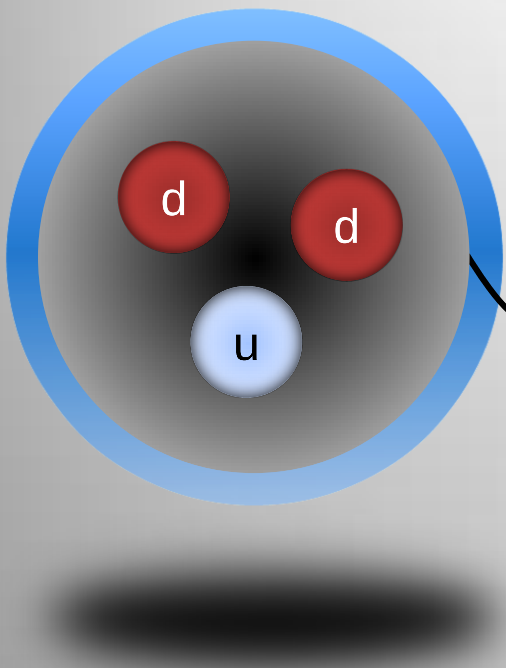
The Uniqueness and Impact of Using Neutrons to Characterize Semiconductor Materials

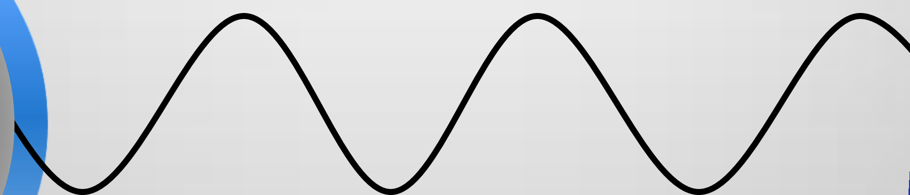
R. Gregory Downing

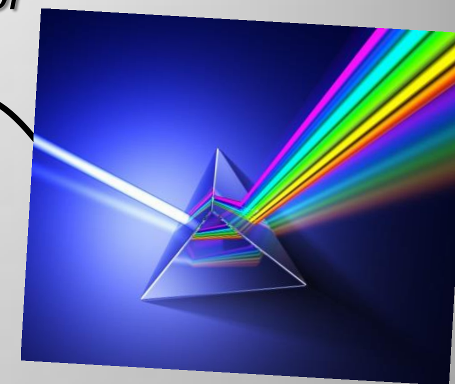
National Institute of Standards and Technology
Chemical Science Division
100 Bureau Drive, Gaithersburg, MD 20899

