Aspects of
μ^+SR in Semiconductors

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With Acknowledgements to many many many others !

Lecture 11, TSI, Aug 12 2011

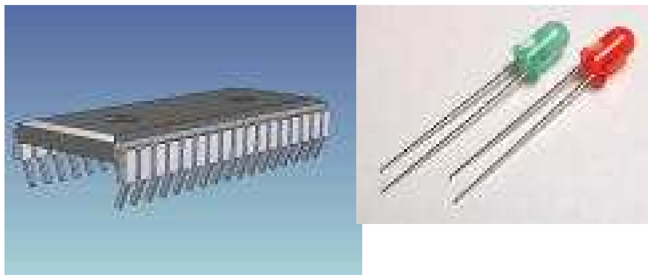
Outline

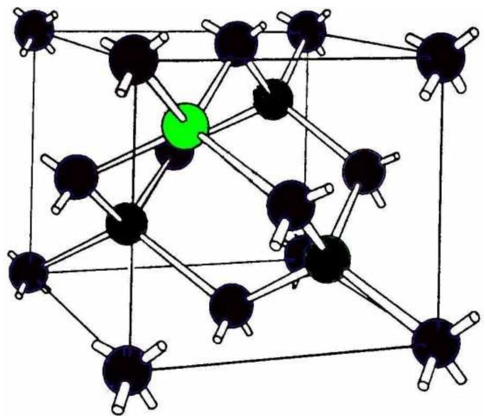
- Physics of Semiconductors
  - ➢Role of impurities in semiconductors
  - ➢ Hydrogen as an impurity
- Muon vs Proton
- Some Experimental Examples
- Summary

PART 1

Impurities in semiconductors

Modern Technology....





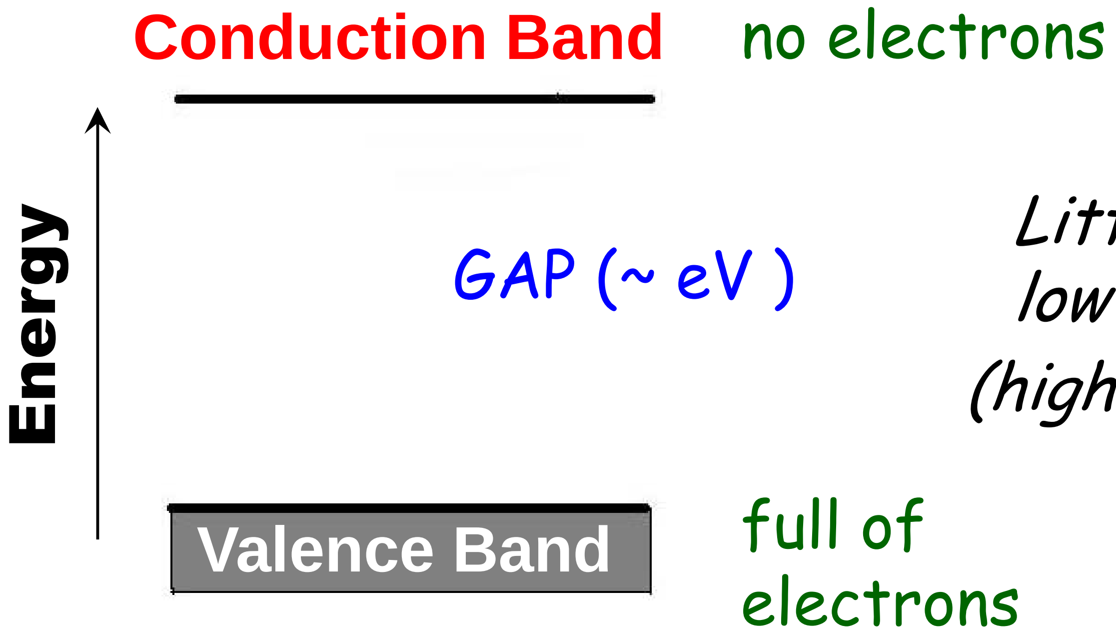
solid state devices

semiconductors

Why use semiconductors ?

- Examples of semiconductors:
  - **- Group IV elements:** **C, Si, Ge, etc**
  - **- Group III-V elements:** **GaAs, GaP, GaN, etc**
  - **- Group II-VI elements:** **ZnO, ZnSe, etc.**

- **Pure semiconductors not that useful…?**

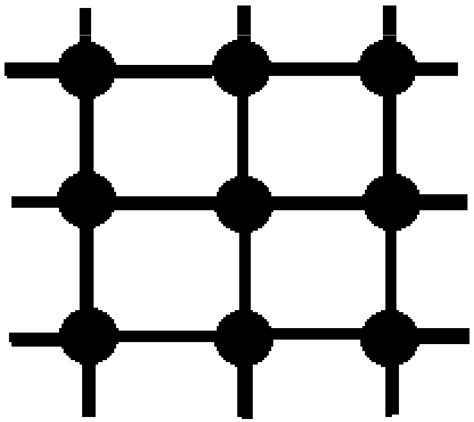


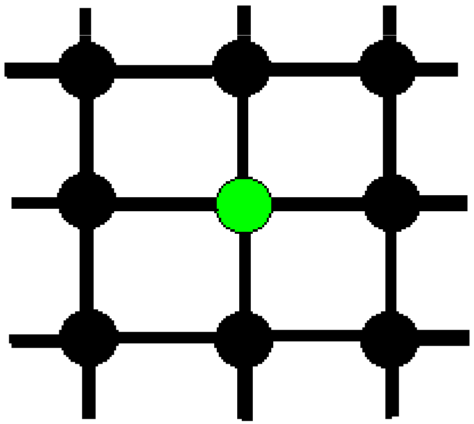
Little current at low temperature (high resistance)

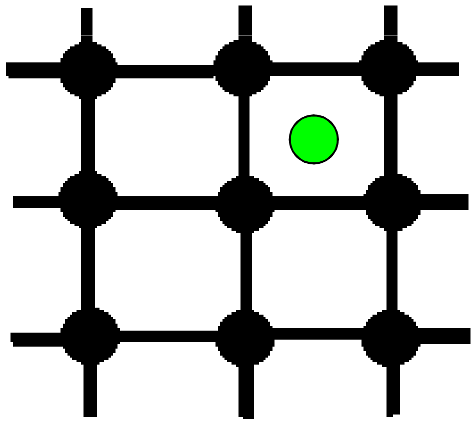
Why use semiconductors ?

- **Electrical conductivity can be varied over many orders of magnitude ….**

- add impurities





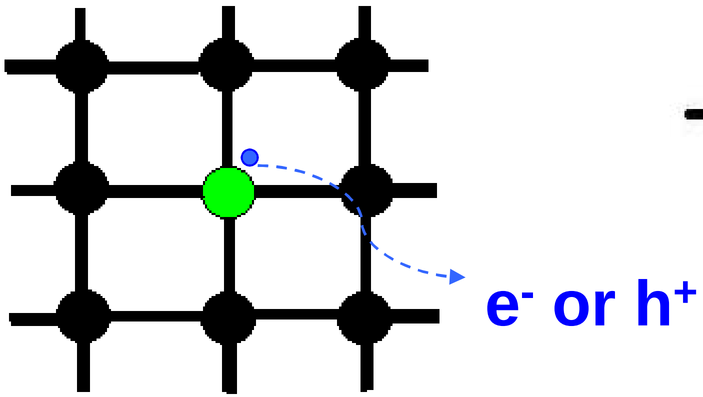


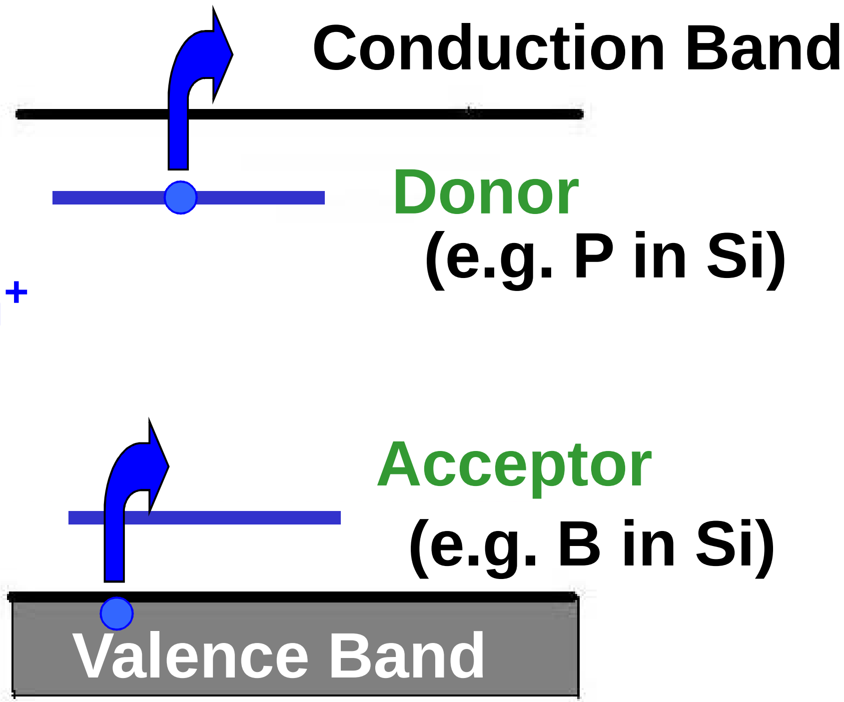
pure

impurity substitutes for a host atom

interstitial impurity

Substitutional Impurities ….





- **Impurities add levels in the band gap**
  - **Donor: *donate* electrons**
  - **Acceptor: *accept* electrons (or *donate* holes)**
- **If levels are close to band edges ("shallow"), current flows at reasonable temperatures as band is populated with electrons (holes)**
- **Vary concentration of impurities = vary conductivity**

Various Impurities…

• ***Solid state electronics depends on CONTROLLED doping of impurities, usually substitutional***

• **Examples of common substitutional impurities:**

"p-type" acceptors	**"n-type" donors**
B in Si	**P in Si**
Zn in GaAs	**Si in GaAs**
Mg in GaN	**Si in GaN**

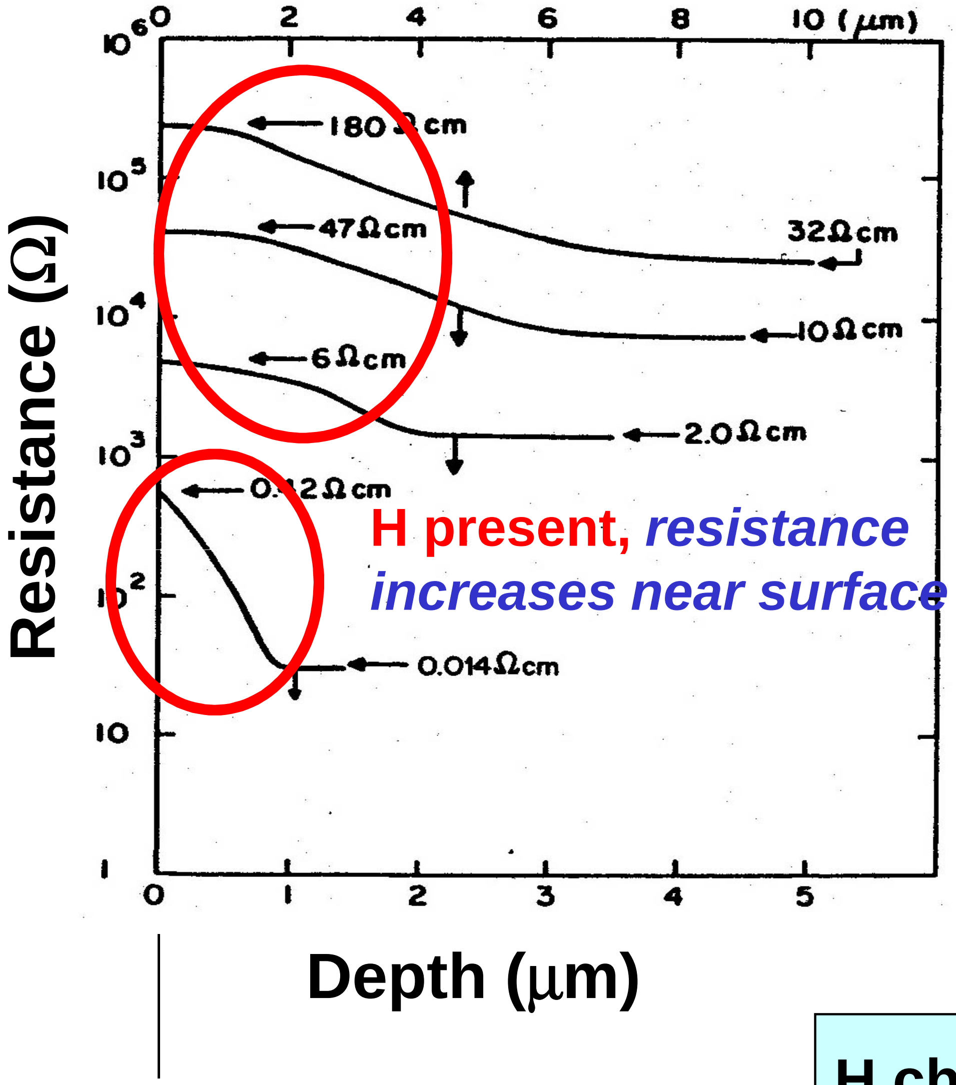
• **How about interstitial Impurities?**

- **Consider HYDROGEN, the most abundant element in the Universe.**
- **H is a fascinating impurity**

PART 2

Hydrogen as an impurity

Example of how H affects semiconductors...



