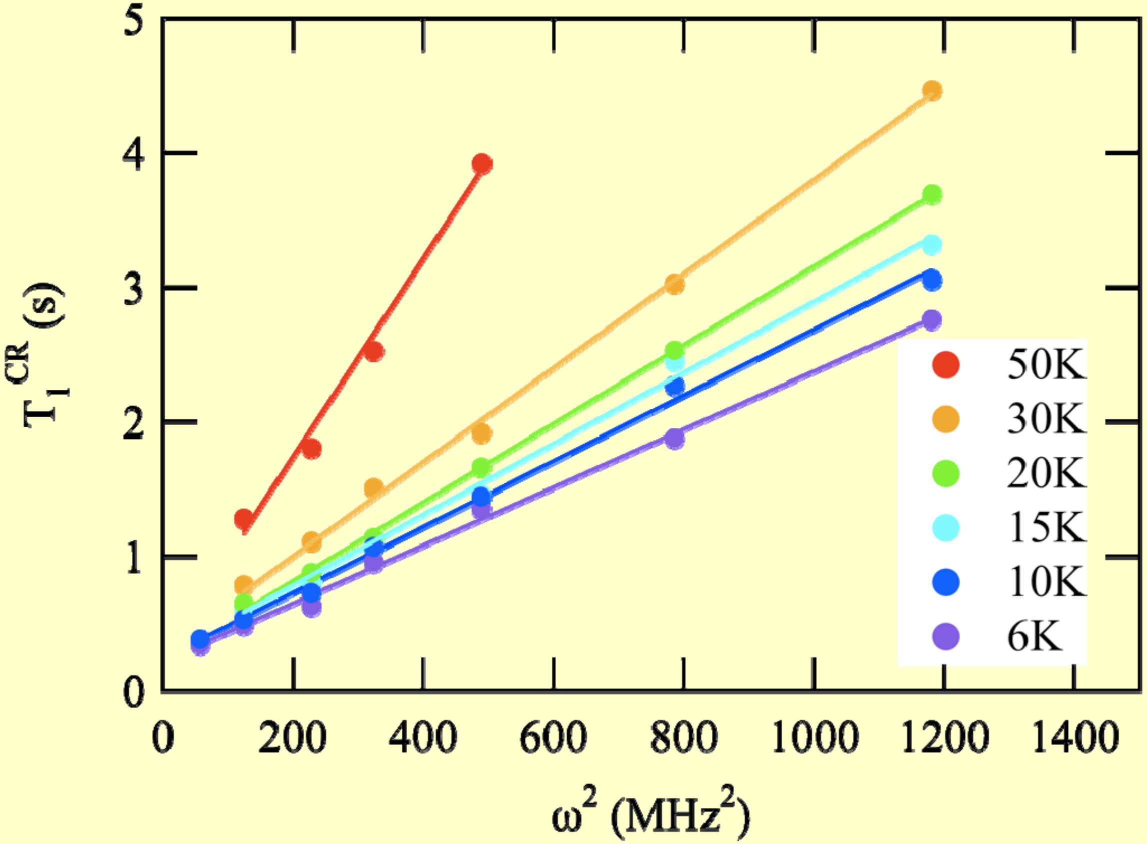
$I_z^{\rm Np}$

$I_\pm^{\rm Np}$



Cross – Relaxation Analysis

$$\frac{1}{T_{1\mathrm{Al}}^{CR}} \sim \frac{\langle \Delta\omega^2 \rangle_\beta T_{1\mathrm{Np}}}{1+\omega_{\mathrm{Al}}^2 T_{1\mathrm{Np}}^2} \Rightarrow T_{1\mathrm{Al}}^{CR} \sim S \times \omega_{Al}^2 + I$$