The Neutron

Exhibits both Particle & Wave Behavior

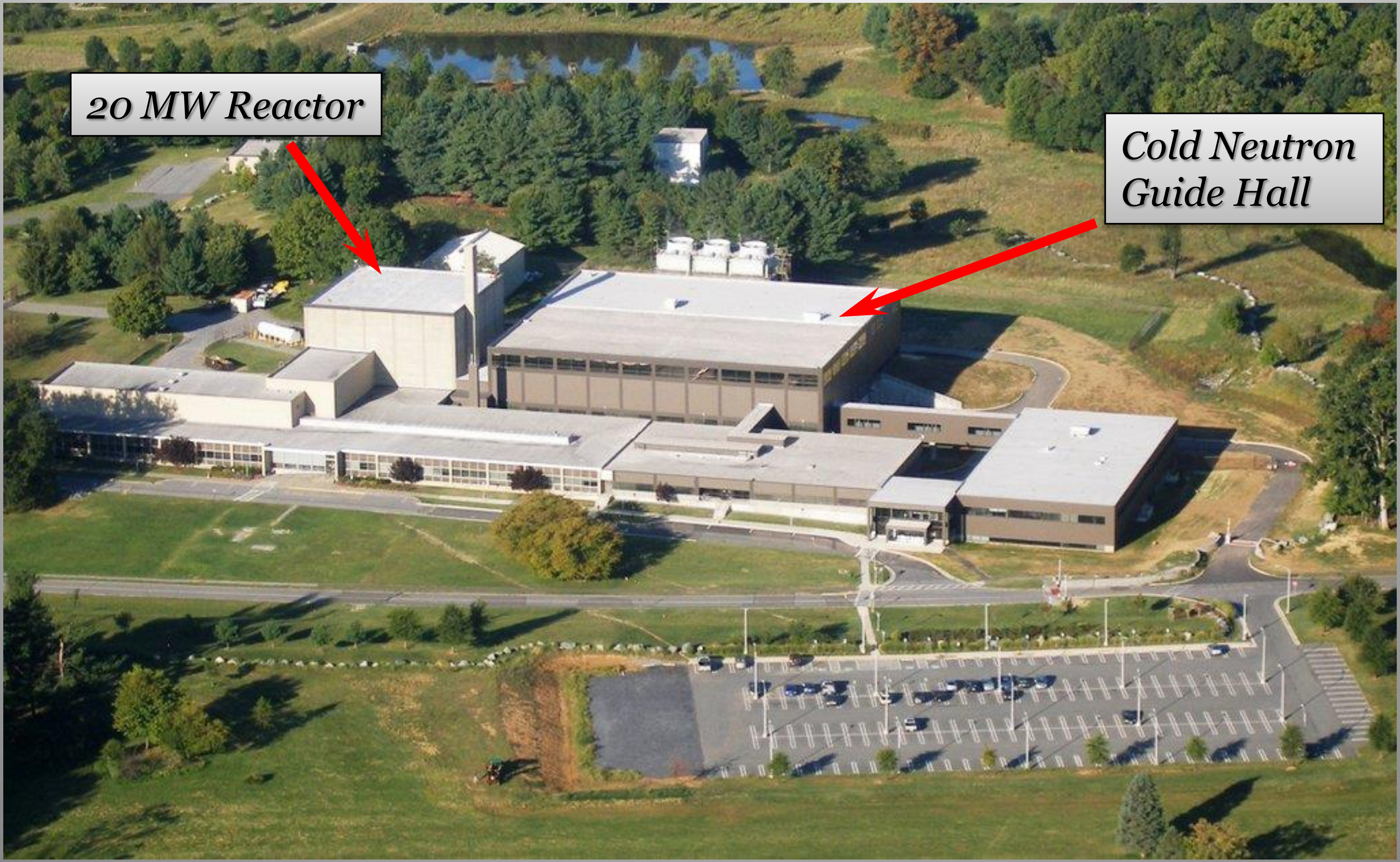




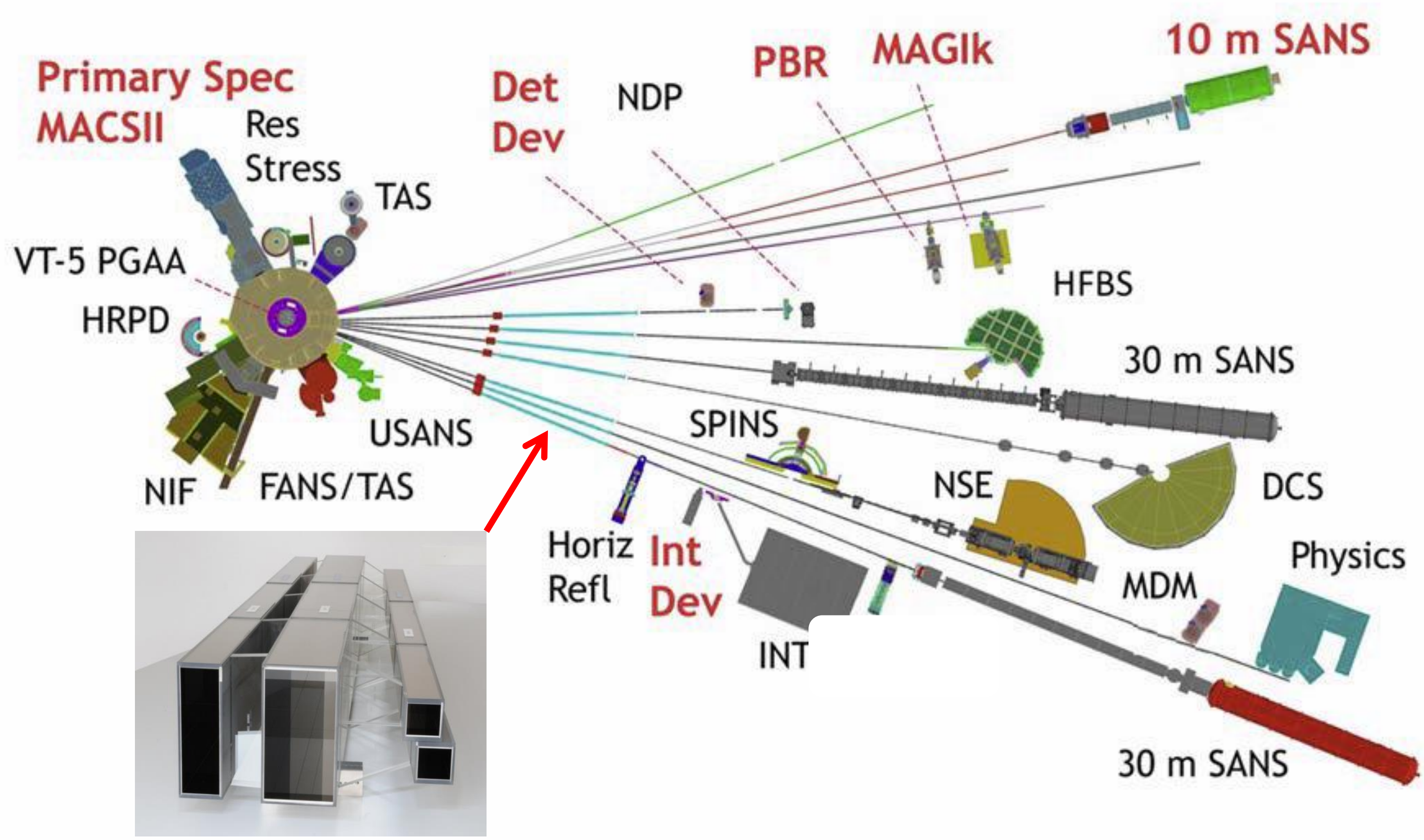


- Mass: $1.674927351(74)\times10^{-27}$ kg
- Net Charge: ~ 0
- Magnetic Dipole Moment: $-0.96623647(23)\times10^{-26}$ J·T−1
- Electric Dipole Moment: $<2.9\times10^{-26}$ e·cm
- Neutron Decay: 885.7 s mean life time

NIST Center for Neutron Research



NCNR Today & Looking to the Future



Major Neutron Research Facilities – World Wide

Asia and Australia – 7 Facilities

- Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, Australia
- China Advanced Research Reactor, Fangshan, Beijing
- High-flux Advanced Neutron Application Reactor (HANARO), Korea
- Japan Atomic Energy Research Institute (JAERI), Tokai, Japan
- Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan
- Kyoto University Research Reactor Institute (KURRI), Kyoto, Japan
- Reactor Triga Puspati (RTP), Malaysian Nuclear Agency, Malaysia

Europe – 13 facilities

- Budapest Neutron Centre, AEKI, Budapest, Hungary
- Berlin Neutron Scattering Center, Helmholtz-Zentrum Berlin, Germany
- Frank Laboratory of Neutron Physics, Joint Institute of Nuclear Research, Dubna, Russia
- FRM-II Research Reactor, Garching, Germany
- Institut Laue Langevin, Grenoble, France
- ISIS Pulsed Neutron and Muon Facility, Rutherford-Appleton Laboratory, Oxfordshire, UK
- JEEP-II Reactor, IFE, Kjeller, Norway
- Laboratoire Léon Brillouin, Saclay, France
- Ljubljana TRIGA MARK II Research Reactor, J. Stefan Institute, Slovenia
- Nuclear Physics Institute (ASCR), Rez nr Prague, Czech Republic
- Reactor Institute Delft, Delft University of Technology, Netherlands
- St. Petersburg Nuclear Physics Institute, Gatchina, Russia
- Swiss Spallation Neutron Source (SINQ), Villigen Switzerland

North and South America – 11 facilities

- Centro Atomico Bariloche, Rio Negro, Argentina
- Canadian Neutron Beam Centre, Chalk River, Ontario, Canada
- High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory, Tennessee, USA
- Los Alamos Neutron Science Center (LANSCE), New Mexico, USA
- Low Energy Neutron Source (LENS), Indiana University Cyclotron Facility, USA
- McMaster Nuclear Reactor, Hamilton, Ontario, Canada
- MIT Nuclear Reactor Laboratory, Massachusetts, USA
- NIST Center for Neutron Research, Gaithersburg, Maryland, USA
- Peruvian Institute of Nuclear Energy (IPEN), Lima, Peru
- Spallation Neutron Source, Oak Ridge National Laboratory, Tennessee, USA
- University of Missouri Research Reactor, Columbia, Missouri, USA

Neutrons as Metrological Probes

- Neutrons are **NEUTRAL** charged particles
  highly penetrating … compared to typical x rays
  yet are useful for mapping surface properties
  are nondestructive probes for structure
  are used to study samples in severe environments
  (hot, cold, pressure, vacuum, dynamic conditions
  … or a combination of environments)

- Neutrons are available in a wide range of **ENERGIES**
  similar to the elementary excitations in solids
  or molecular vibrations,
  or lattice modes,
  or the dynamics of atomic motion

- Neutrons have a **MAGNETIC** moment
  used to map magnetic structure of matter
  Profile magnetic domains covering multiple dimensions
  Measure dynamic magnetic fluctuations