Introduce atomic H @ 122 °C to surface of Si:B samples

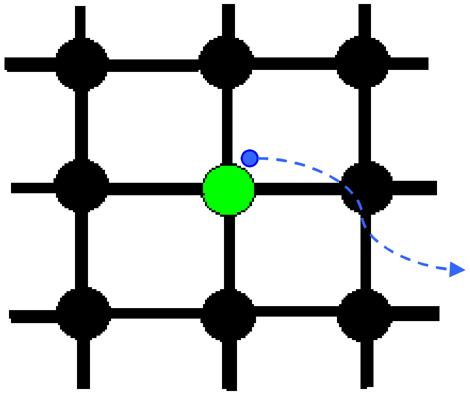
Pankove (1985)

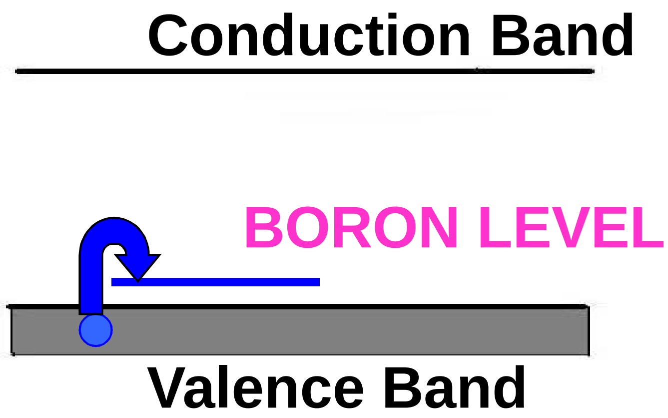
CONCLUSION:

H changes resistance dramatically!

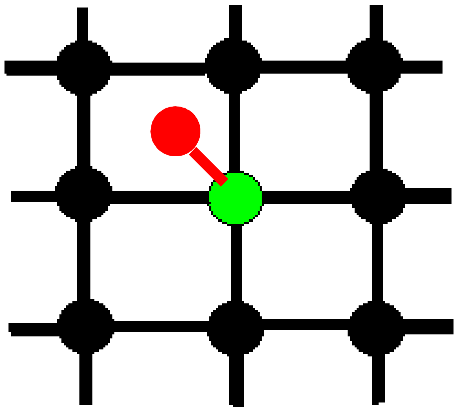
What is the mechanism?

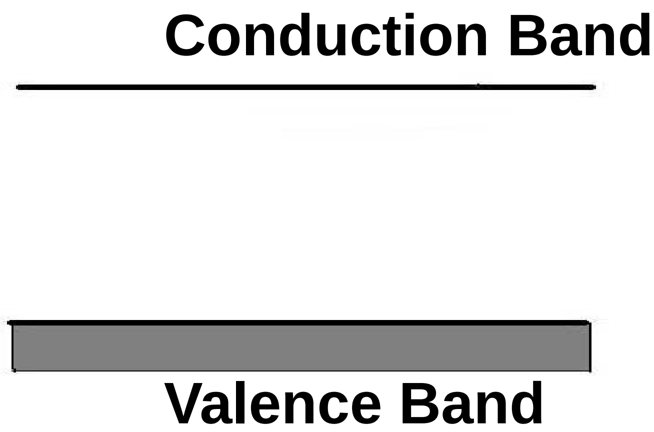
- **H absent**





- **H present: reacts with dopant**





- ties up free carrier

- impurity level removed

Hydrogen, a technologically relevant impurity…

- **H is everywhere, and enters a semiconductor easily**
  - **Boiling in water, device fabrication steps, etc.**

  - unintentional = BAD

  - controlled = GOOD

  e.g. solar cells, surface passivation, etc.

- **H can be H^0 (neutral), H^+ (positive), H^- (negative)**

- **H reacts rapidly with:**

  - dangling bonds **- itself** **etc.**

  - other dopants **- extended defects**

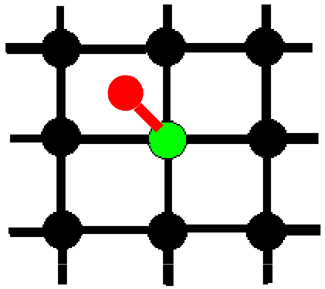
- **H can also act as a dopant ?**

H affects optical & electrical properties dramatically

Atomic Hydrogen ….

- **the role that H plays has prompted many theoretical and expt'al studies of H inside semiconductors**
    - **- resistivity**
    - **- secondary ion mass spectroscopy**
    - **- deep level transient spectroscopy**
    - **- local vibrational mode spectroscopy**
    - **- electron paramagnetic resonance**

etc.



- **lots of exptal info on H-dopant complexes**

BUT…..

- **almost none on:**

(1) *ISOLATED, atomic* H (H^0, H^+ or H^-)
e.g. electronic structure, mobility

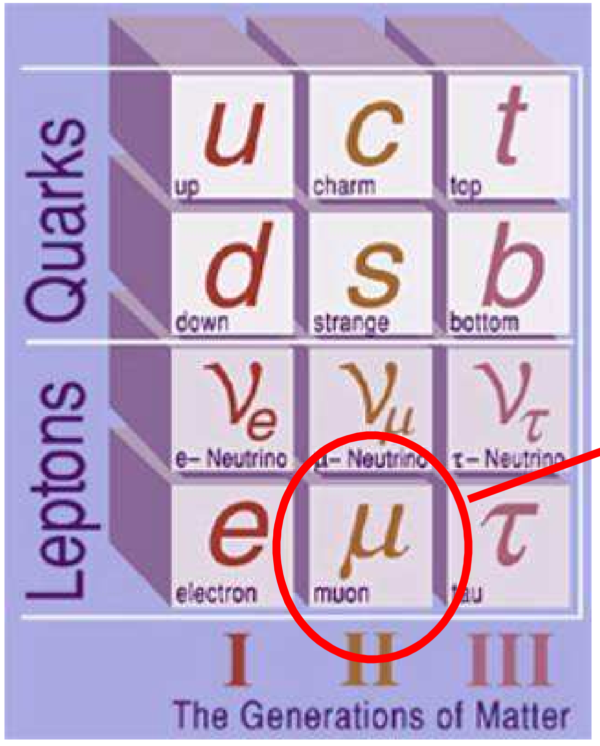
(2) Reaction *as-it-happens*.

H too reactive, forms complex quickly

Problem: cannot study H on short timescale directly…..

Solution: use a short-lived isotope that "acts" like isolated H

The "isotope": a fundamental particle of nature



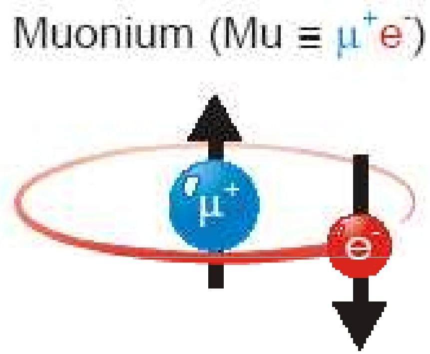
Use
Muon = μ^+
to mimic H^+

PART 3

Muon vs Proton

Compare μ^+ & H^+ ?

	H^+	μ^+
Charge	+1	+1
Mass	m_H	1/9 m_H
Stability	Stable	2.2 μs
Spin	1/2	1/2



- μ^+ & H^+ have same spin and charge
- H^o (= p^+e^-) & Mu^o (= μ^+e^-) have rather different masses *but* nearly identical *reduced* mass

  - *Potential Energy Surface*
  - Electronic Structure (Bohr radius, etc.)

  } VERY SIMILAR

Compare μ^+ & H^+ (con't)

	H^+	μ^+
Charge	+1	+1
Mass	m_H	1/9 m_H
Stability	Stable	2.2 μs
Spin	1/2	1/2

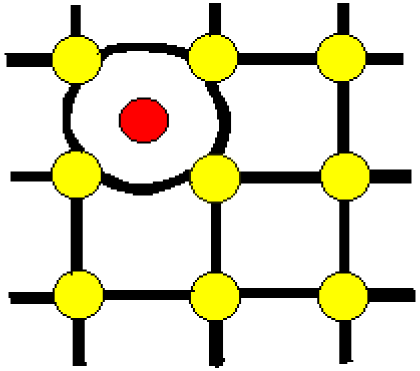
- ***Short lifetime*** **of μ^+ = does not have time to react**

$\Rightarrow$ much easier to study *ISOLATED* "muonium": Mu^+, Mu^o, Mu^- than highly reactive H

- **Most of the info. on isolated H comes from studying Mu**

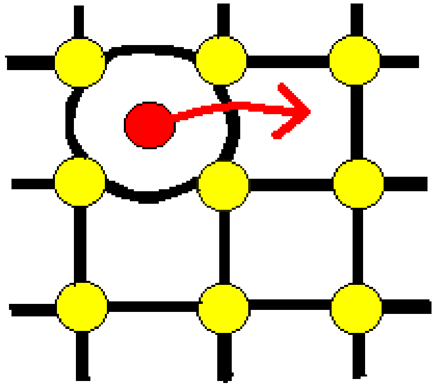
Information we are trying to get

- **Atomic level information on Mu:**



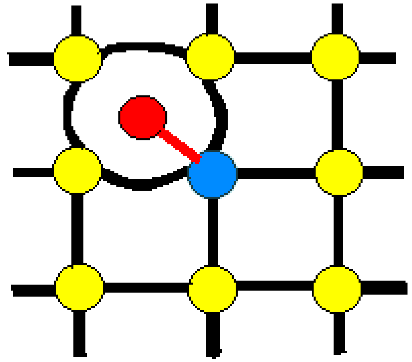
(a) Structure:

- Existence?
- formation?
- charge states?
- sites?
- Energy level in gap?
- stabilities?



(b) Motion:

- how fast?
- influence of T?
  charge state?
- path?



(c) Interactions:

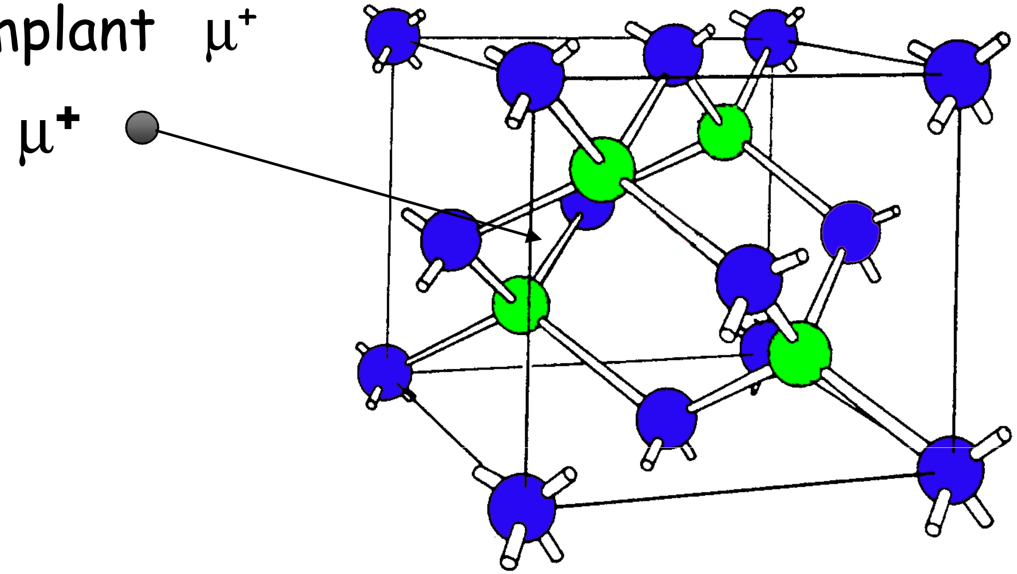
- with free carriers?
- with host?
- External Stimuli?

