Magnetic Order and Muon Diffusion in VO_2

Rick Mengyan, Ph.D.

Research Associate
Texas Tech University, Physics
Lubbock, TX 79409-1051 USA

Collaboration:
R.L. Lichti, B.B. Baker, G. Jayarathna
Texas Tech

Support:
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Experimental Facility:
ISIS: EMU
TRIUMF:
- M15 - HiTime
- M20 - Helios

Basic Properties of VO_2

Transitions

- Reversible, Metal-Semiconducting at T_{MST} = 340 K
- Structural: Rutile ($T>T_{MST}$) → Monoclinic (M1, $T<T_{MST}$)

	Metallic	**Semiconducting**
Band Gap	~0 eV	~1 eV
Optical Property	Reflective (Near IR)	Translucent
Conductivity	$\sim 10^3 - 10^4\ (\Omega\text{cm})^{-1}$	$\sim 10^{-1} - 10^{-3}\ (\Omega\text{cm})^{-1}$

Triggered by:

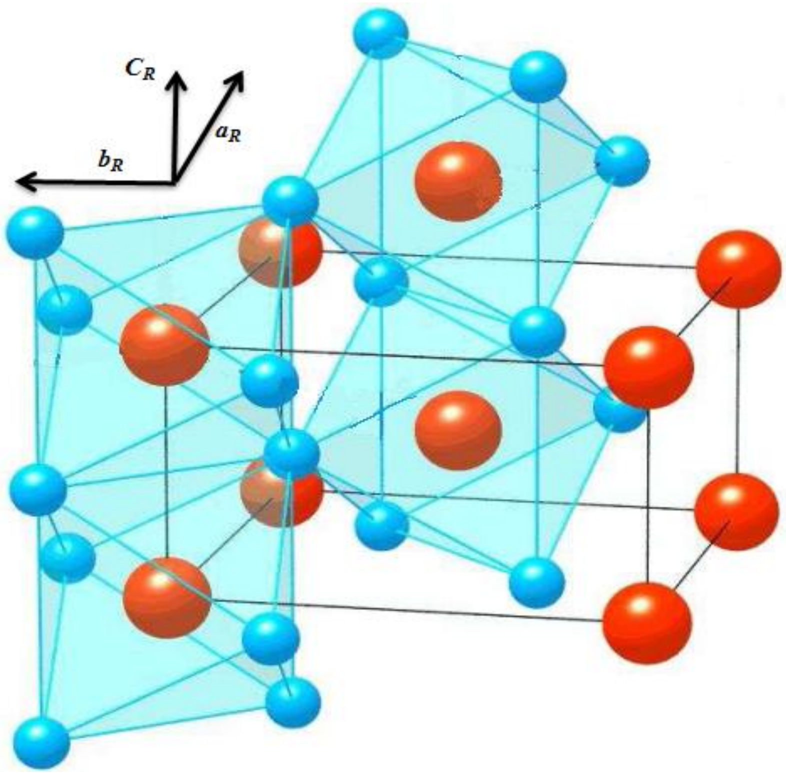
- Temperature, **E**-field, Optical Excitation, Pressure

Potential Applications

- Microwave wave guides, smart-windows, reconfigurable and switchable antennae, ultra-fast optical filters

F. J. Morin, *Phys. Rev. Lett.* **3** (1959) 34; A. Cavalleri *et al*, *J. Phys Soc Japan* **75** (2006) 011004
B. J. Kim, et al *Appl Phys Lett* **90** (2007) 023515; M. M. Qazilbash, et al *Appl Phys Lett* **92** (2008) 241906
M. Imada, et al *Rev Mod Phys* **70** (1998) 1039; J. B. Goodenough, *J. Solid State Chem.* **3** (1971) 490

Structure: Metallic ($T > T_{MST}$)



•Tetragonal body-centered unit cell

•V surrounded by octahedron of O atoms

•V^{4+} has single e^- near Fermi level, occupies lowest 3*d* level

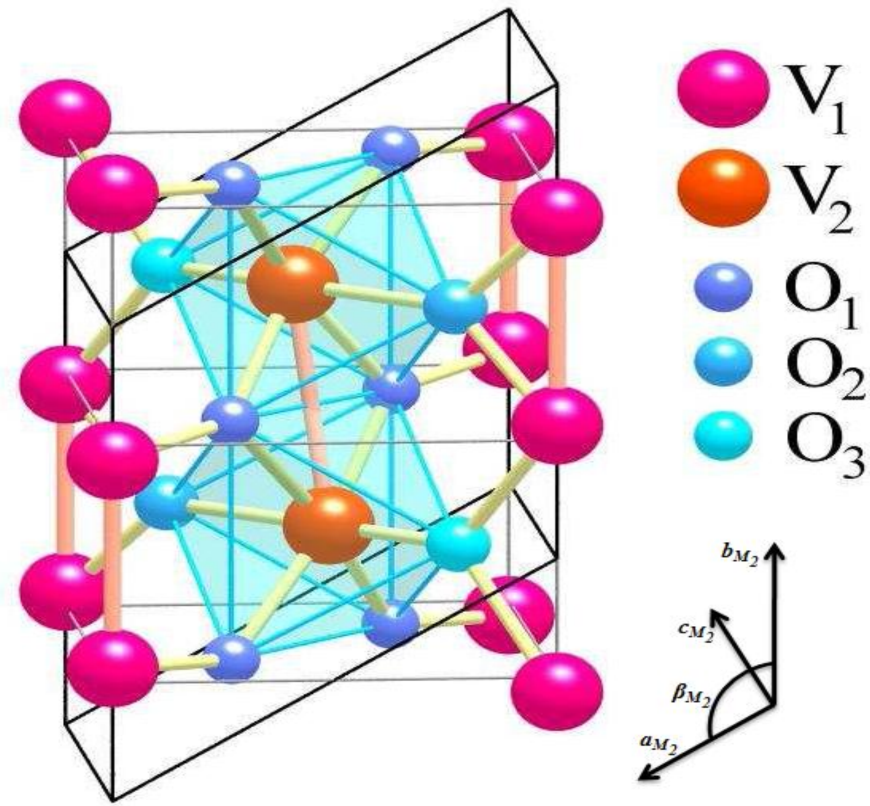
•Asymmetry in crystal field splits 3*d* states with lowest orbital aligned along c-axis ($\rightarrow$ higher conductivity)

Images from: M. Nazarri, PhD Dissertation, Texas Tech, 2013;

P.W. Mengyan, et al. MuSR (2014)

Structure: Semiconducting ($T < T_{MST}$)