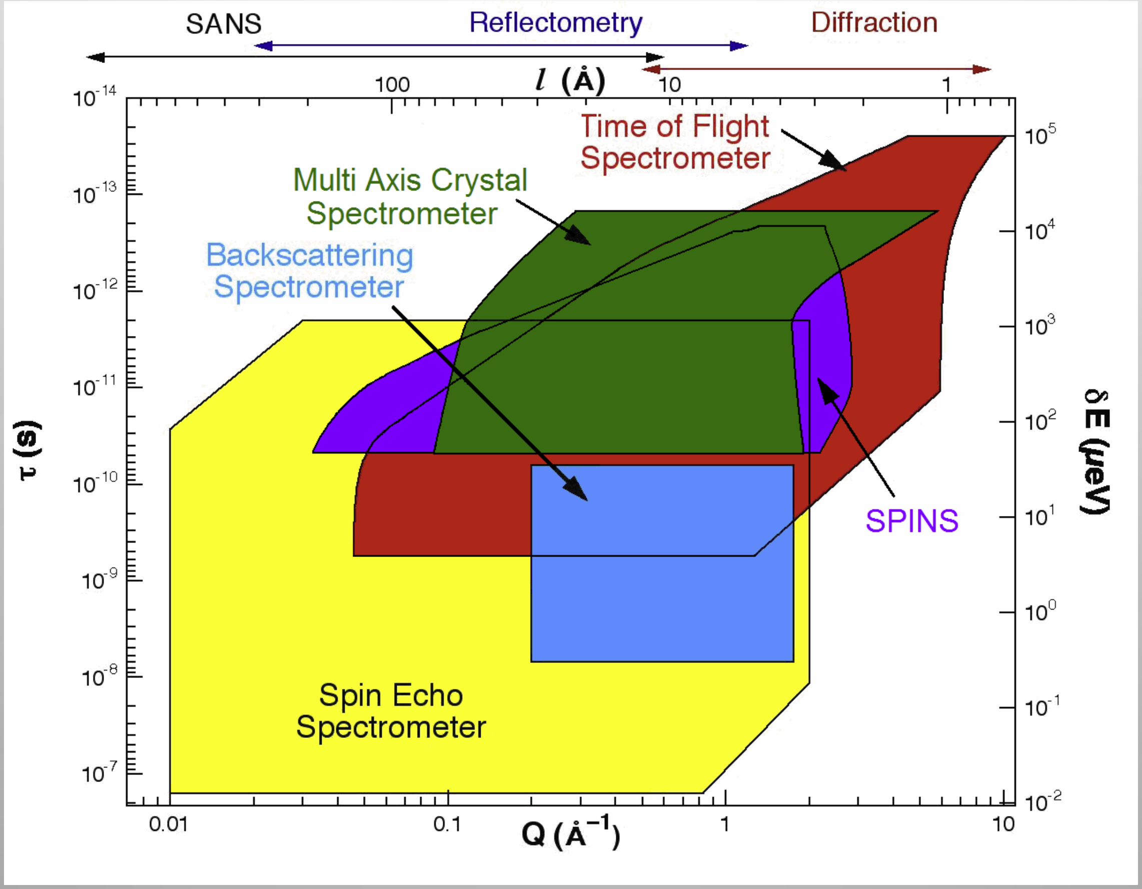
Neutrons Properties Continued

- Neutrons have **SPIN** (1/2) properties
  Polarized neutron beams are available
  used to study nuclear (atomic) orientation, and
  used for coherent and incoherent scattering

- Neutron have **WAVELENGTHS** (0.1 Å to 1000 Å)
  are comparable to atomic sizes
  and the inter-distance spacings of materials
  for the determination of structural variations

- Neutrons may be **CAPTURED** by nuclei
  to detect up to 74 elements – most of the periodic table
  detection limits of 10^{-7} g/g to 10^{-15} g/g (with caveats)
  notably sensitive to several of the light atoms

Scale of Structure and Dynamics



Updated version of fig. by Nickolas Rosov

NCNR instrument probes span:

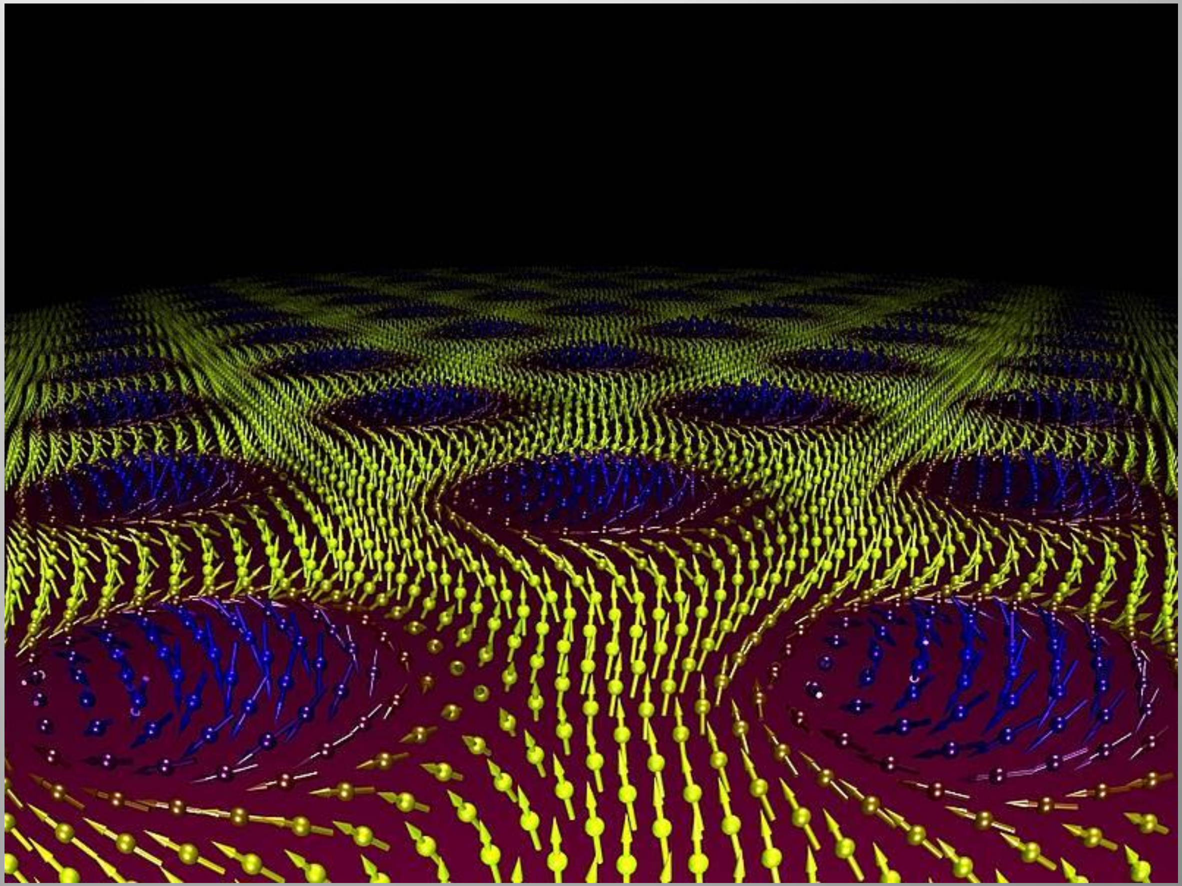
- 5 spatial orders (0.01 nm - 10 µm)
- 7 dynamic orders (10 neV - 100 meV)

Magnetic Vortices
“Imaged” by Neutron Scattering

Christian Pfleiderer (TUM) and his team had discovered a novel form of magnetic order consisting of magnetic vortices using neutrons at the FRM II. While this work triggered high

A second discovery of his group soon followed. Using neutron scattering, they showed that the magnetic vortices could be altered using a very low electric current.