PART 4

A set of (very incomplete) Experimental examples

Existence
&
Electrical Activity

Implant μ^+



Semiconductor

various "Muonium" states (co)exist:

Mu^+

Mu^0

Mu^-

- *depends on semiconductor (dopant type and conc)*
- *depends on Temperature*
- Over 30 distinct muonium states in many semiconductors…

(e.g. Si, Ge, GaAs, GaP, ZnO, ZnSe, SiC, GaN, etc etc etc.)

Charged and Neutral states – *simple signatures in vacuum*

- **Charged Mu centers have no unpaired electron nearby:**

Mu^+

Mu^-

$$\nu_\mu = \gamma_\mu H_{applied}$$

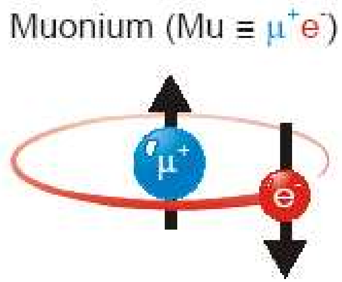
(Larmor frequency in a TF-μSR expt)

- **A neutral Mu center has an unpaired electron nearby:**

Mu^0

$$\nu_\mu = \gamma_\mu H_{applied} + A_{hf} / 2$$

$$= \gamma_\mu H_{applied} - A_{hf} / 2$$

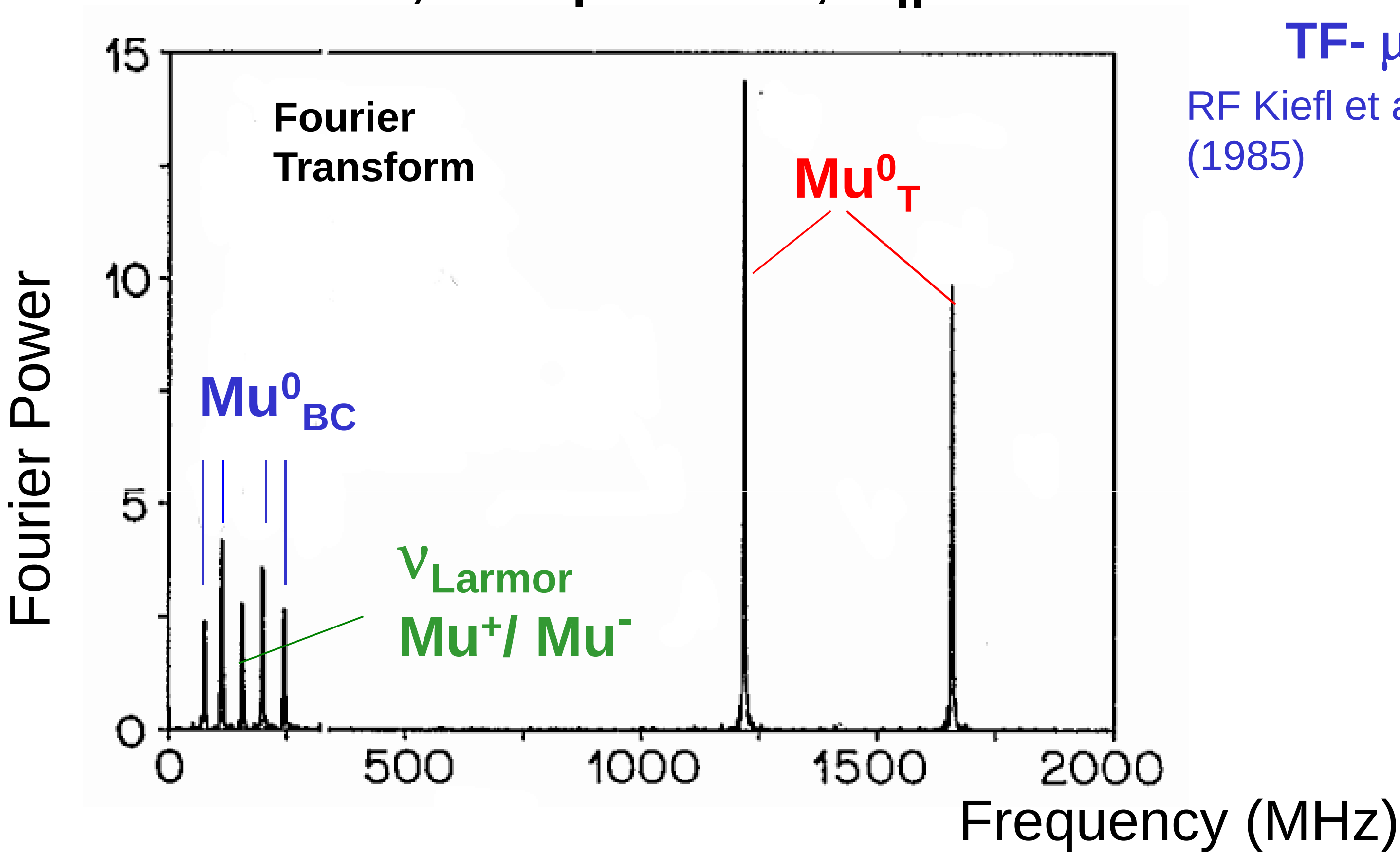


A_{hf} = "Hyperfine interaction" $\propto |\psi_e(0)|^2$ = unpaired electron spin density at muon

***Note:* A_{hf} = 4400 MHz in vacuum**

Example of Co-existing Mu^0 states:

T = 10 K, Undoped GaAs, B || <110>



TF- μSR

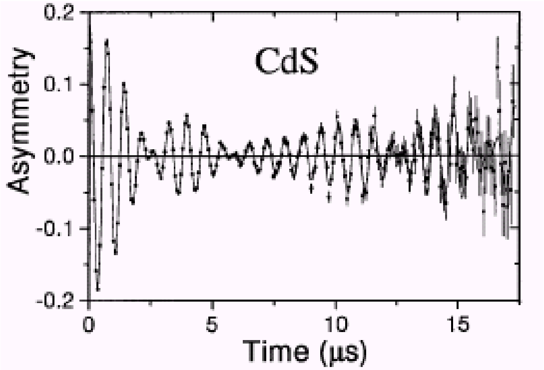
RF Kiefl et al., PRB v32, 530 (1985)

- **One charged center: Mu^+ or Mu^-**
- **Two distinct "deep" neutral centers with large hyperfine interactions: Mu^0_T & Mu^0_{BC}**

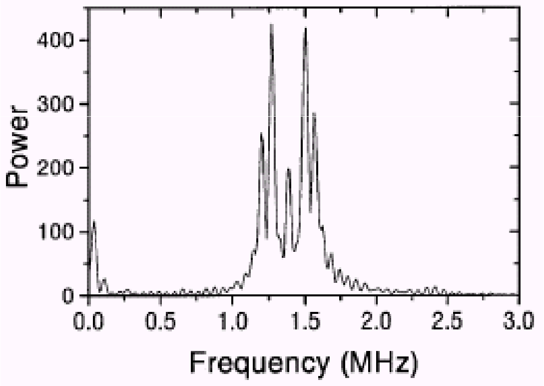
Shallow neutral centers:

J.M. Gil *et al.*, PRL v83, 5294 (1999)

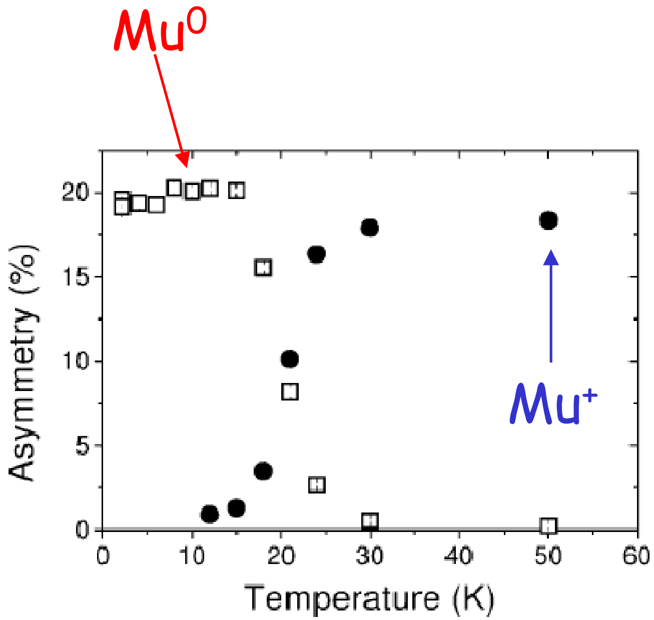
TF- µSR, CdS, T = 2.1 K

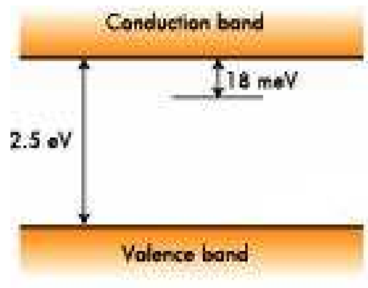


TF-µSR



Fourier Transform





- **Mu^0 with very small muon hyperfine interaction (0.01% vacuum) & low activation energy**
- **H can act as a donor**
- **Shallow Mu^o centers are being very actively studied**

Universal alignment of hydrogen levels in semiconductors, insulators and solutions

NATURE | VOL 423 | 5 JUNE 2003 |

Chris G. Van de Walle* & J. Neugebauer†

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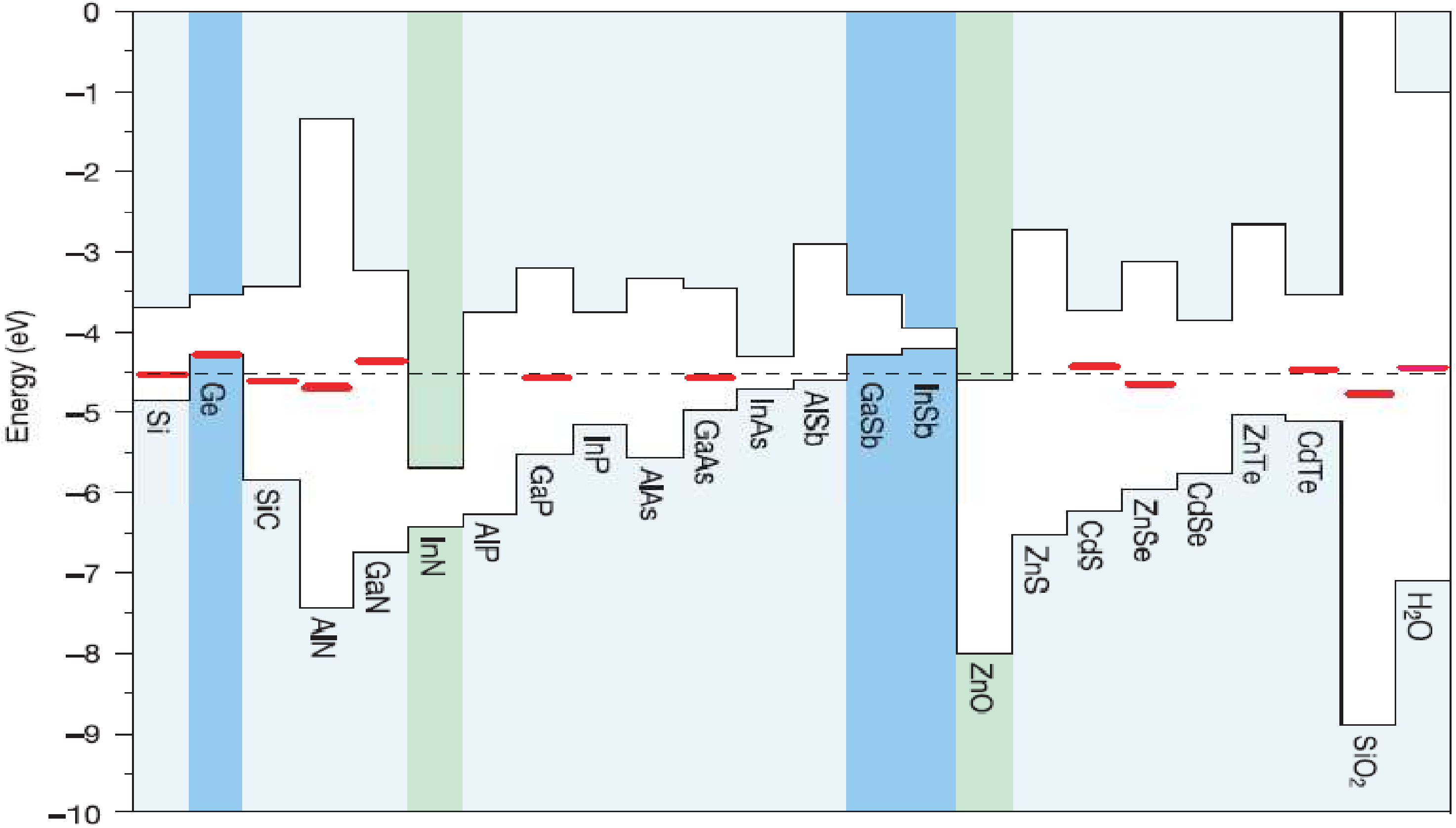
† *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany*

1) Is there a common H(+/-) level?