- V−V dimerization → doubled unit cell
- V atoms pair along *c*-axis
- One V per pair:
  - Shift in *a*−*b* plane
  - Closer to partner along *c*
- Dimerization pairs e^- into singlet state, lead to
  - High resistivity
  - Non-zero bandgap



Semiconducting (Monoclinic)

Pink V1 paired with twisting
Orange V2 paired without twisting

Images from: M. Nazarri, PhD Dissertation, Texas Tech, 2013;

P.W. Mengyan, et al. MuSR (2014)

Background

H investigated as a dopant (~0 to 3.8% H)

- Nominal resistivity change; remains metallic down to 200 K (at 3.8% H)
- Effect has been observed but role H *actually* plays needs investigation [C. Wu, et al. *J. Am. Chem. Soc.* **133** (2011) 13798]

Dopants introduced, modify transition temperature

- W, Ti, Au: Lower transition temperature
- Cr, Al: Raise transition temperature
- **Minimal effects** on properties other than T_{MST}
- *Actual* role dopants play needs additional thorough investigation [ie: P. Kiri, et al. *Adv Mat Lett* **1** (2010) 86; Burkhardt, et al. *Thin Solid Films* **345** (1999) 229; A. Kaye, *private communication*, Texas Tech University (May 2013); C. Tang, et al. *Phys Rev B* **31** (1985) 1000]

Applications require exposure to H

- Long-term effects of H has not been studied
- Intentional H incorporation into VO_2 has major effect on transition → Important to understand:
  - *How H may propagate into & Behavior in bulk VO_2*

Project Focus: VO_2 Compounds

- General study of Mu in VO_2
  ie: Unique contribution to H defect studies (early time)
  - Stability, Charge & Site dynamics, Energy Barriers, Diffusion Parameters, etc
- Local environment of VO_2 [vs VO_2:*X*]
  - Role dopants play in modifying various phases and transition
  - Sensitive magnetic probe:
    Dimer $S_{net} = 0$
    Magnetic moments introduced by disruption of V-V dimerization
- Local probe of yet to be understood transition
  - Mechanism (Mott-Hubbard vs Peierls)
  - Role Dopants play (c.f. Modification of environment, etc)

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Experiment Details

ZF-MuSR

EMU (ISIS), HiTime and Helios (TRIUMF)

- Mu diffusion 8 K to 560 K
- Dynamics (field fluctuations or mu motion)
- Local magnetic environment

wTF-MuSR

EMU, B_{TF} = 100G

- ZF α calibration
- Basic character info

HTF-MuSR

- HiTime, B_{ext} up to 6.5 T
- Identify & characterize sites
- Investigate Mu^0/Mu^0-like states & formation
- Characterize magnetism

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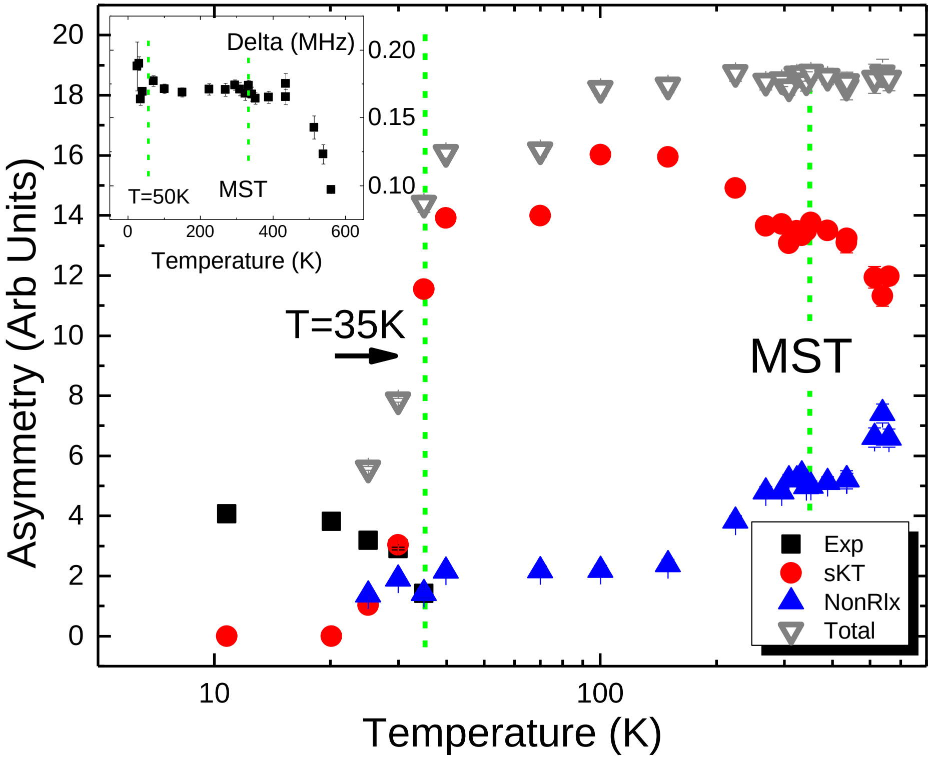
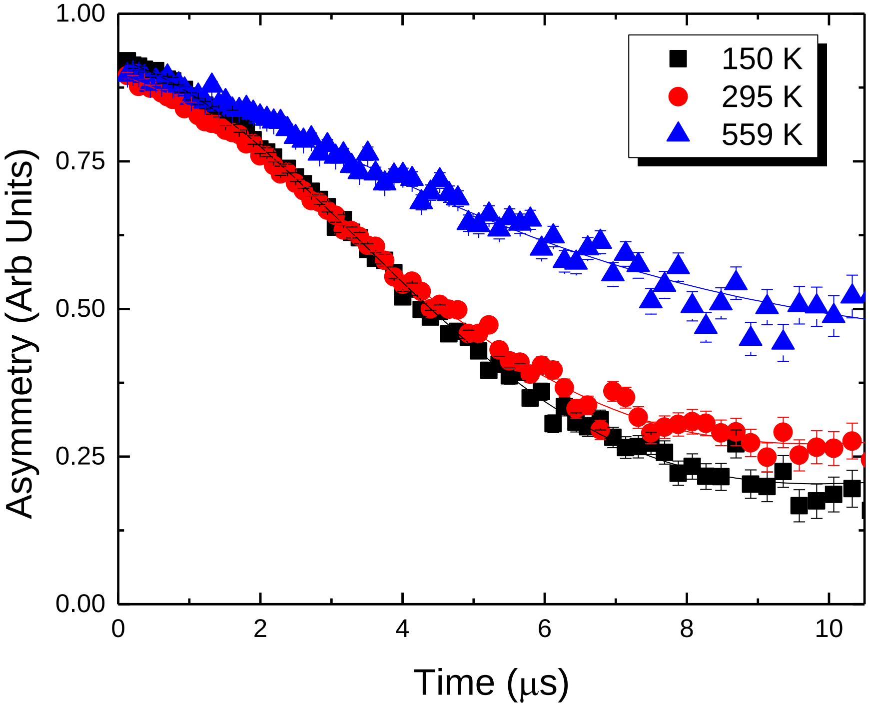
Results and Discussion