The magnetic vortices are promising candidates for applications to information technology.



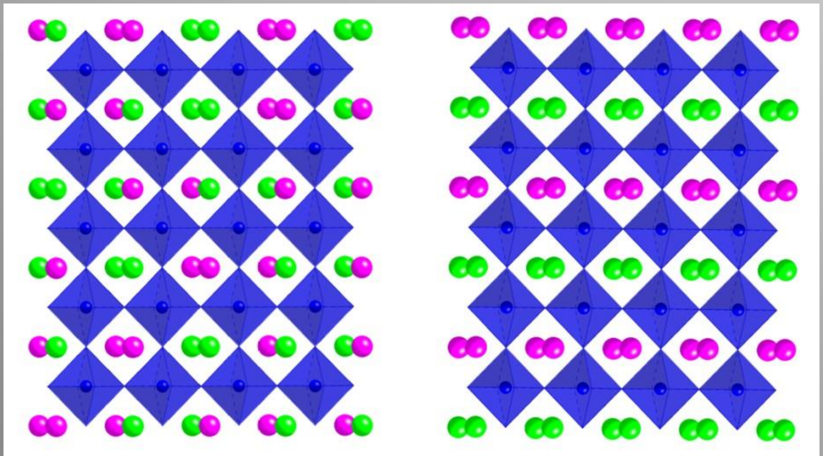
esciencenews.com/articles/2010/12/17/electric.current.moves.magnetic.vortices

Understanding the role of oxygen vacancies in spintronics semiconductor

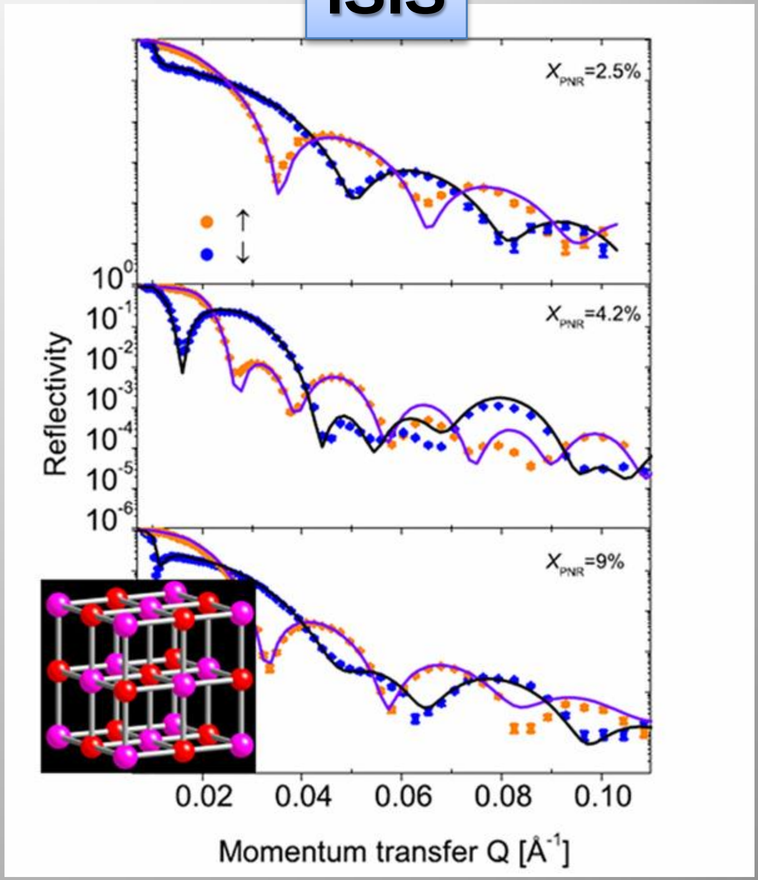
ISIS

Polarized *neutron reflectivity* data and model calculations as a function of oxygen deficiency.

Electron-doped europium oxide (EuO) is a semiconductor which undergoes a simultaneous ferromagnetic and metal-to-insulator phase transition, creating resistivity drops by 8 to 13 orders of magnitude.



http://www.nist.gov/ncnr/spintronic-101911.cfm



The inset shows the crystal structure of stoichiometric EuO.

M. Barbagallo et al., Phys. Rev. B. 84 (2011) 075219

NAA – RNAA – PGAA – NDP Standard Reference Materials

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2133

Phosphorus Implant in Silicon Depth Profile Standard

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2134

Arsenic Implant in Silicon Depth Profile Standard

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2137

Boron Implant in Silicon Standard for Calibration of Concentration in a Depth Profile

National Institut

Report of Investigation

Reference Material 8095

$Si_{1-x}Ge_x$ Films on Si

Neutron Transmutation Doping

National Institute of Standards & Technology

Certificate

Standard Reference Material® 2547

Silicon Resistivity Standard - 200 ohm·cm Level

SRM 2546 & 2547 are single Si wafers float zone (111) orientation and phosphorus-doped by the neutron transmutation doping process

Neutron Transmutation Doping (NTD) Needs (2012)

Materials for NTD are Si, Ge, GaAs, GaN, GaP, InP, InSe, HgCdTe, etc.

NTD float-zone Si *produces highest quality (most uniform) product among all doping methods,* devices with IGBTs are used to control electric traction motors in hybrid electric vehicles (HEV).

$$^{30}Si + n \rightarrow {}^{31}Si \rightarrow (\beta^-) \rightarrow {}^{31}P$$

*HEV and other **Green Technologies** continue to drive the demand for NTD Si and the demand is expected to out pace production.*

Ge doped by the NTD method is used for the far-infrared p-Ge laser and sensors including extremely low temperature devices like germanium cryogenic thermistors.

$$^{70}Ge + n \rightarrow {}^{71}Ge \rightarrow (EC) \rightarrow {}^{71}Ga$$

GaAs NTD with **Se** has some superior electronic properties over silicon for microwave frequency integrated circuits, infrared light-emitting diodes, laser diodes and solar cells.