2) Will H be a shallow dopant?

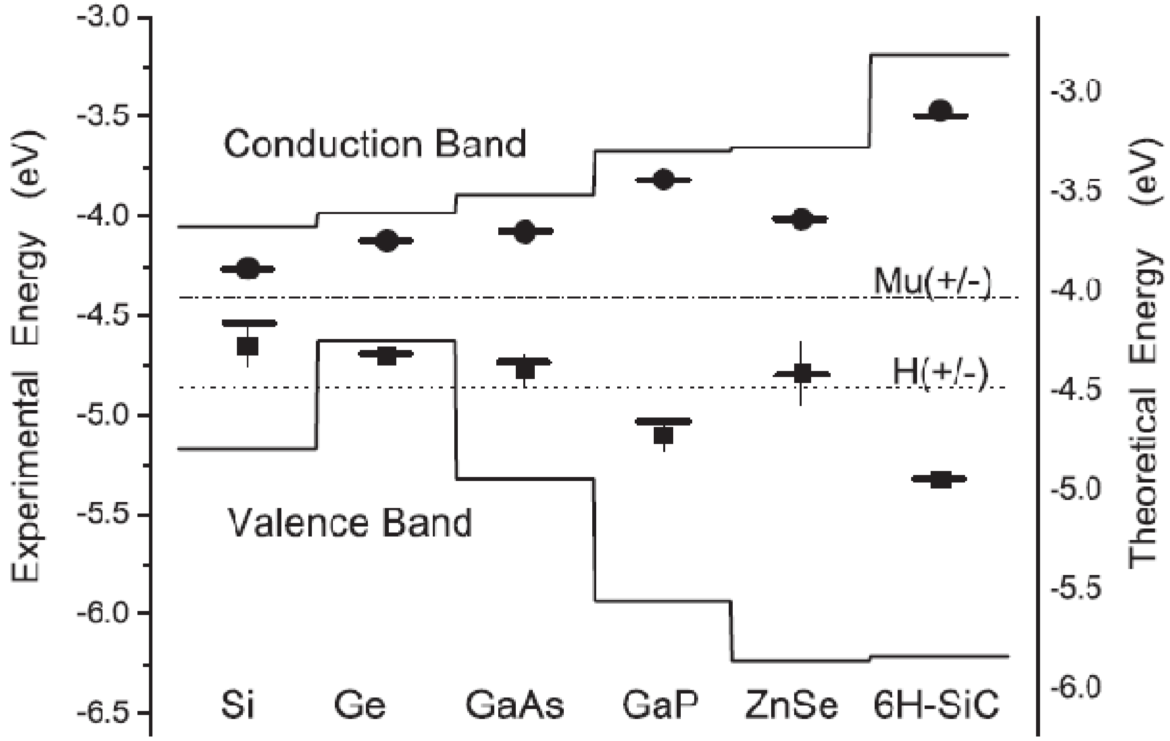


PRL 101, 136403 (2008) PHYSICAL REVIEW LETTERS week ending 26 SEPTEMBER 2008

Hydrogen Defect-Level Pinning in Semiconductors: The Muonium Equivalent

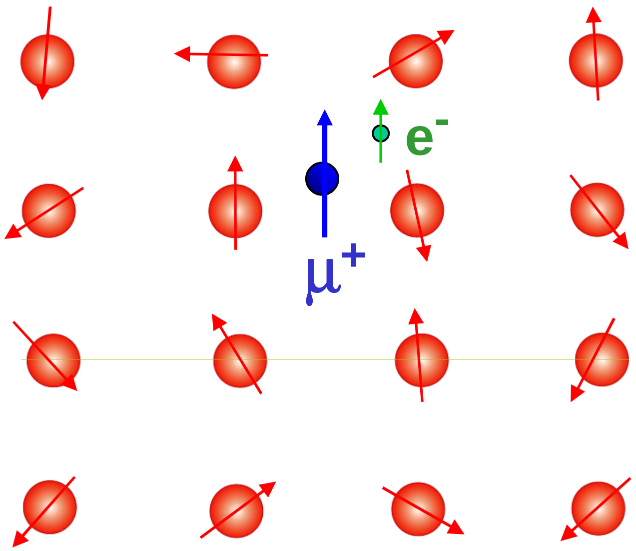
R. L. Lichti,[1,*] K. H. Chow,[2] and S. F. J. Cox[3,4]

- Use T dependence of various Mu states to estimate energy level:



Site
&
Other Structural Info

Structural info: **study interactions with the host**



Useful interactions:

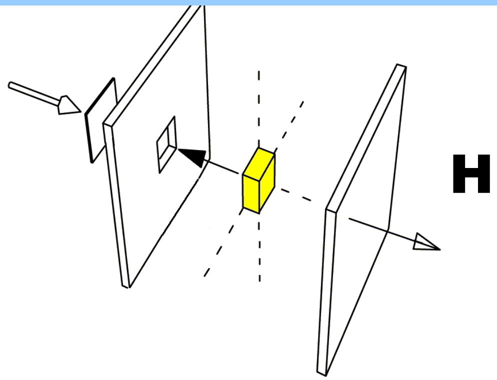
- μ^+ **& host:**
  - muon induced quadrupole
  - dipole-dipole

- μ^+ **&** e^- **& host:**
  - nuclear hyperfine

$$
\begin{aligned}
\mathcal{H} \;&=\; h\tilde{\gamma}_e \mathbf{B}\cdot\mathbf{S} - h\tilde{\gamma}_\mu \mathbf{B}\cdot\mathbf{I} + \mathbf{S}\cdot\tilde{\mathbf{A}}^\mu\cdot\mathbf{I} + \\
&\sum_i [\mathbf{I}\cdot\tilde{\mathbf{D}}^i\cdot\mathbf{J}^i + \mathbf{S}\cdot\tilde{\mathbf{A}}^i\cdot\mathbf{J}^i - h\tilde{\gamma}_n^i \mathbf{B}\cdot\mathbf{J}^i + \mathbf{J}^i\cdot\tilde{\mathbf{Q}}^i\cdot\mathbf{J}^i]
\end{aligned}
$$

Avoided Level Crossing / Cross Relaxation

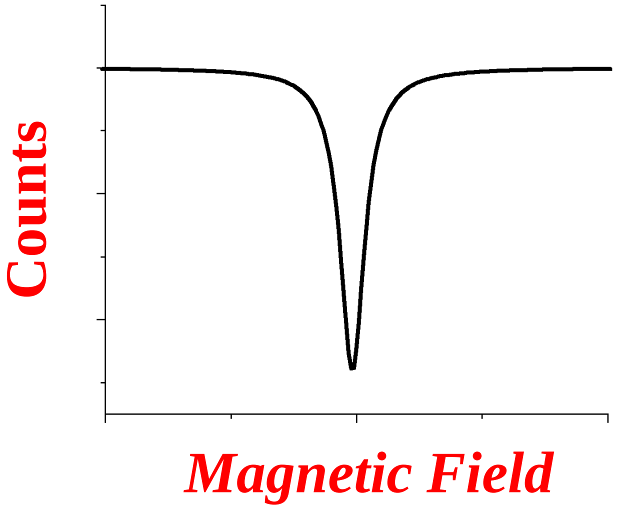
eg. $Mu^{+/-}$ - Nuclear Cross-Relaxation



- Scan longitudinal magnetic field, and look for instances where

Muon energy level splittings = Nuclear energy level splittings
(muon Zeeman interaction) (nuclear Zeeman interaction, muon-induced electric field gradient)

- Muon and Nuclear spin "flip-flop"

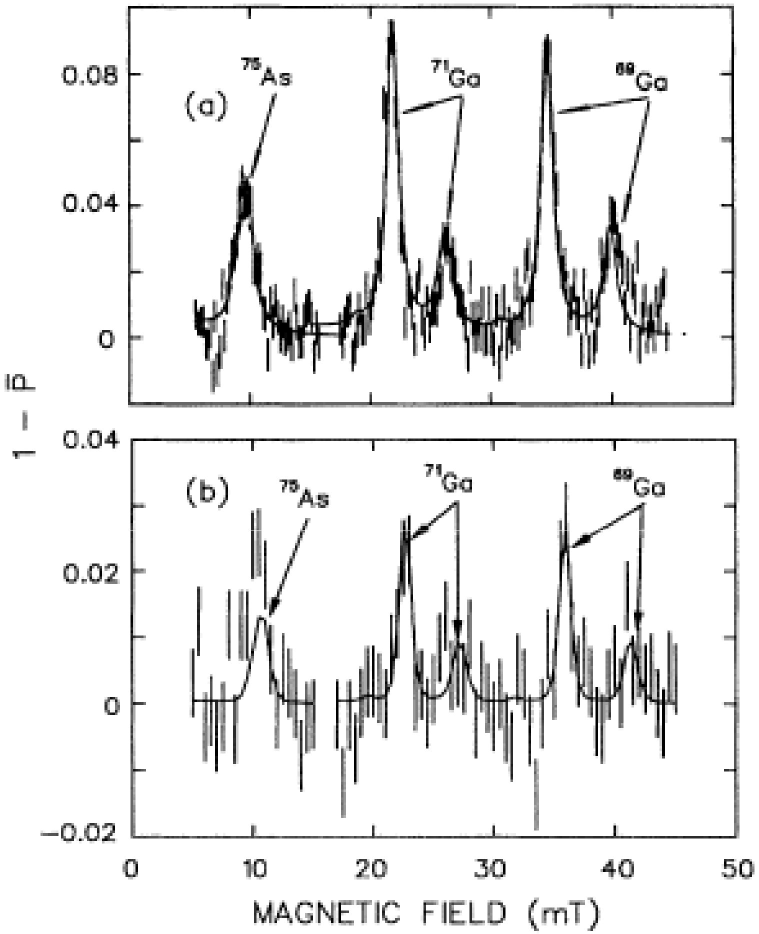


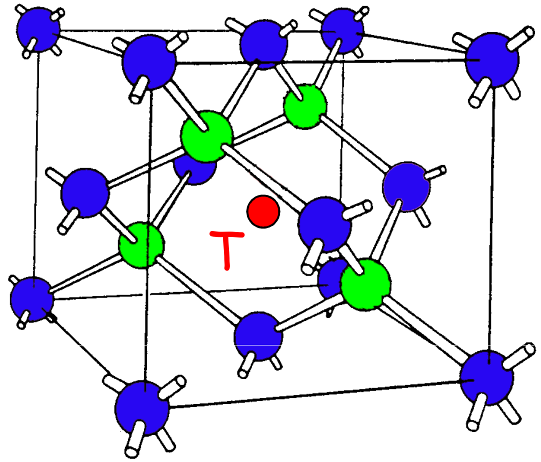
Details of signal …

- **Identifies nearest neighbors**
- **Gives info on their position wrt muon**

Location of isolated Mu^- in n-type GaAs:

KH Chow et al., PRB **51**, 14762 (1995)



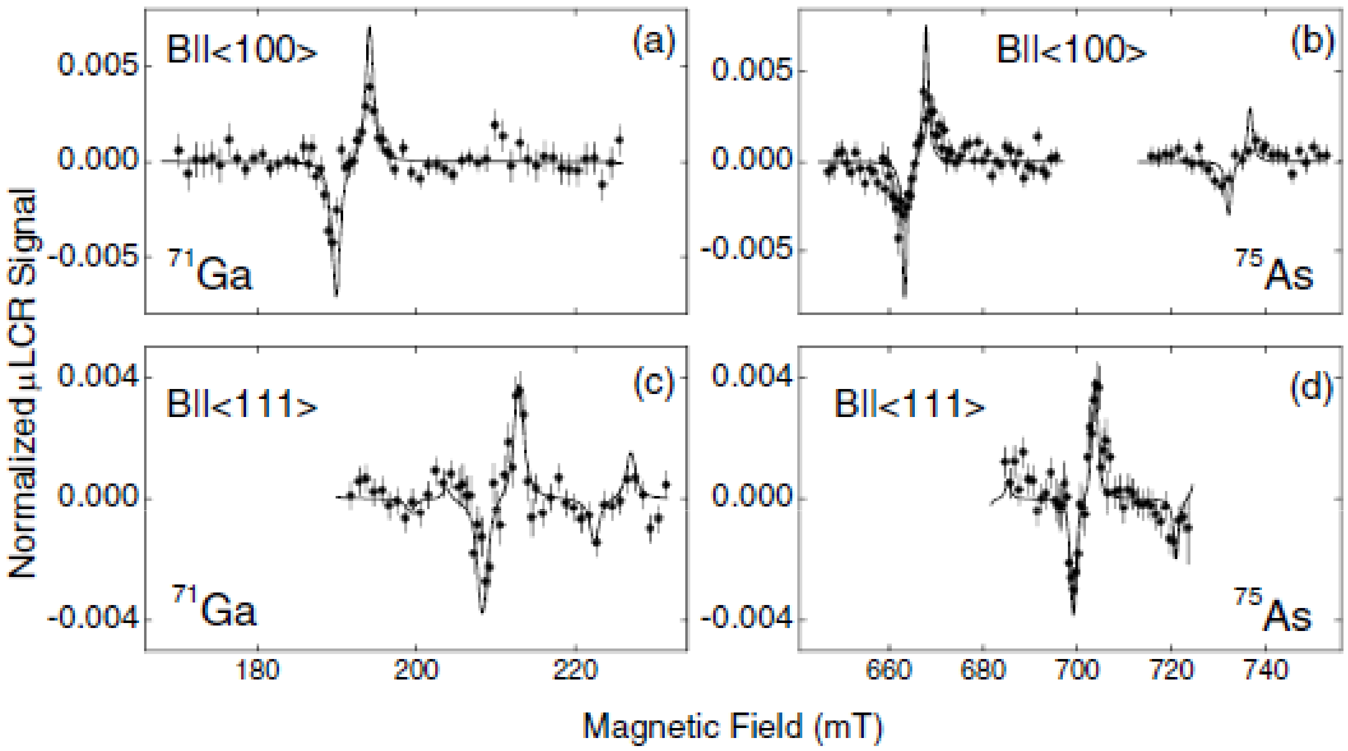


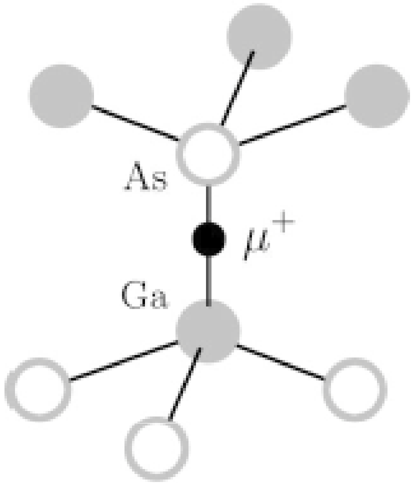
- Mu^- prefers regions with low electron density
- Located @ T_{Ga} site

Location of isolated Mu^+ in p-type GaAs:

B.E. Schultz et al., PRL 95, 086404 (2005)

50 K





$r_{Ga} = 1.84 \pm 0.08$ Å

$r_{As} = 1.76 \pm 0.05$ Å

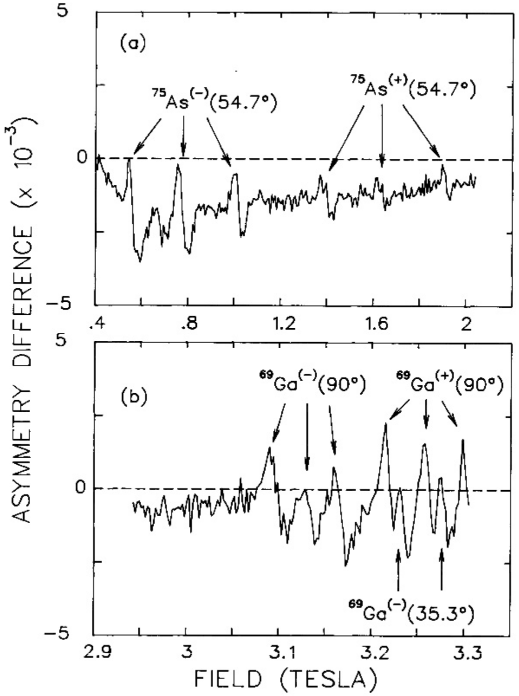
- Mu^+ prefers regions of high electron density
- squeezes into Bond-Center position
- stretches Ga-As bond by ~ 50 %

Location of Mu^0_{BC} in Si and GaAs

Mu^0_{BC} in GaAs

R.F. Kiefl *et al.*,

PRL v58, 1780 (1987)

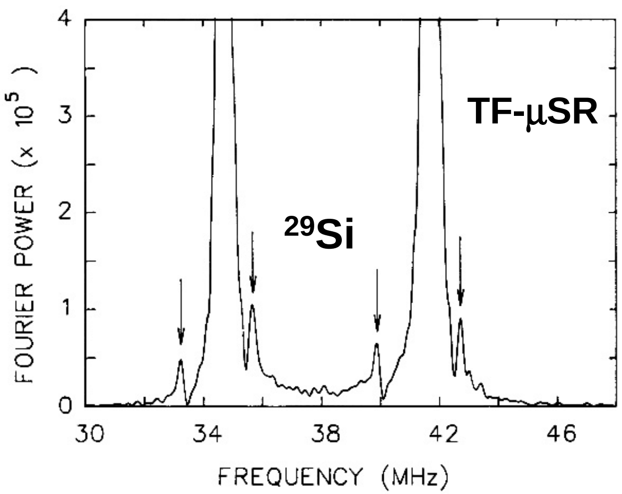


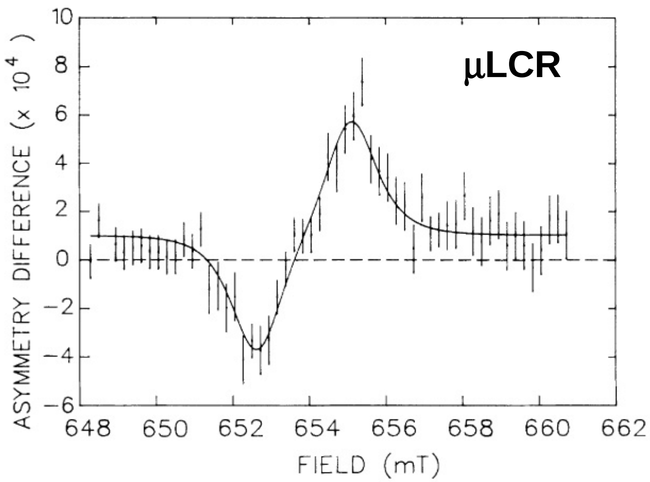
μLCR

Mu^0_{BC} in Si

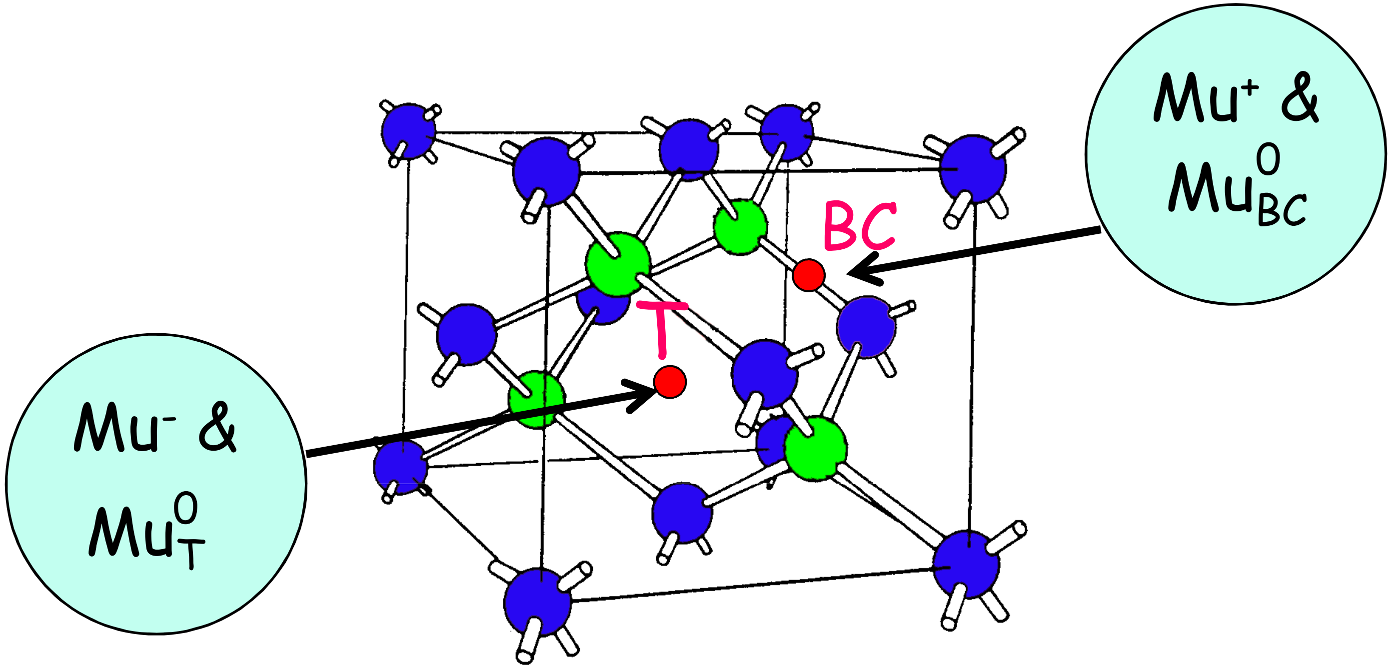
R.F. Kiefl *et al.*,

PRL v60, 224 (1988)