1) Static between 100 K and ~300 K
$\Delta = 0.171 \pm 0.004$ MHz

2) Detect change in mu site around MST
$\Delta(T > T_{MST}) = 0.165 \pm 0.005$ MHz

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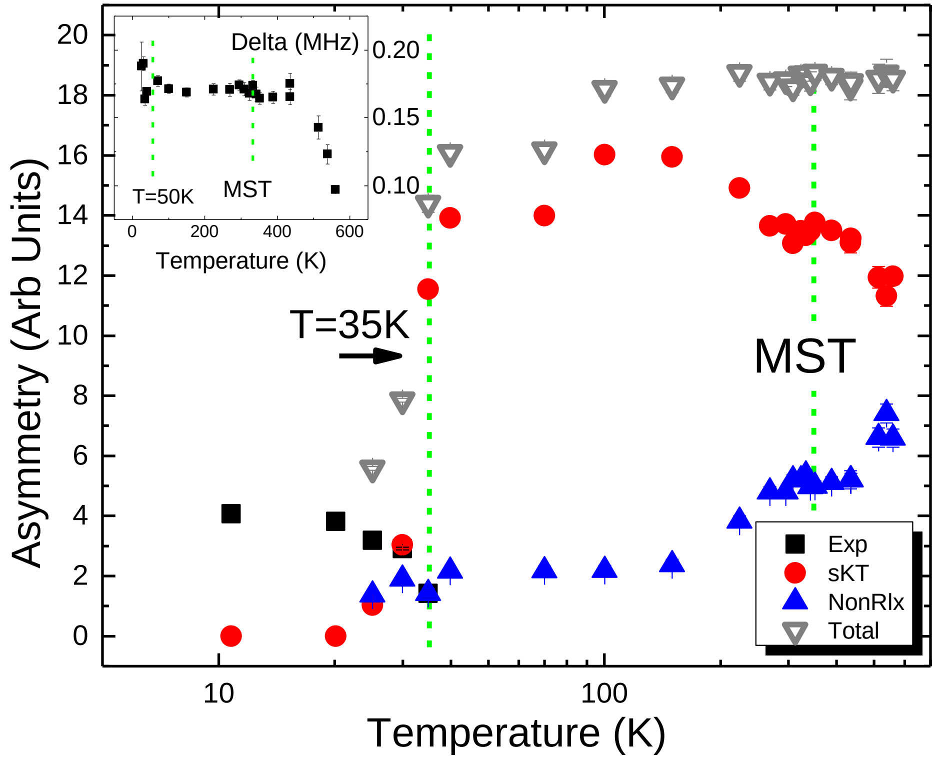
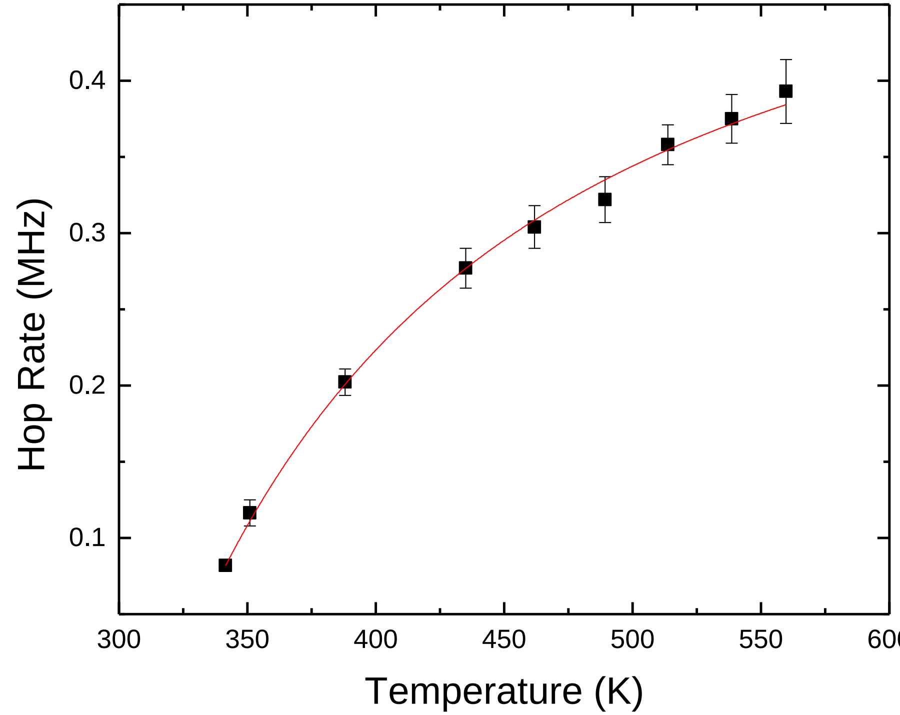
Results and Discussion





3) Dynamic at higher T, fit down to ~340 K

4) T < 35 K, trade off in Asy; $B_{loc,max} = 0.62 \pm 0.08$ kG

5) Small fraction fits to same B_{loc} between 35 K & 100 K suggesting small fraction of high local order starting ~100 K