GaN is transmuted into an n-type semiconductor by NTD with Ge

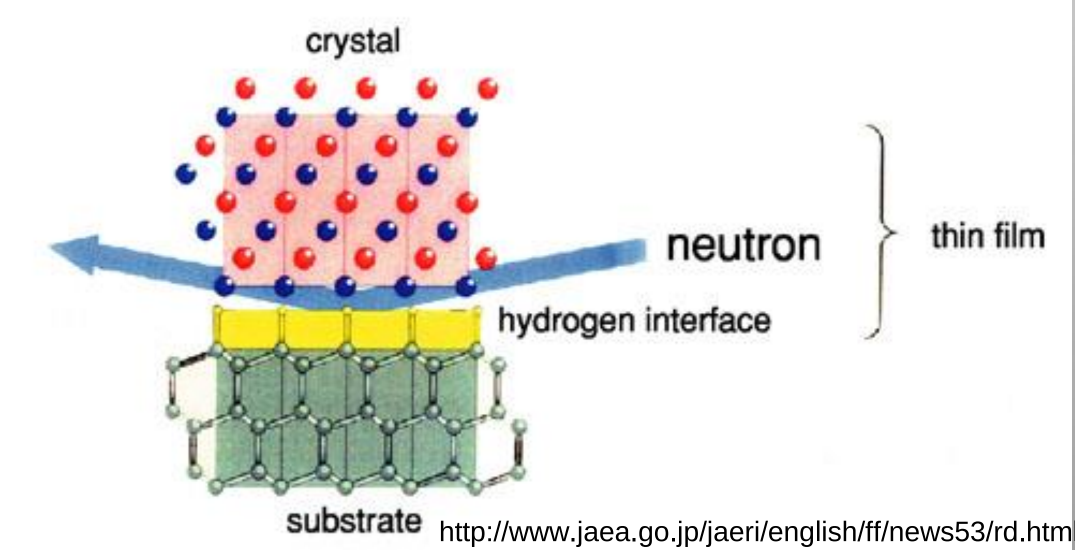
HgCdTeSe is converted by NTD into p-type material

$$^{74}Se + n \rightarrow {}^{75}Se \rightarrow (\beta^-) \rightarrow {}^{75}As$$

http://www-pub.iaea.org/MTCD/Publications/PDF/TE_1681_web.pdf

Neutron Reflectometry

JAERI researchers examine semiconductor structures and their properties with neutron reflectometry at JRR-3. They are able to *interrogate* the interface between a semiconductor substrate and a *monatomic hydrogen layer* introduced to facilitate lattice mismatched crystal growth. The H serves as an interfacial buffer layer that has less bonding energy than that between the substrate and the growing crystal. Findings feed back into improved manufacturing methods of thin films.



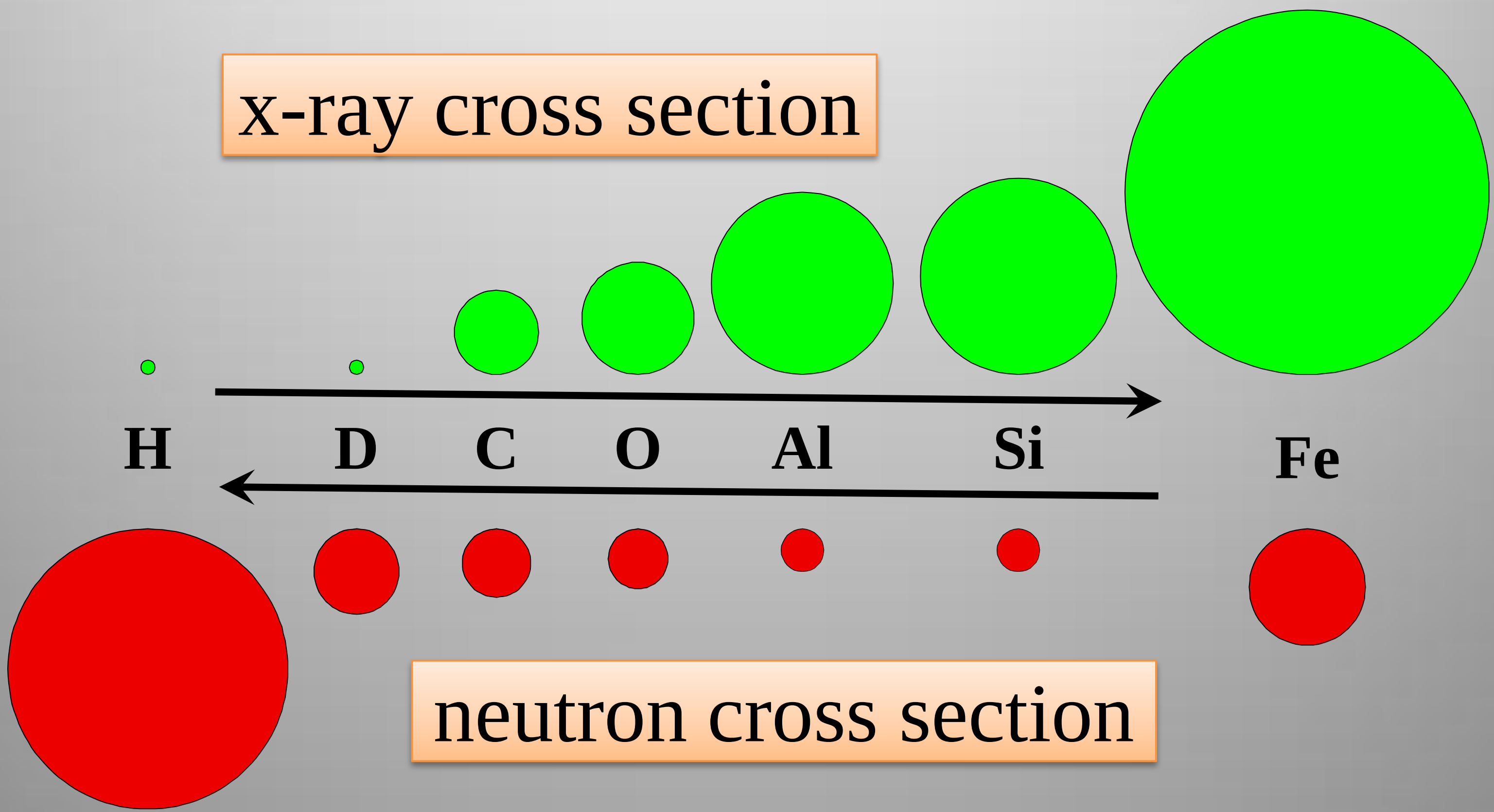
http://www.jaea.go.jp/jaeri/english/ff/news53/rd.html