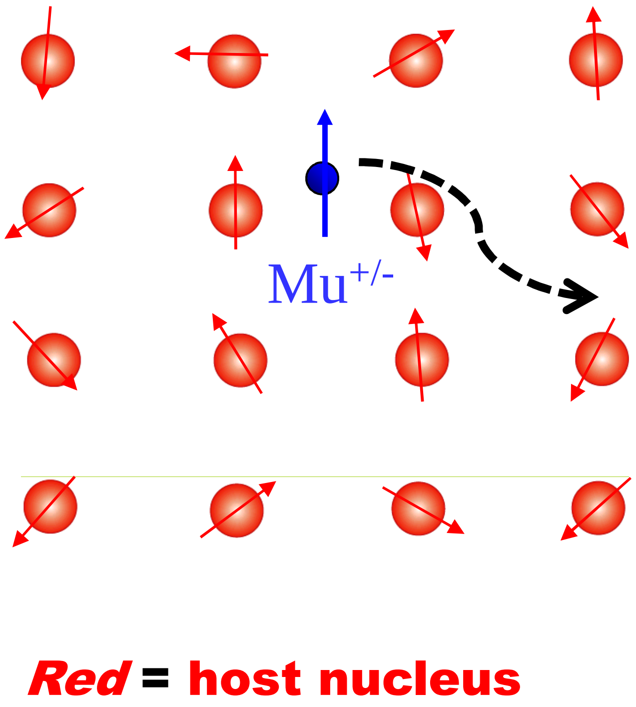


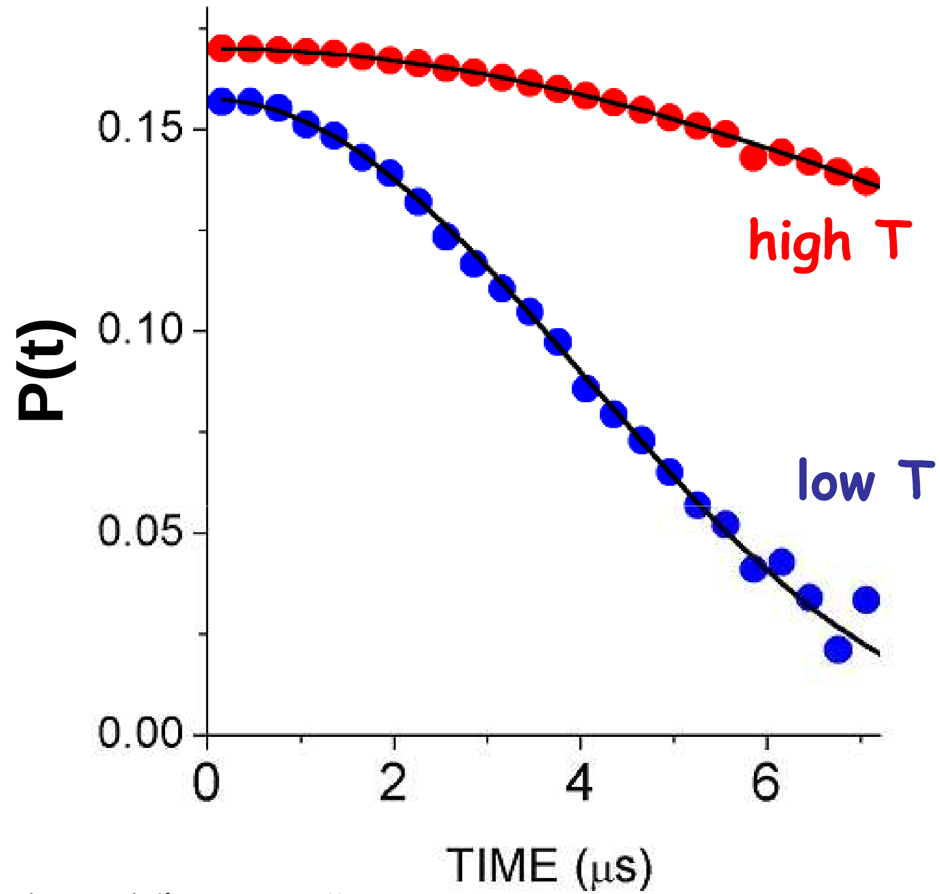
In many semiconductors…



Motion
&
Reactions

eg. Motion of Isolated Mu^+ or Mu^-





- host spins are randomly oriented and "static"
- each μ^+ sees a slightly different internal magnetic field (~ Gauss)
- leads to "relaxation", characterized by relaxation parameter Δ
- **motion** *averages* these spread in magnetic fields

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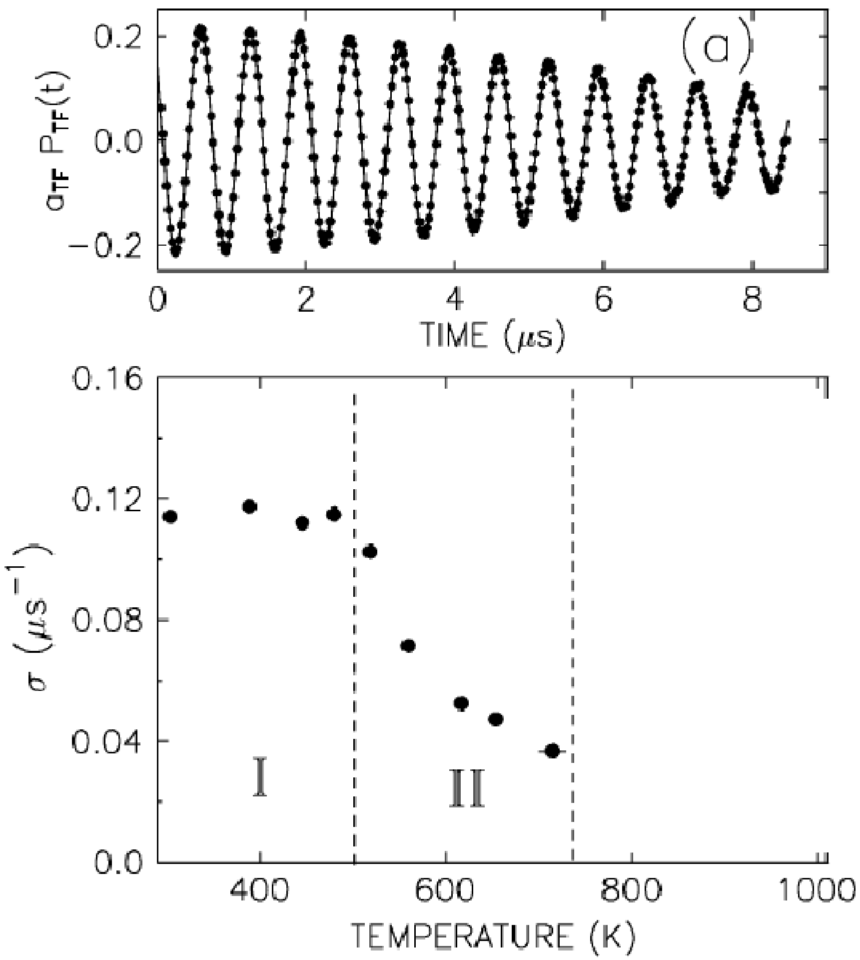
Diffusion and Charge Dynamics of Negatively Charged Muonium in *n*-Type GaAs