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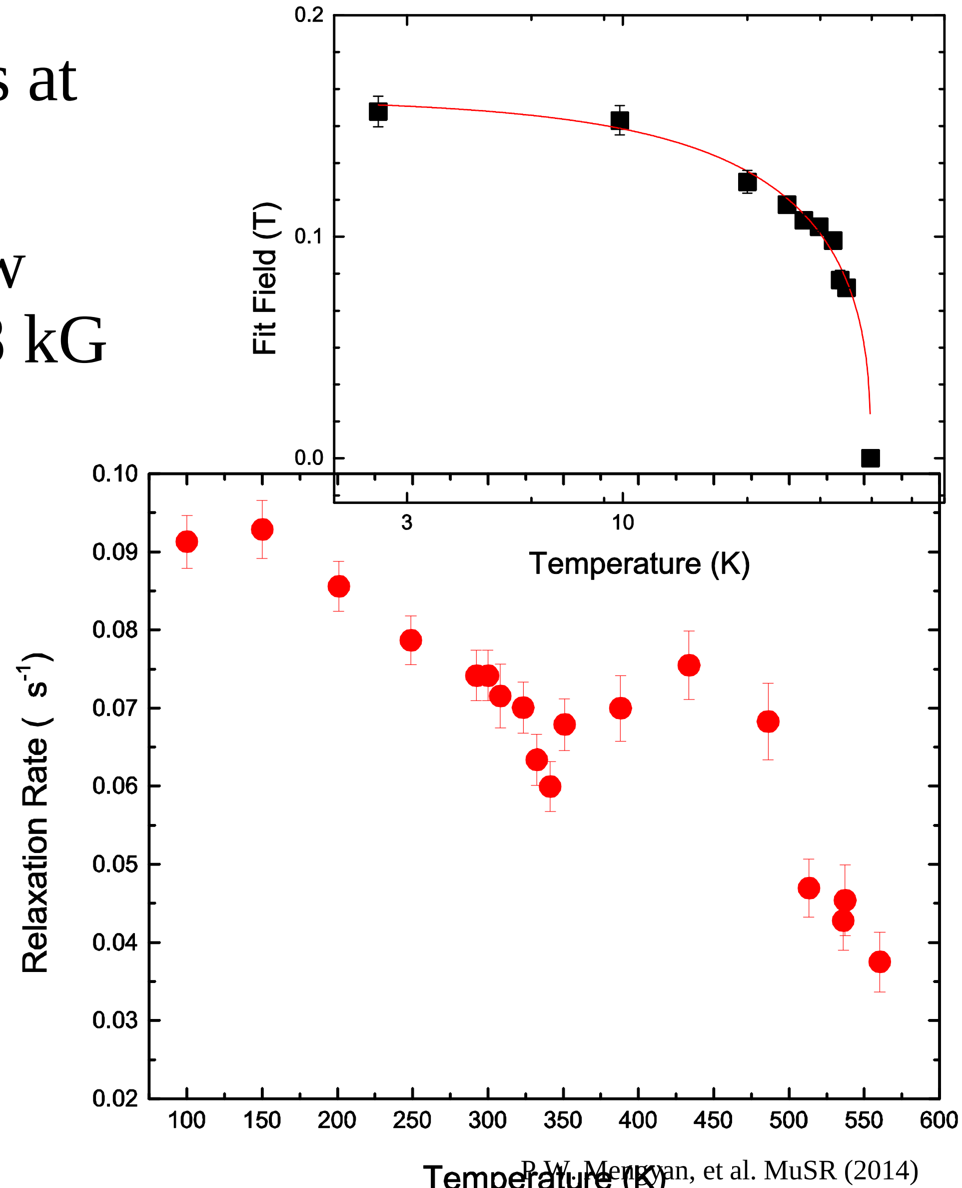
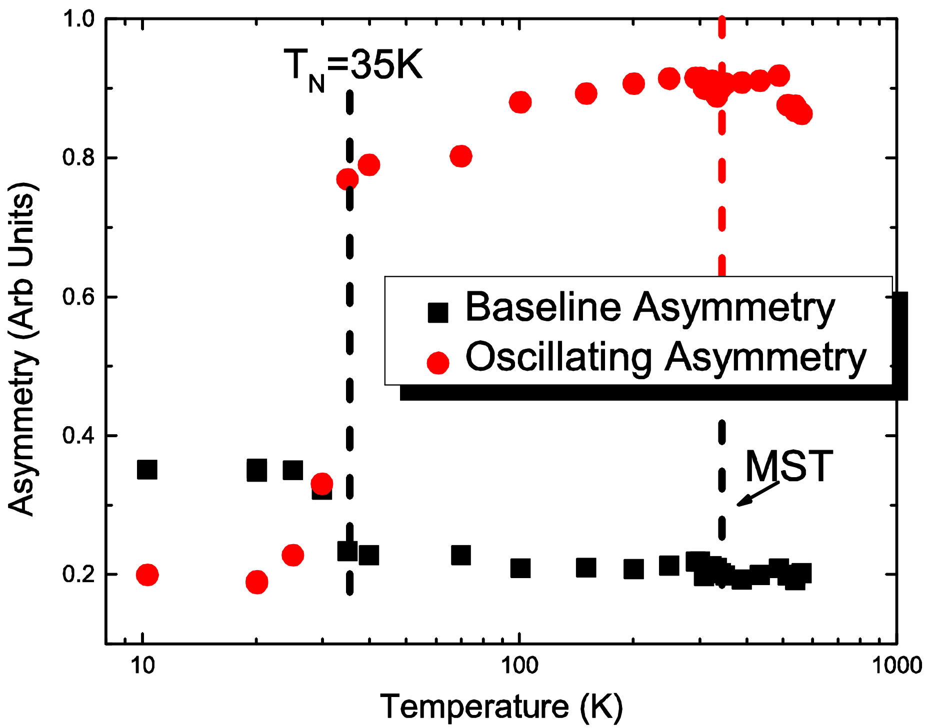
Results and Discussion