Hydrogen interface characterized by using neutron reflectometry

http://www.jaea.go.jp/jaeri/english/ff/news53/rd.html

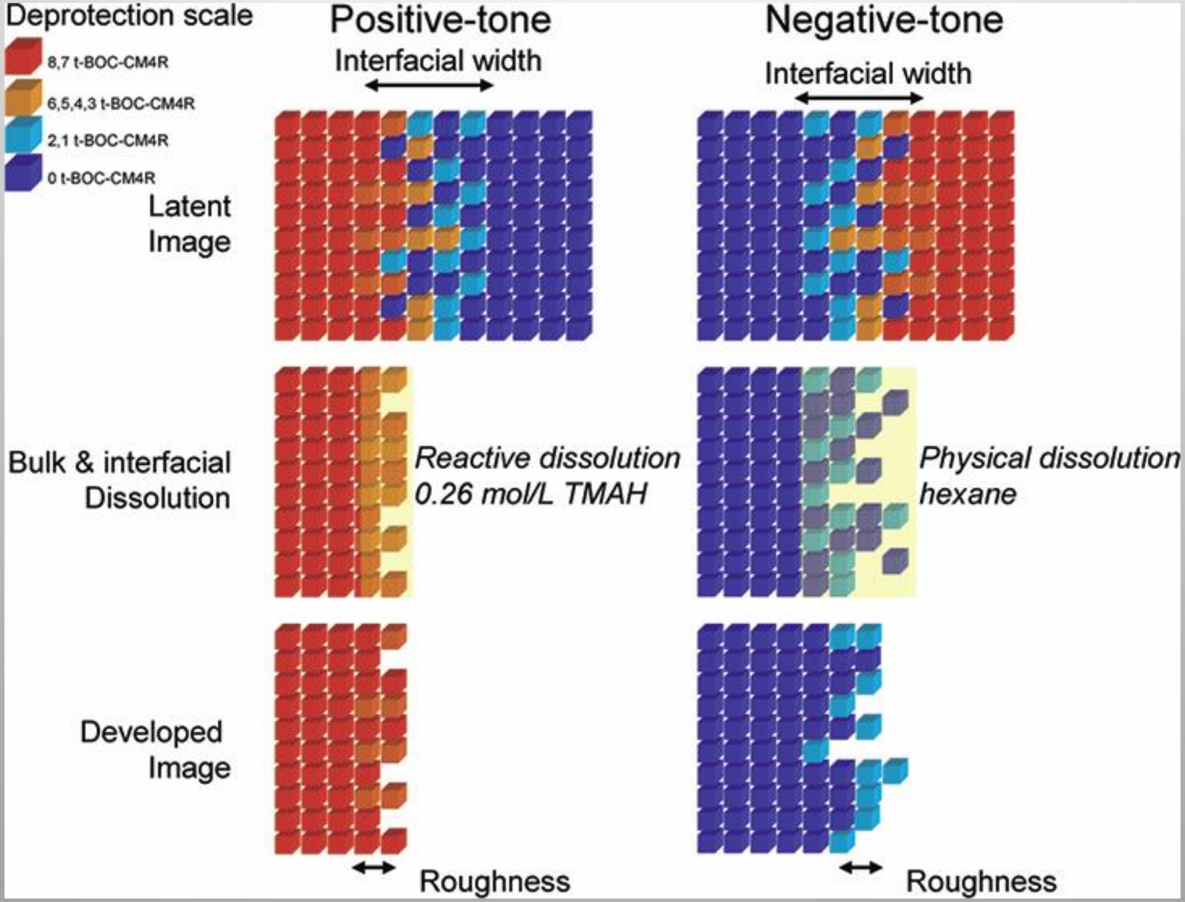
Neutrons vs. X-rays

Relative magnitude of x-ray and thermal neutron scattering cross sections for select elements



Updated version of fig. by D. Jacobson

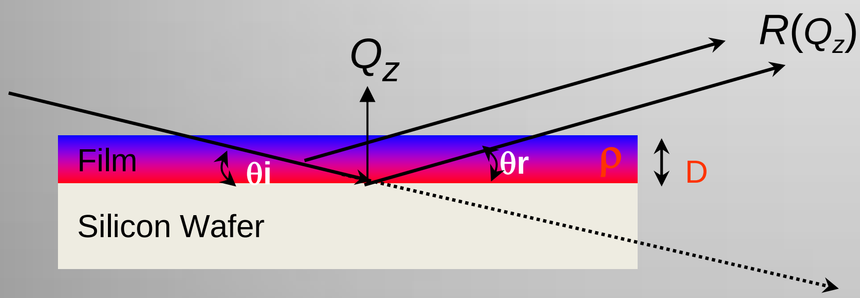
Very few techniques directly measure the nanometer-scale swelling at diffuse soft interfaces – but neutron reflectometry does.



"Neutron Reflectivity Characterization of the Photoacid Reaction-Diffusion Latent and Developed Images of Molecular Resists for Extreme Ultraviolet Lithography," Vivek M. Prabhu, Shuhui Kang, Jing Sha, Peter V. Bonnesen, Sushil Satija, Wen-li Wu, and Christopher K. Ober, **2012** Langmuir 7665-7678.

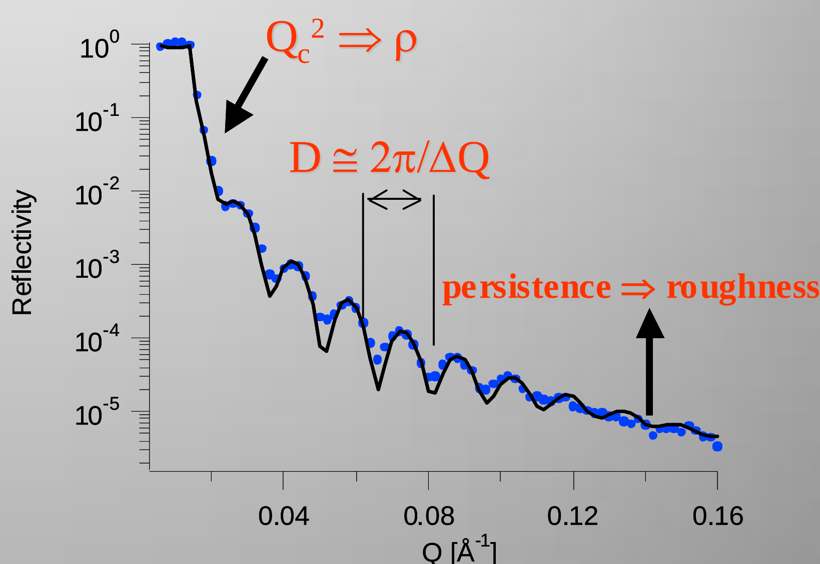
Specular Reflectivity (Neutrons or X-rays)

NR provides detailed information about the structure of the sample surface, including the ***thickness, density, roughness, or magnetic make-up*** of any thin films layered on the substrate – notably H, C, N, O, …