K. H. Chow,[1] B. Hitti,[2] R. F. Kiefl,[3,4] S. R. Dunsiger,[4] R. L. Lichti,[5] and T. L. Estle[6]

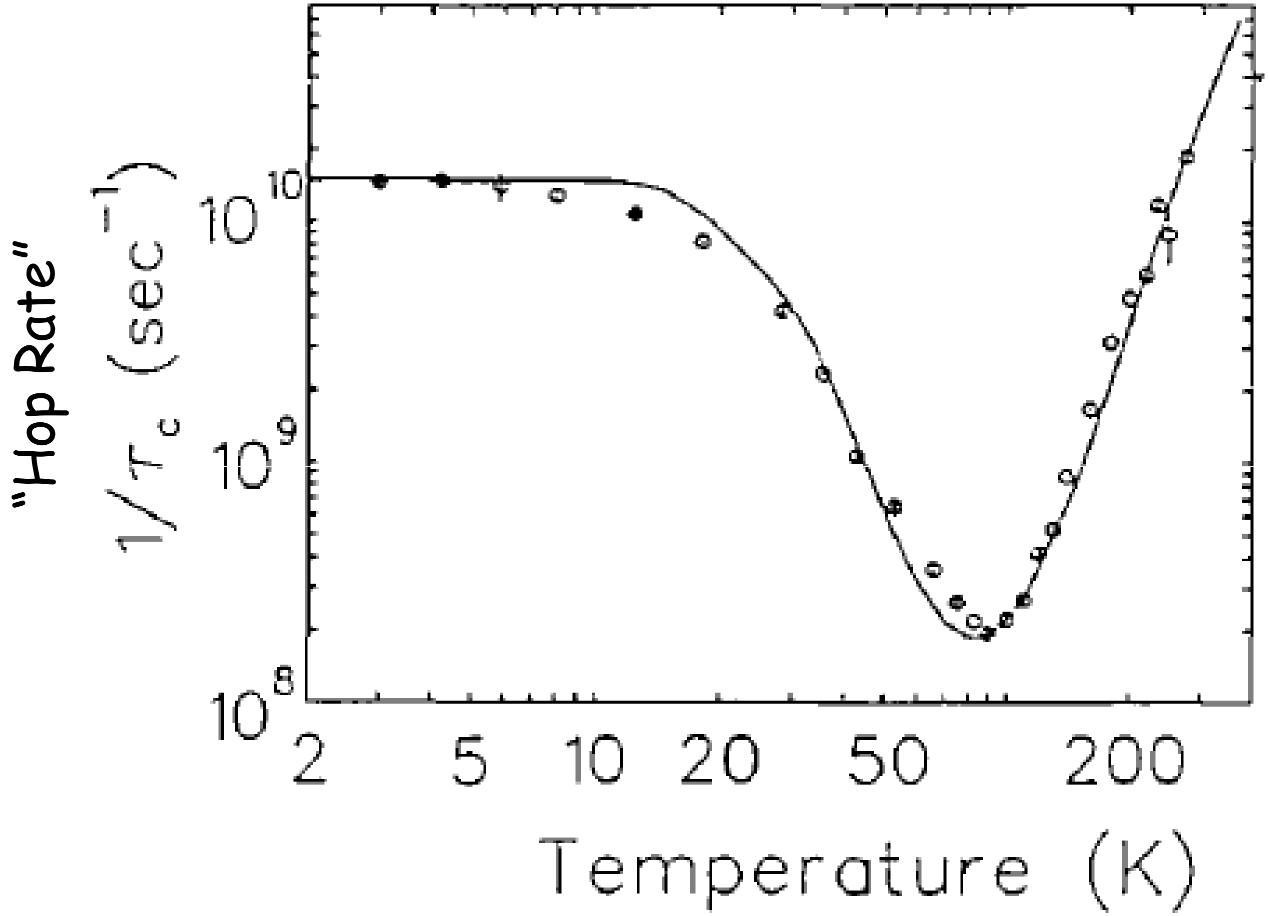


- Mu_T^- in heavily doped n-GaAs

- *Static* in Region I
- *Moving* in Region II

Contrast with Diffusion of Mu_T^0 in undoped GaAs

R. Kadono *et al.*, Hyperfine Interactions **64**, 635 (1990)

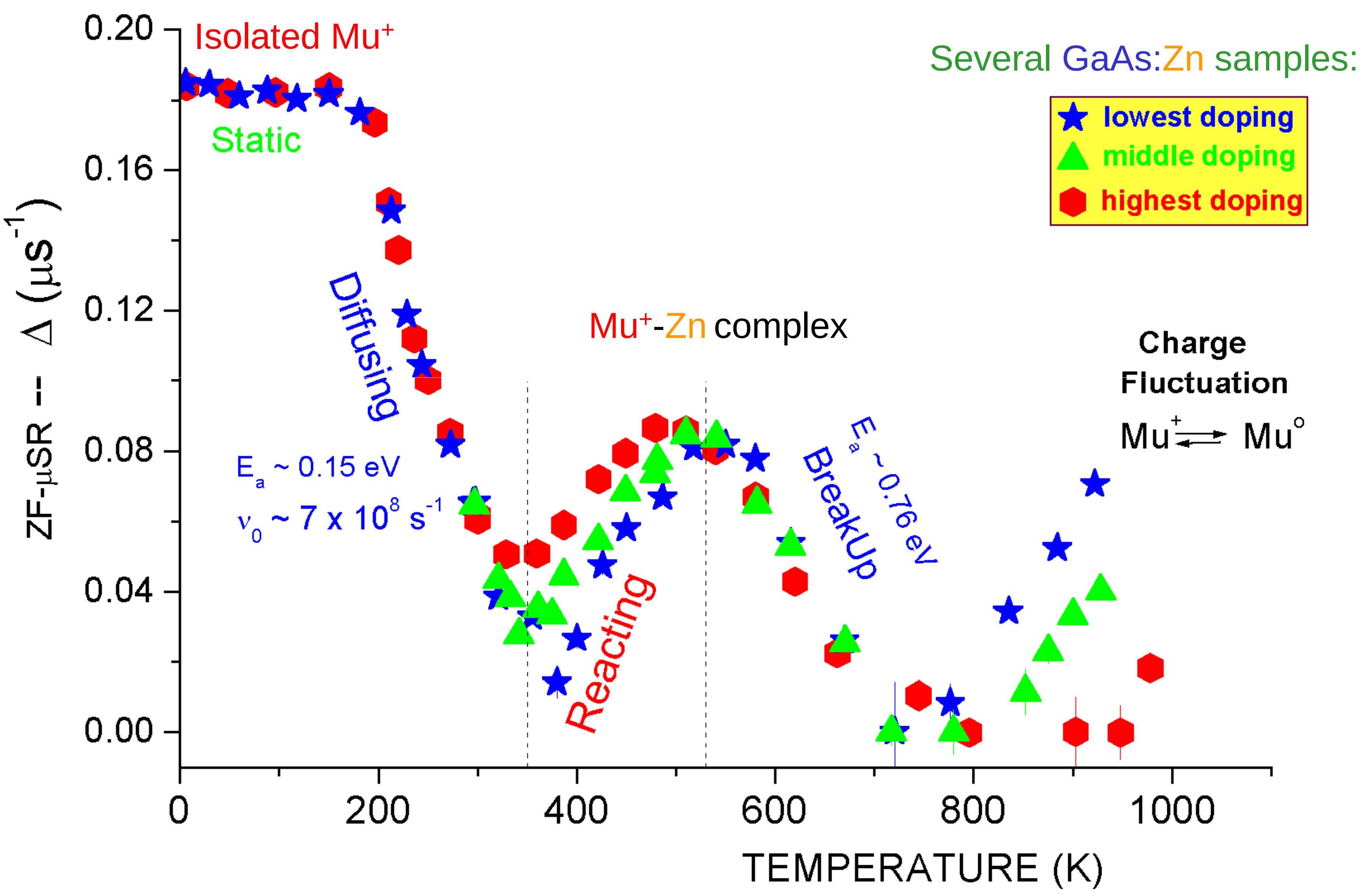


- Diffusion depends dramatically on charge state

Mu⁺ in heavily doped p-GaAs:Zn

Muonium Analog of Hydrogen Passivation

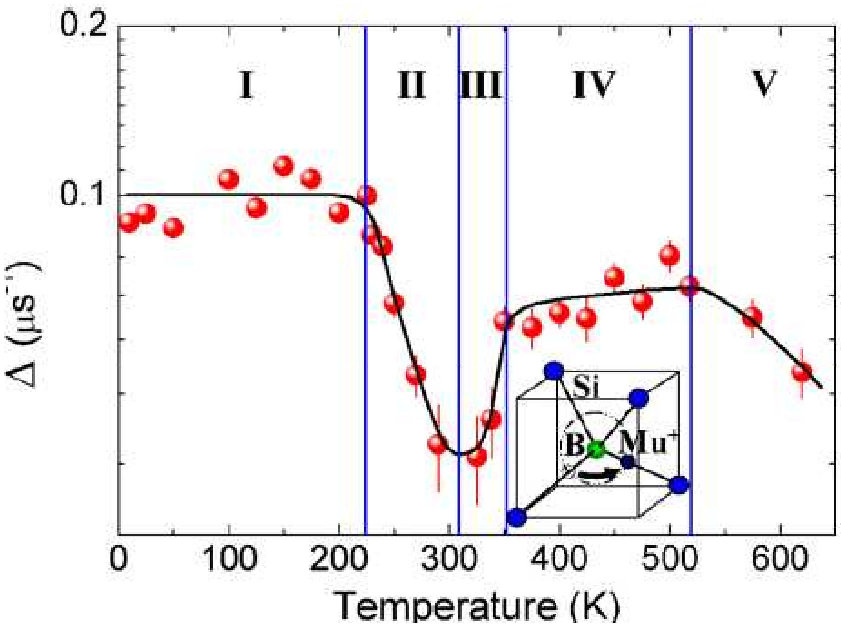
Chow, Hitti, Kiefl, Estle, Lichti, *PRL* ***87***, 216403 (2001)

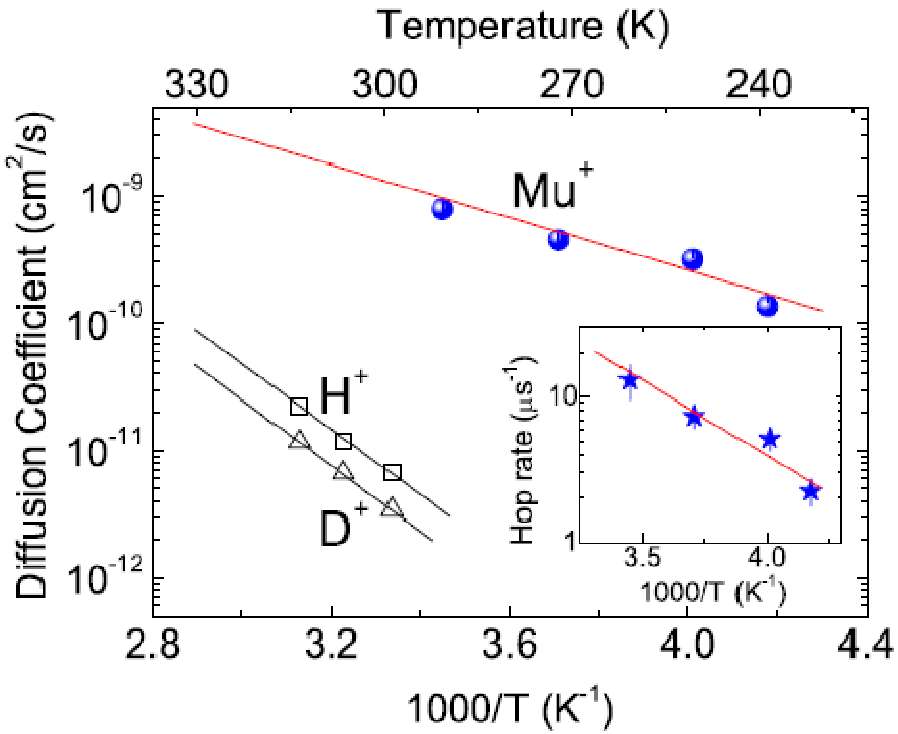


PRL 100, 257602 (2008) PHYSICAL REVIEW LETTERS week ending 27 JUNE 2008

Dynamics and Reactivity of Positively Charged Muonium in Heavily Doped Si:B and Comparisons with Hydrogen

A. I. Mansour,[1,*] Z. Salman,[2,3] K. H. Chow,[1,†] I. Fan,[1] P. J. C. King,[3] B. Hitti,[4] J. Jung,[1] and S. P. Cottrell[3]





- **Reaction of Mu^+ with intentional impurity**
- **Zero point motion of Mu^+**

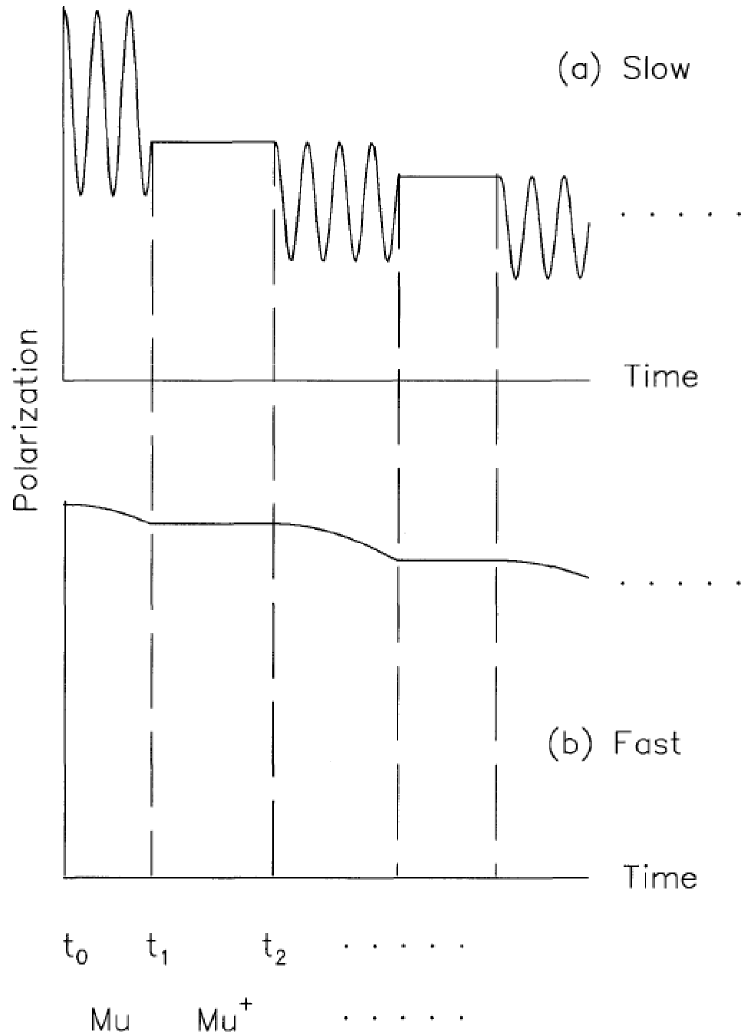
Fluctuation Dynamics

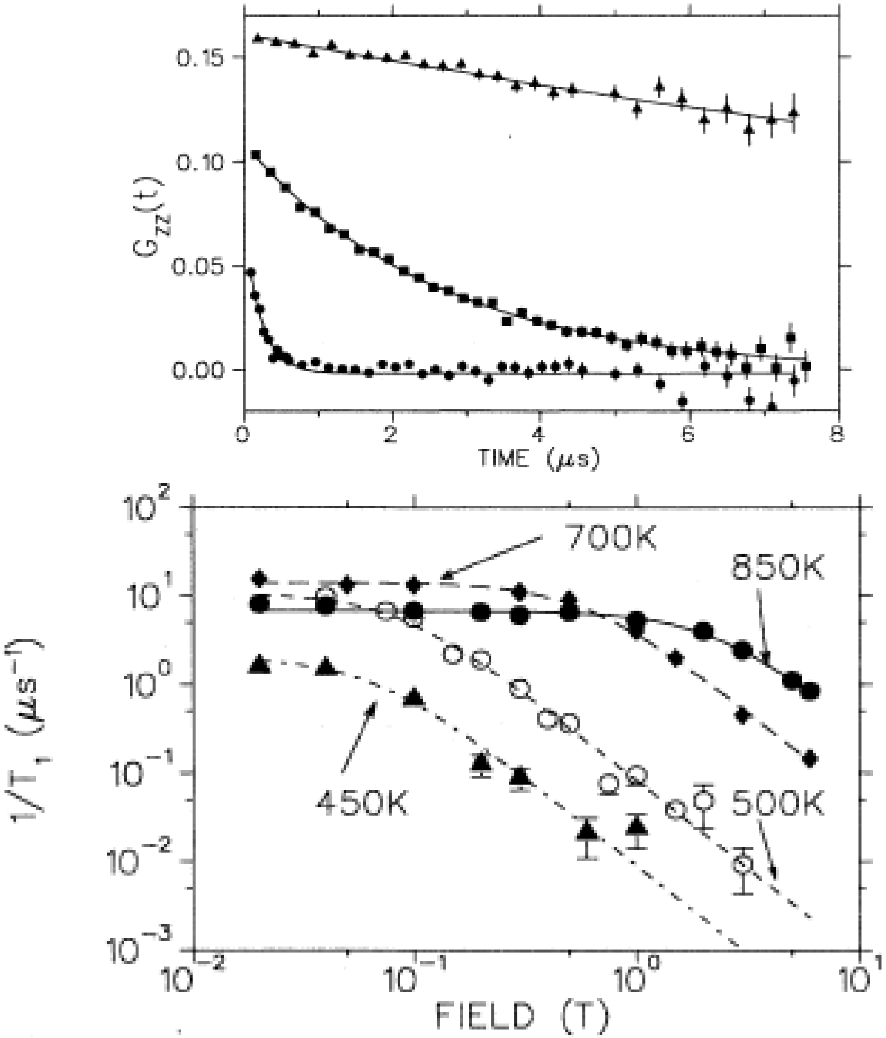
Muonium dynamics in undoped Si at high temperatures

Chow et al., PRB **47**, 16004 (1993)