$$S = T_{1\mathrm{Np}} / \langle \Delta\omega^2 \rangle_\beta$$

$$I = (T_{1\mathrm{Np}} \langle \Delta\omega^2 \rangle_\beta)^{-1}$$

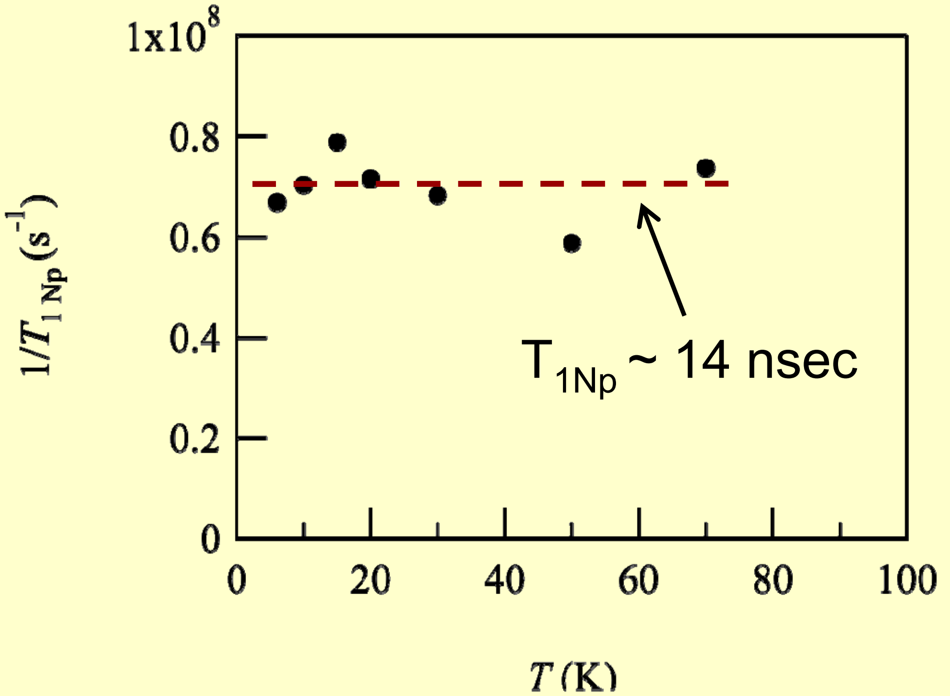
$$1/T_{1\mathrm{Np}} = (I/S)^{1/2}$$

^{237}Np spin-lattice relaxation rate

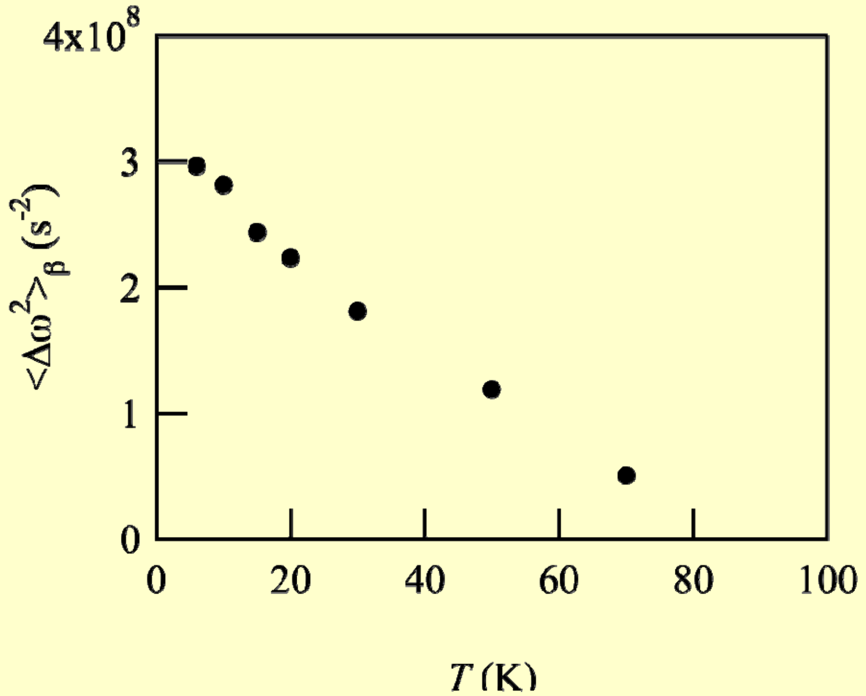
$$\langle \Delta\omega^2 \rangle_\beta = (SI)^{-1/2}$$

unlike-spin second moment

Results of Cross-Relaxation Analysis



T_{1Np} ~ 14 nsec



- First measurement of T_1 for the magnetic ion nucleus of a heavy fermion system.
- Result: T_{1Np} ~ constant (Moriya process?)
- 5f electrons: localized?
- Which electrons are heavy fermions?