$$Q_z = \frac{4\pi}{\lambda}\sin(\theta_i)$$

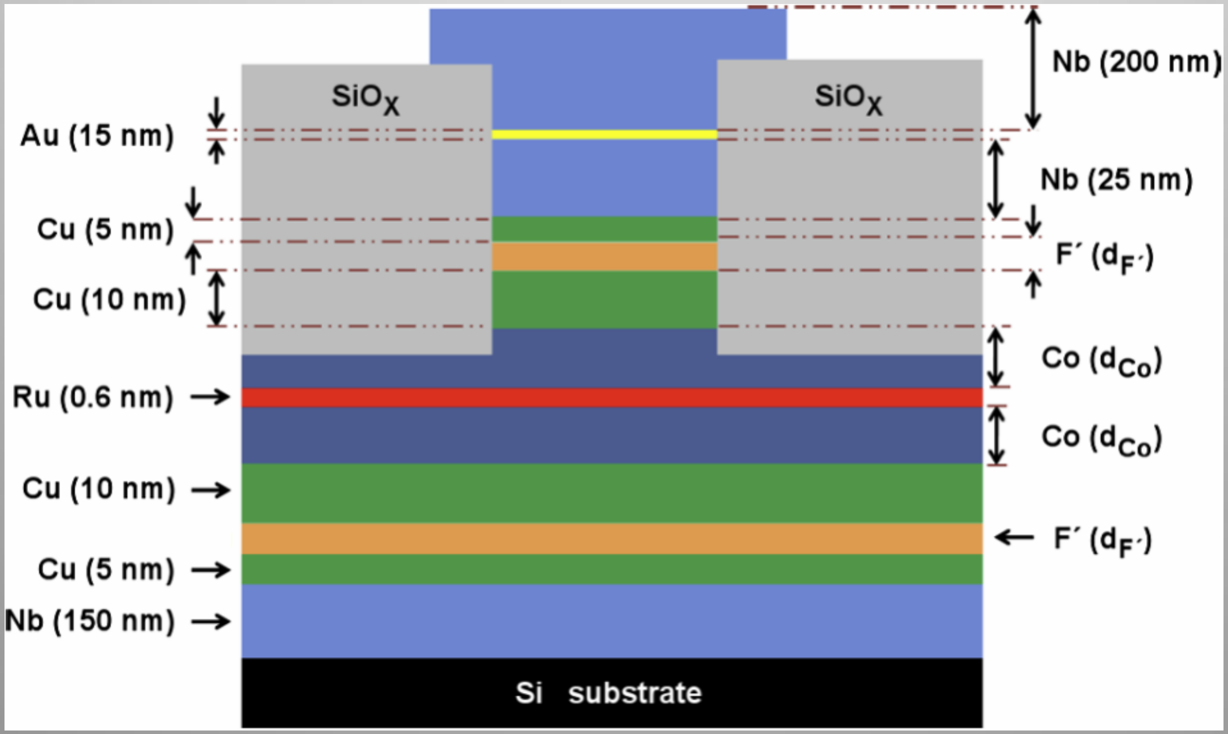
Neutrons: λ = 0.475 nm
X-ray: λ = 0.154 nm



$R[q] \xleftarrow{\text{model}} \rho[z]$

Spin-polarized Neutron Reflectometry

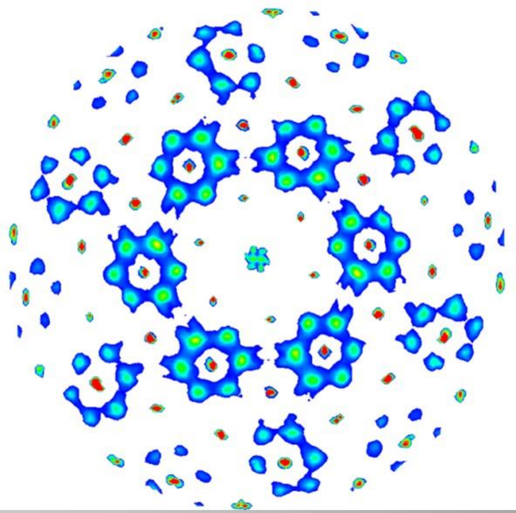
Superconductivity and ferromagnetism rarely coexist. In work performed at NIST, researchers observed long-range spin-triplet supercurrents in Josephson junctions containing ferromagnetic(F) materials, … *They showed that the spin-triplet supercurrent is enhanced up to 20 times after samples were subjected to a large in-plane field*. … direct experimental evidence was obtained for the spin-flop transition using both scanning electron microscopy with polarization analysis and spin-polarized neutron reflectometry. These results suggest experimental control of spin-triplet supercurrents are possible.



Optimization of Spin-Triplet Supercurrent in Ferromagnetic Josephson Junctions, Carolin Klose, et al., Phys. Rev. Lett. 108,127002 (2012)

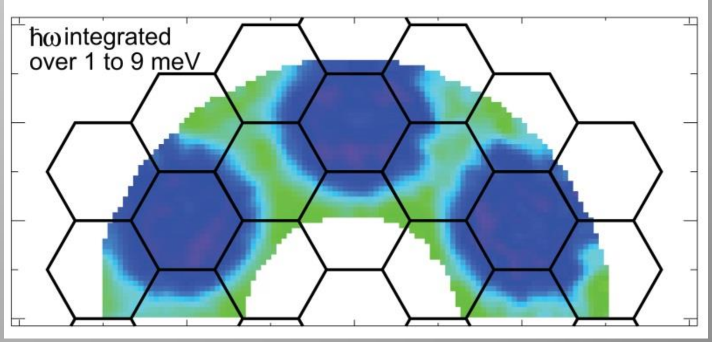
Discovery of Novel Quantum Spin-“Liquid”

"In this particular structure the copper atoms exhibit unusual properties generally associated with liquids. Specifically, their magnetic orientation remains in a constant state of flux… Magnetic neutron scattering gave us a clear indication of some sort of quantum mischief in this compound," Broholm says. "The data show the spins don't develop static long-range order, but instead ***behave as a magnetic quantum fluid*** …This could provide new opportunities in materials science and engineering "