6) TF show relaxation features at 340 and near 450 K

7) Fit field – critical power law
Bloc= $B_{loc,max}$ = 0.62 ± 0.08 kG





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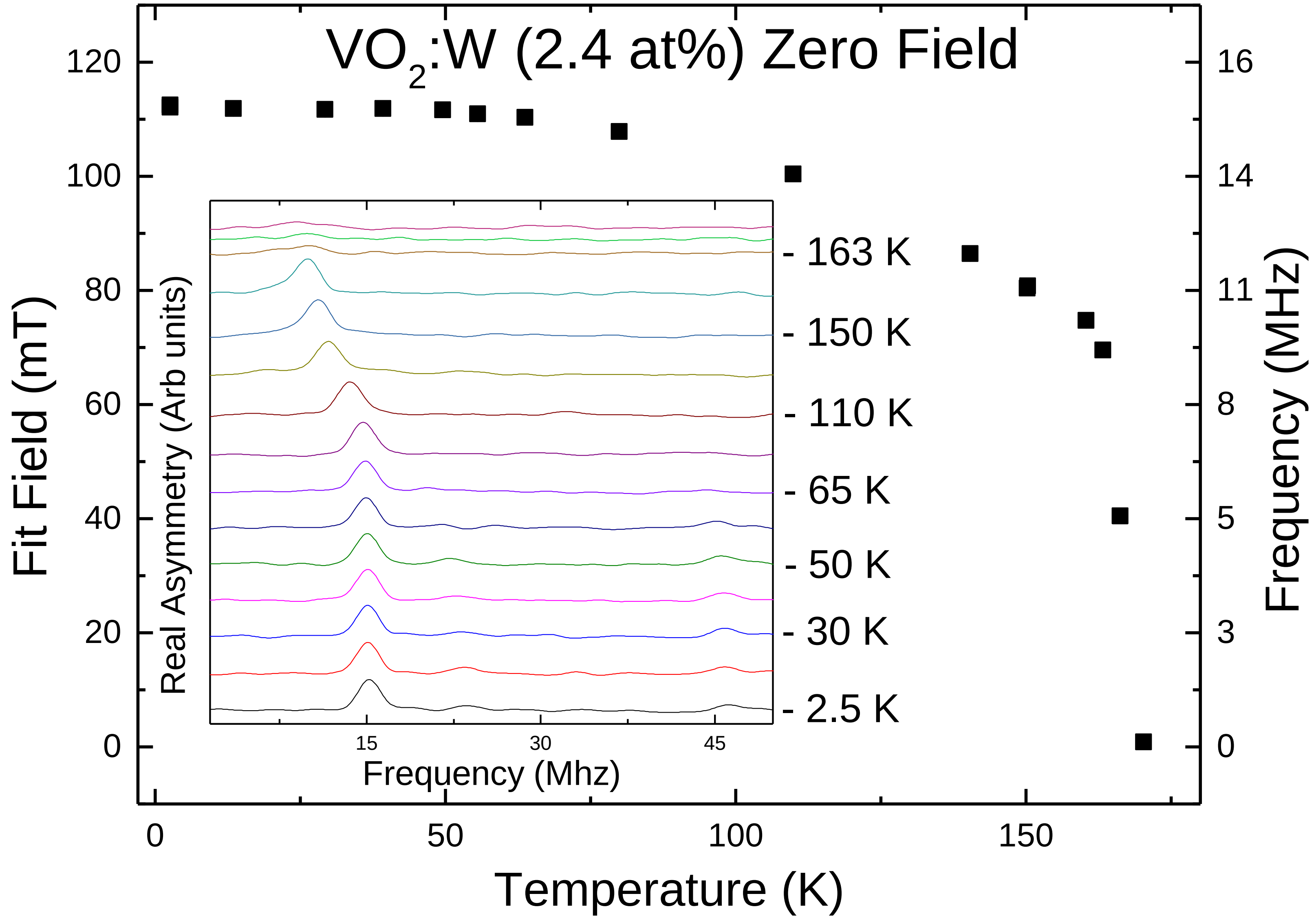
ZF-MuSR: VO2:W (97.6:2.4 at%)



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Summary

- Mu is sensitive to a feature near the MST and low temperature magnetism
- T < 35 K Magnetic phase B_{loc}=0.62 +/- 0.08 kG in VO_2
- 35 K to ~100 K localized magnetic features
- Static between 100 K − 300 K
- Significant dynamics above 450K;
  possibly starting near 340K -- just above MST
- 5 at% Ti & 2.4 at % W show T_c ~ 175 K with
  B_{loc} ~ 1.1 kG

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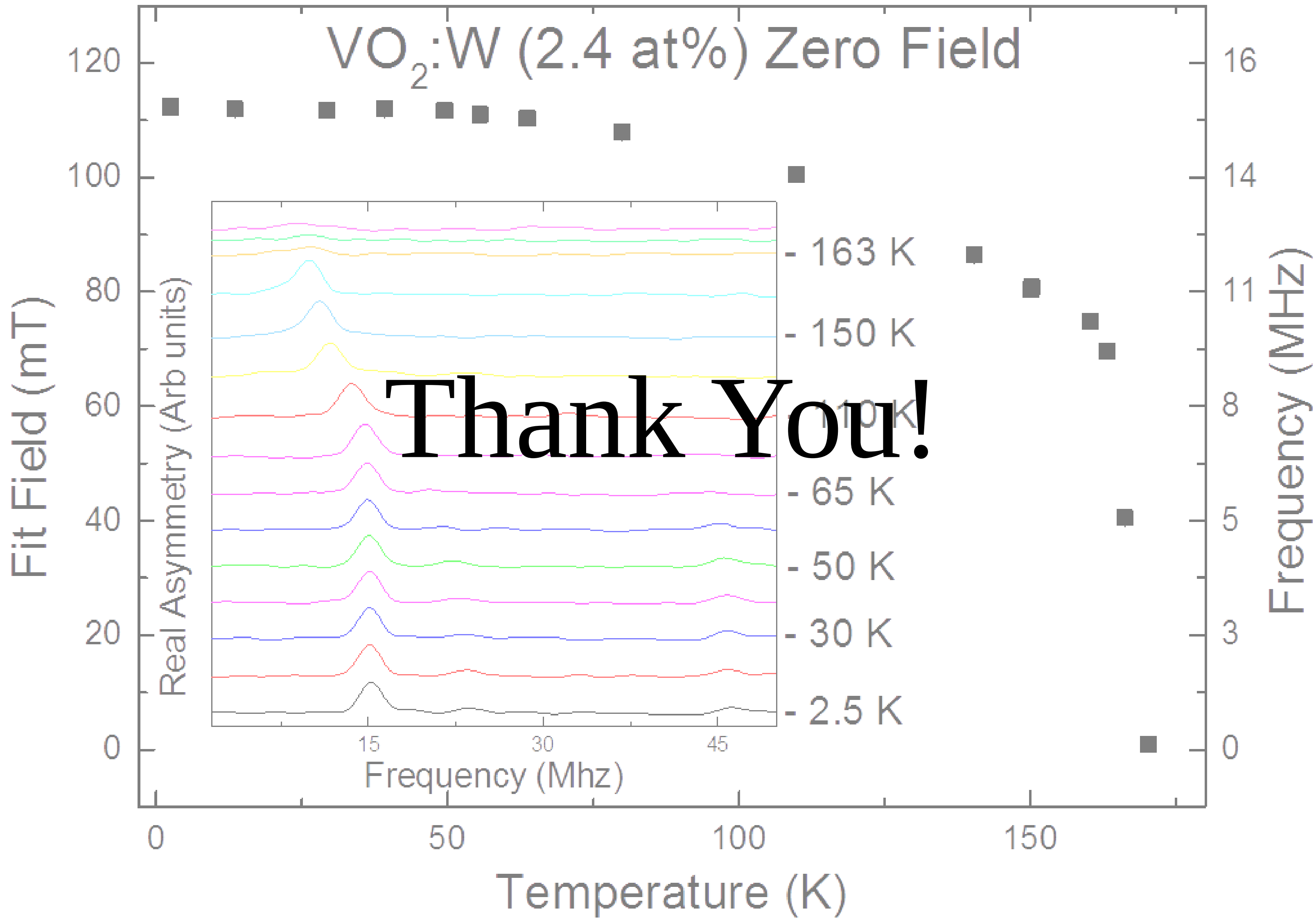
Thank You!