Charge State Fluctuations: $Mu_T^0 \rightleftarrows Mu^+$

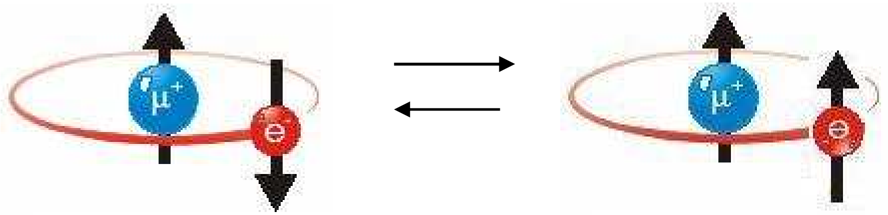
LF-μSR



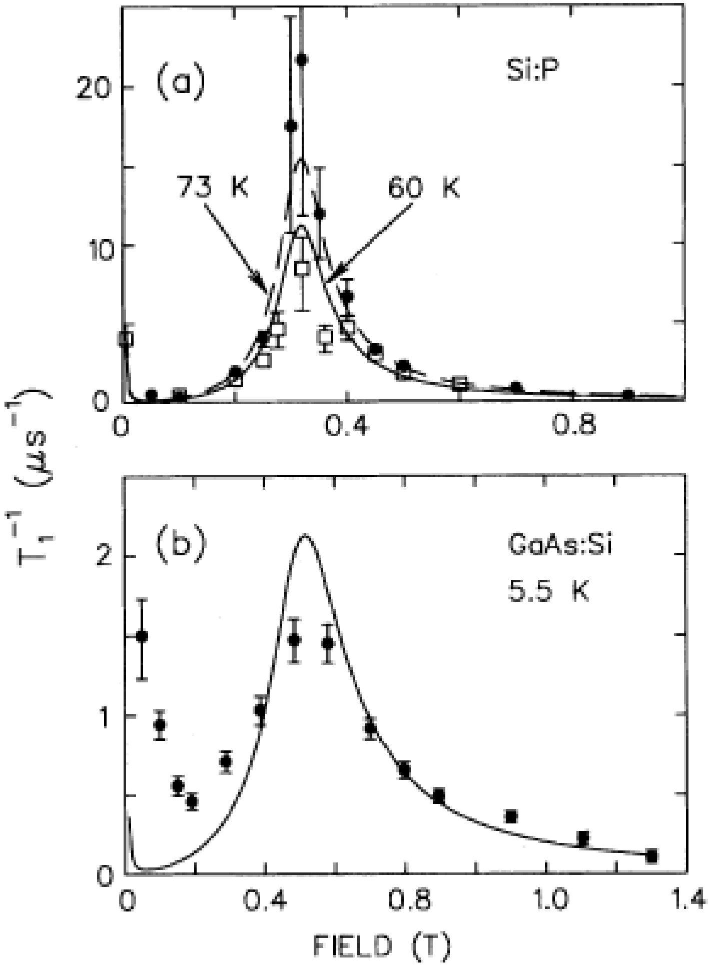


Identification of Mu_{BC}^0 in n-type semiconductors by LF-muSR
Chow et al., PRB **50**, 8918 (1994).

Spin Fluctuations of Mu_{BC}^0:



LF-μSR



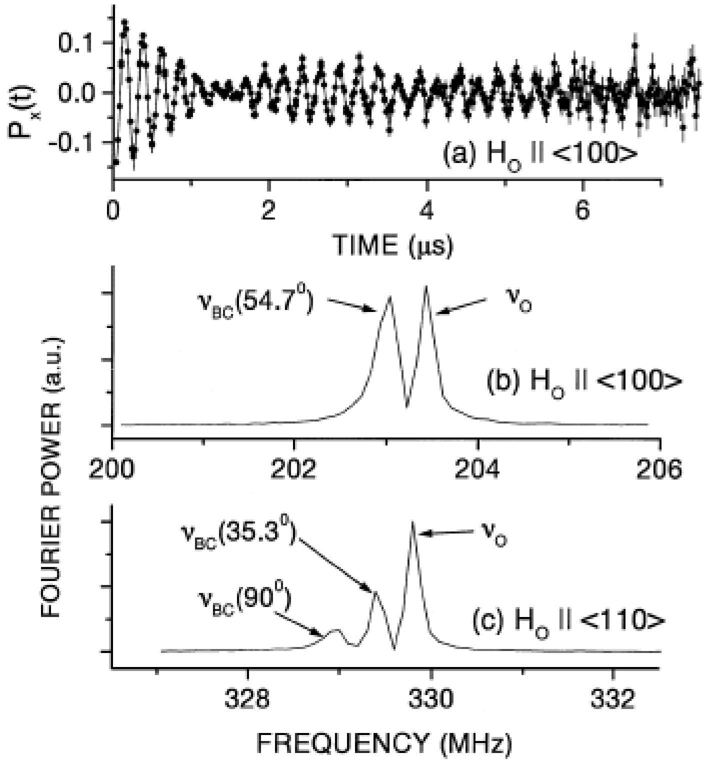
- Peak in relaxation with field

- Signature of Mu_{BC}^0 undergoing spin fluctuations

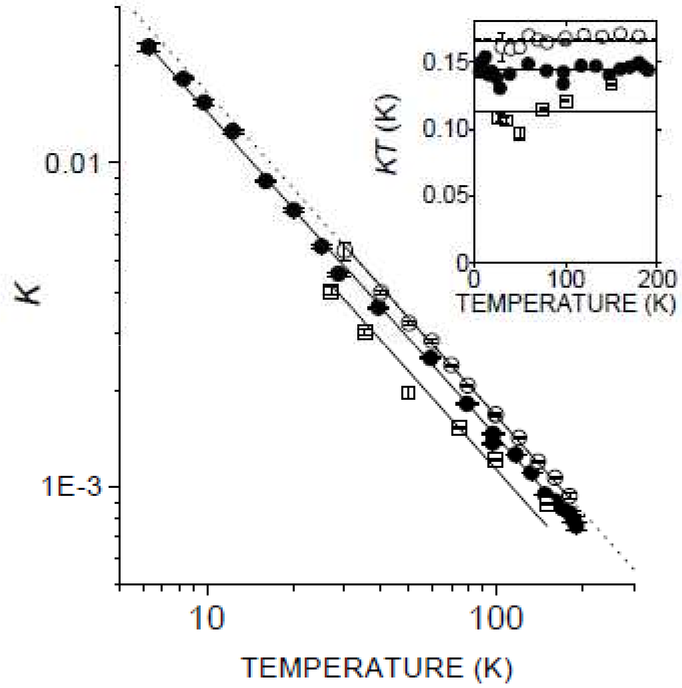
VOLUME 84, NUMBER 10 PHYSICAL REVIEW LETTERS 6 MARCH 2000

Novel Behavior of Bond-Centered Muonium in Heavily Doped n-Type Silicon: Curie-Like Spin Susceptibility and Charge Screening

K. H. Chow,[1] R. F. Kiefl,[2] B. Hitti,[3] T. L. Estle,[4] and R. L. Lichti[5]



Increasing Doping

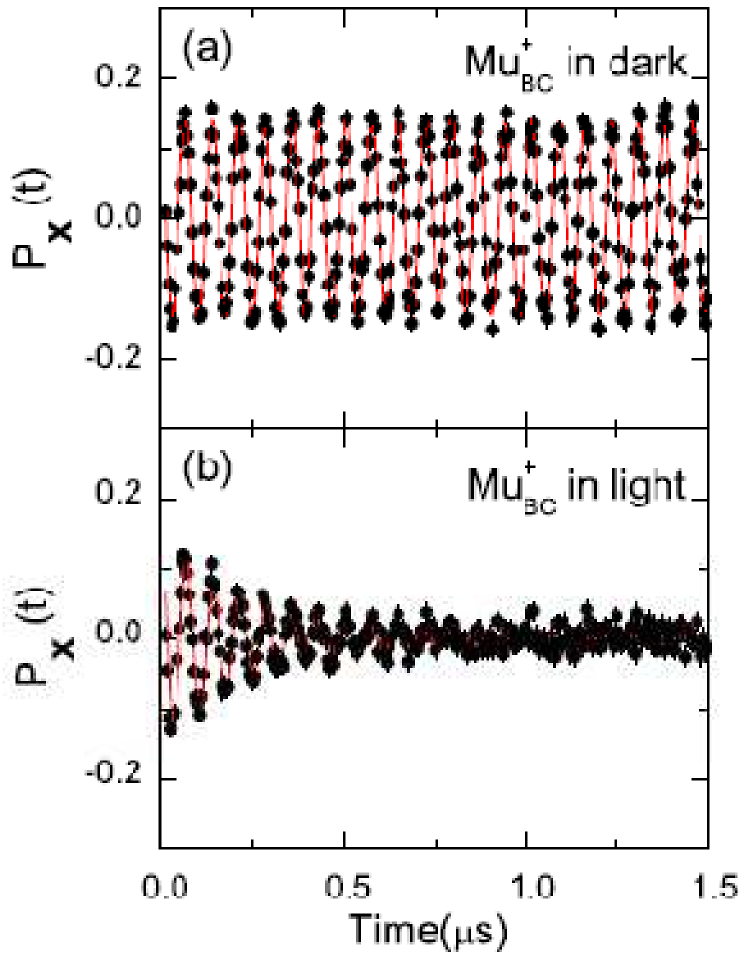


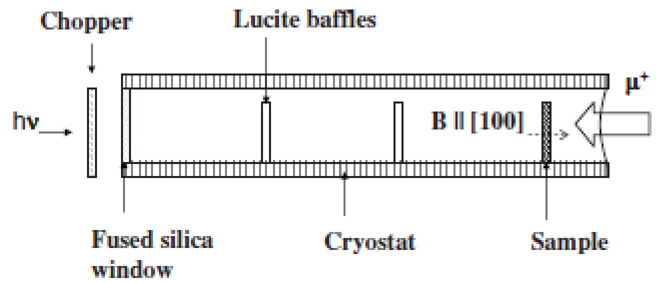
-Screening of an isolated impurity
with increasing electron concentration

Optical Excitation

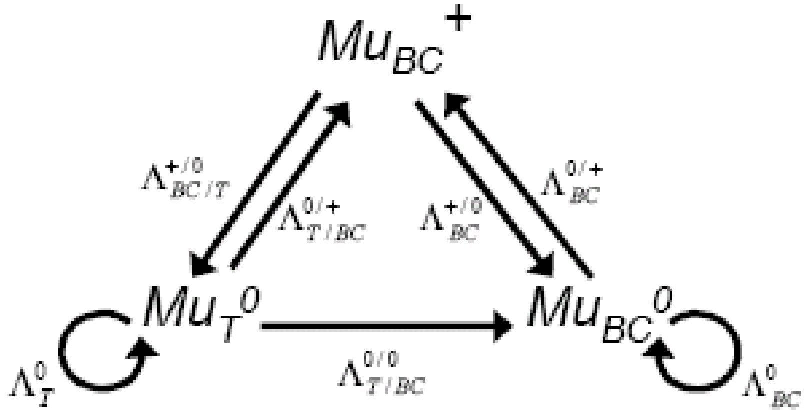
[*Si:* Fan et al., PRB **77,** 035203 (2008)]

[*Ge:* Fan et al., PRB **78,** 153203 (2008)]





Optically induced transitions:



PART 5

Summary

Examples of Reviews

- BD Patterson, *Reviews of Modern Physics* **v60**, 1 (1988).
- RF Kiefl & TL Estle, *Semiconductors and Semimetals* **v34**, 547 (1991).
- KH Chow, B Hitti, RF Kiefl, *Semiconductors and Semimetals* **v51**, 137 (1998).
- RL Lichti, *Semiconductors and Semimetals* **v61**, 311 (1999).

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter 18 (2006) 1079–1119 doi:10.1088/0953-8984/18/3/022

Oxide muonics: II. Modelling the electrical activity of hydrogen in wide-gap and high-permittivity dielectrics

S F J Cox[1,2], J L Gavartin[2], J S Lord[1], S P Cottrell[1], J M Gil[3], H V Alberto[3], J Piroto Duarte[3], R C Vilão[3], N Ayres de Campos[3], D J Keeble[4], E A Davis[5], M Charlton[6] and D P van der Werf[6]

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[5] Department of Materials Science and Metallurgy, University of Cambridge, CB2 3QZ, UK
[6] Department of Physics, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK

IOP PUBLISHING REPORTS ON PROGRESS IN PHYSICS
Rep. Prog. Phys. 72 (2009) 116501 (130pp) doi:10.1088/0034-4885/72/11/116501

Muonium as a model for interstitial hydrogen in the semiconducting and semimetallic elements

S F J Cox

ISIS Muon Facility, Rutherford Appleton Laboratory, Chilton, OX11 0QX UK
and
Condensed Matter and Materials Physics, University College London, W1E 6BT UK

- Muons provide important information on isolated H in semiconductors .... *and more!*

End of Presentation