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Thank you

Transition Mechanism Question

- Basic properties of stoichiometric VO_2 well into each phase are well understood
- Driving mechanism of transition highly debated
  - *(1) instability in Fermi surface caused by periodic lattice deformations (V-V pairing) which causes an energy gap to open (Peiels Mechanism)*

    OR
  - *(2) is it related to strong e^- -- e^- correlations that introduce an energy gap from the mutual repulsion (Mott-Hubbard mechanism)*
- Understanding of this transition is required for better control and optimization of the properties for any application

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Goals with MuSR

Use μ^+ as experimentally accessible analog to hydrogen

- Probe Mu^0/H like states
- Mu/H diffusion

Mu as sensitive local probe to investigate local magnetic environment

- Through transition
- Well into each phase

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Experimentally Accessible Analog to Hydrogen

	Muon	**Proton**
Mass (m_p)	0.1126 ≈ 1/9	1
Spin	½	½
Gyro. Ratio, γ (s^{-1} T^{-1})	8.51607 x 10^8 ≈3.2 x γ_P	2.67520 x 10^8
Lifetime, τ (μs)	2.19709	Stable
	Muonium	**Hydrogen**
Red. e^- mass (m_e)	0.995187	0.999456
G. S. Radius (Å)	0.531736	0.529465
G. S. Energy (eV)	-13.5403	-13.5984

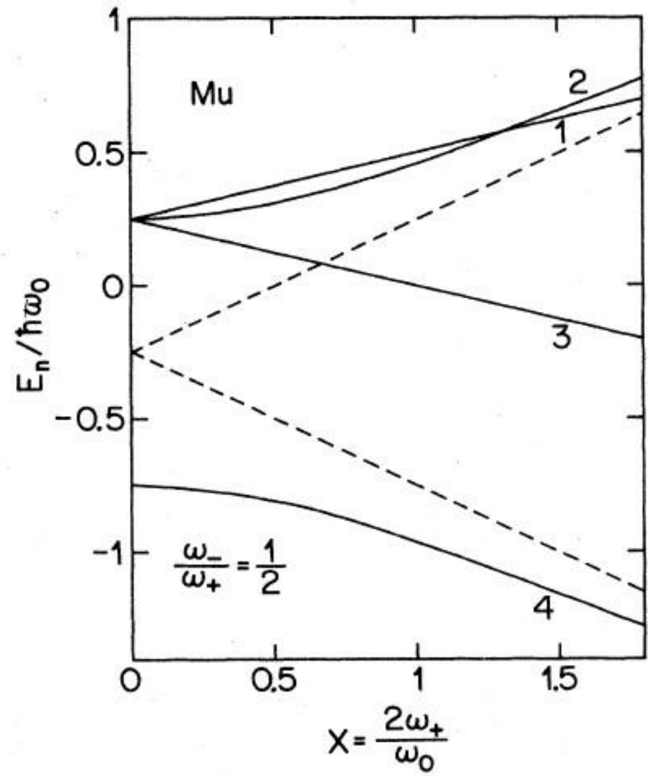
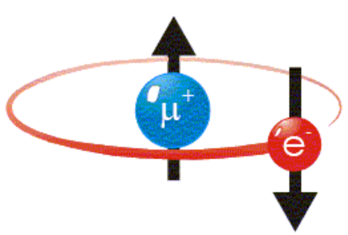


FIG. 1. The hyperfine energy-level (Breit-Rabi) diagram for isotropic 1*s*-Mu as a function of the dimensionless magnetic field $x = B(g_\mu \mu_\mu - g_e \mu_B)/(hA)$. A fictitious value for the quantity ω_-/ω_+ has been used for clarity; its true value is 0.9904. The dashed lines are the high-field asymptotes for levels 2 and 4.

B.D. Patterson, *Rev. Mod. Phys.*, **60**, (1988) 1

Muonium (Mu ≡ μ^+e^-)



Brewer, http://musr.ca →

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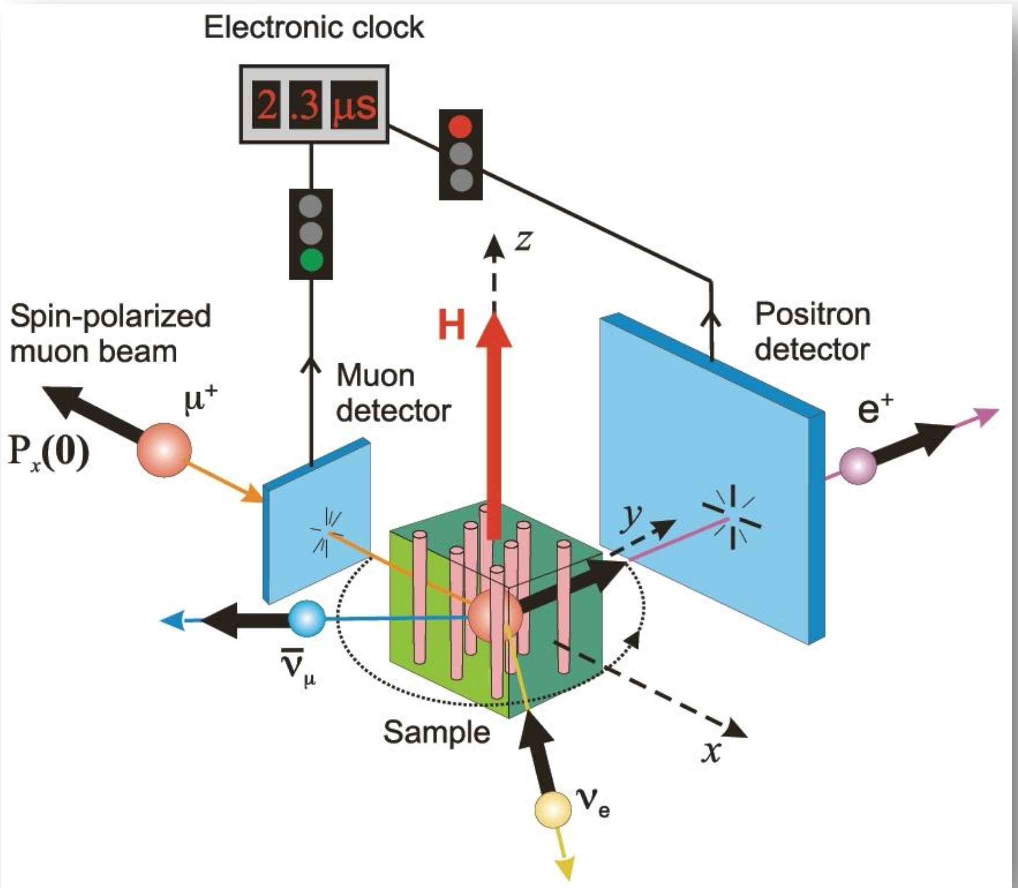
TF-μSR



Brewer, http://musr.ca

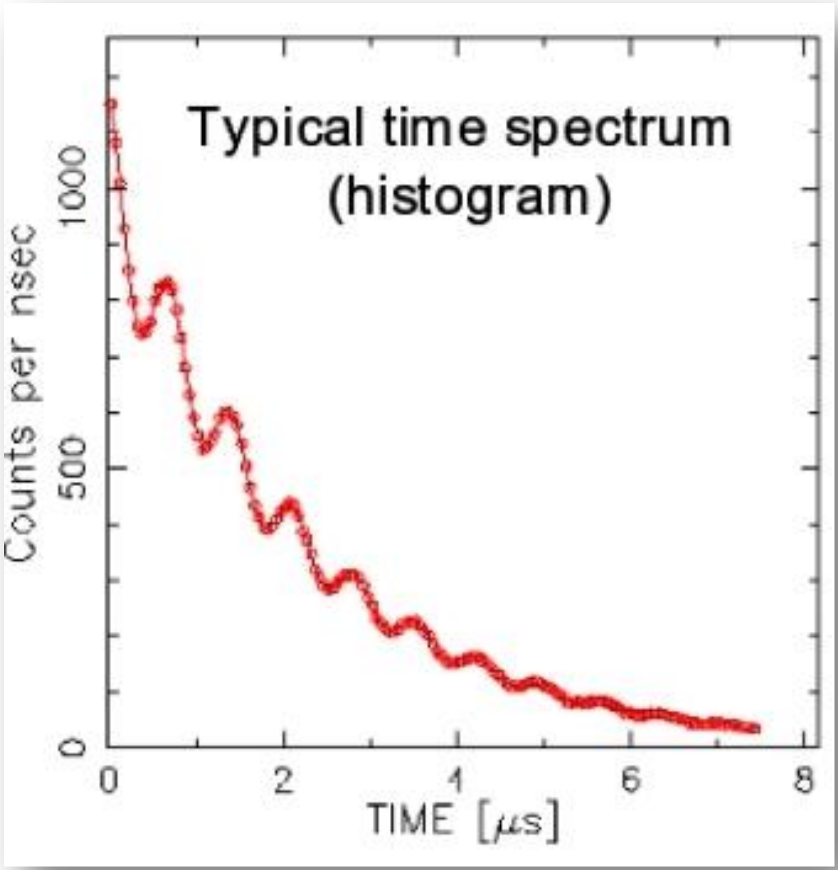
Field applied ⊥ to initial spin polarization
→ μ^+ spin precession about applied field at:

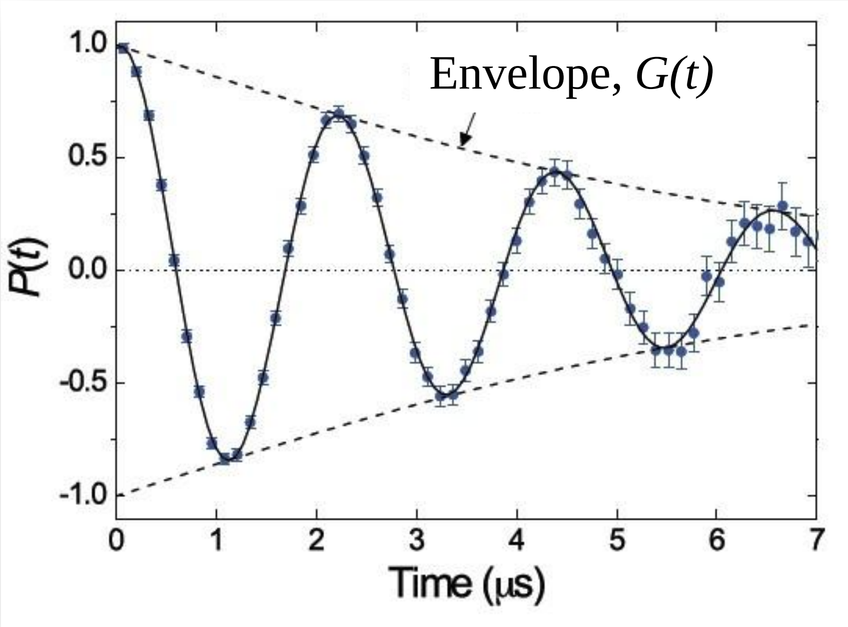
$\nu_{\mu+} = \gamma_\mu \times |\mathbf{B}|$ $|\gamma_\mu = 135.54\text{MHz/T}$

$Mu^0 = \mu^+ + e^-$
→ spin-orbit coupling
→ affects local field of μ^+
→ diff prec. Freq for:
$|\uparrow_\mu\rangle + |\uparrow_e\rangle$ & $|\uparrow_\mu\rangle + |\downarrow_e\rangle$

B.D. Patterson, *Rev. Mod. Phys.*, **60**, (1988) 1

TF-μSR: Sample signal from relaxing μ^+





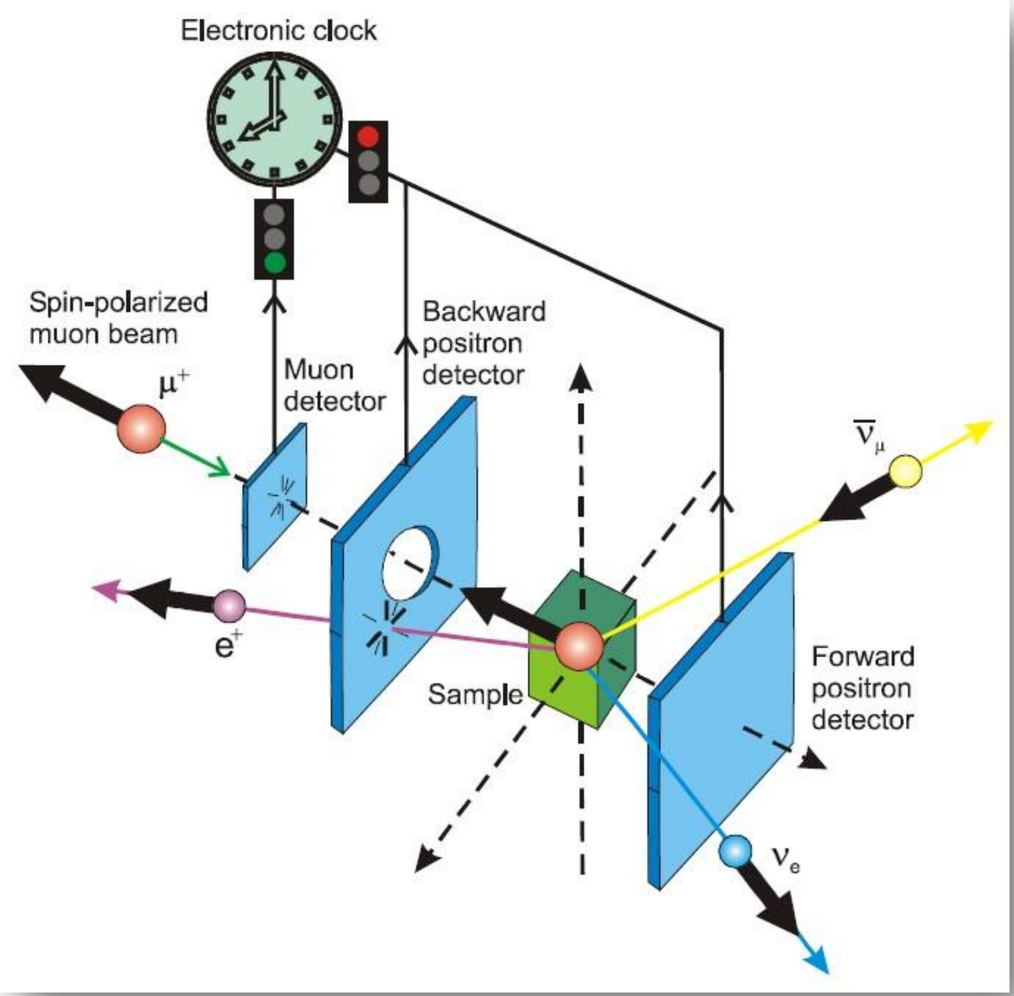
$$P(t) = G(t)\cos\left(\gamma_{\mu^+}\left|\mathbf{B}_{\mu^+}\right| + \delta\right)$$

Brewer, http://musr.ca
P.W. Mengyan, *et al.* MuSR (2014)

LF-μSR

B applied || to μ^+ spin pol.
See time evolution of P(t) along original direction

=> Change in Spin P(t) from:
1) local environment (nearby nuclear moments)
2) muonium motion
(e^- spin-flip w/ each site change, transferring back to μ^+ contributing to Δ P(t))

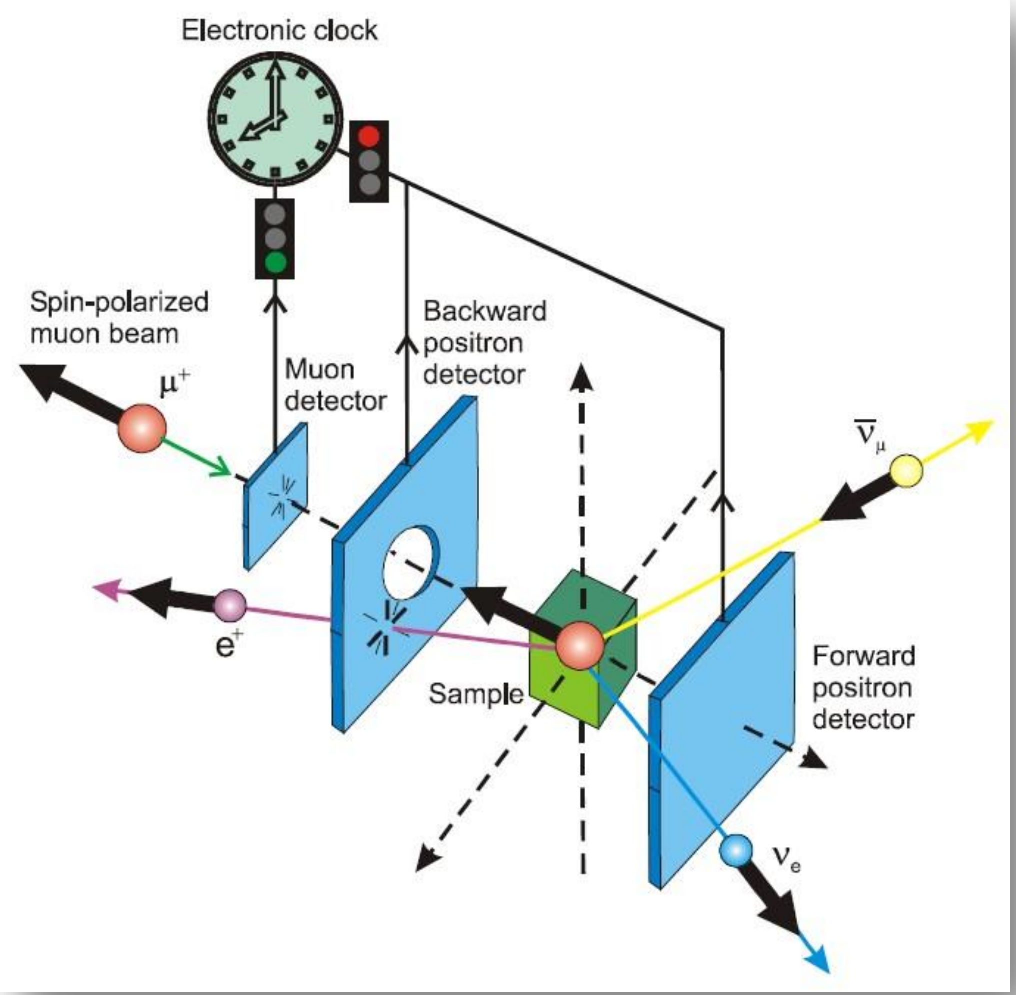


R.F. Kiefl, R. Kadono, et al., *Phys Rev Lett*, **62** (1989) 7

Brewer, http://musr.ca

P.W. Mengyan, et al. MuSR (2014)

ZF-μSR



Brewer, http://musr.ca

No net B applied
See time evolution of P(t) in natural environment

=> Change in Spin P(t) from:
1) local environment (nearby nuclear moments)
2) μ^+ motion

R.F. Kiefl, R. Kadono, et al., *Phys Rev Lett*, **62** (1989) 7
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