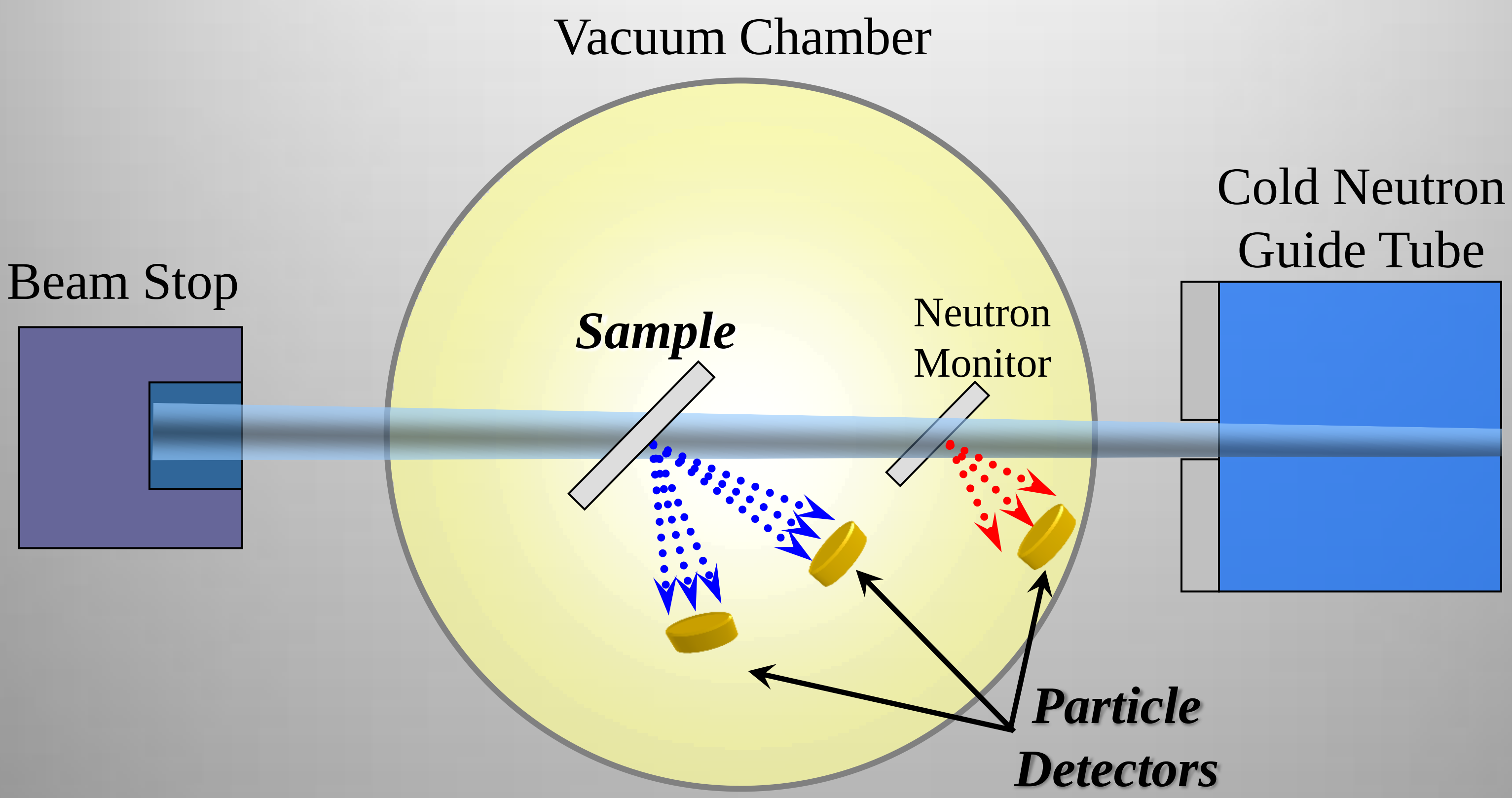
Credit: H. Sawa/Nagoya University

The NIST findings were among the first to be made with the NCNR's ***multi-axis crystal spectrometer (MACS)***, which is supported in part by the National Science Foundation



*S. Nakatsuji, K. Kuga, K. Kimura, R. Satake, K. Katayama, E. Nishibori, H. Sawa, R. Ishii, M. Hagiwara, F. Bridges, T. U. Ito, W. Higemoto, Y. Karaki, M. Halim, A.A. Nugroho, J.A. Rodriguez-Rivera, M.A. Green, and C. Broholm. Spin-orbital short-range order on a honeycomb-based lattice. *Science*, May 4, 2012: Vol. 336 no. 6081 pp. 559-563 DOI: 10.1126/science.1212154

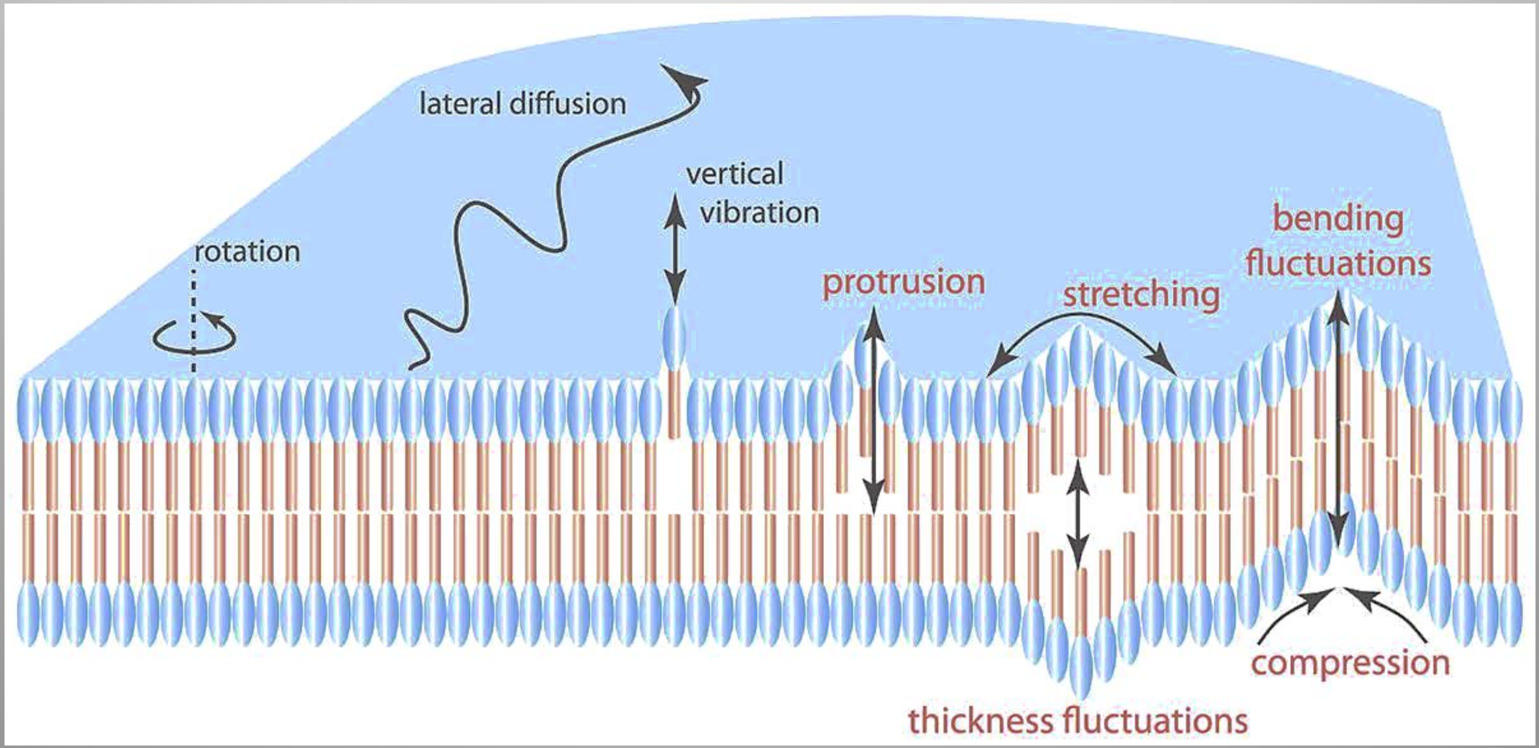
Neutron Depth Profiling



- Determine **concentration vs depth profiles** throughout the first few micrometers of surface
- **Few nanometer depth resolution** depending on the depth, reaction, and material

Fluctuations measured in a biological membrane for the first time directly. **Neutron spin echo spectroscopy** to experimentally reveal such fluctuations in a pure, fully saturated, phosphocholine lipid bilayer system.

The amplitude of the thickness fluctuations is 3.7 Å ± 0.7 Å which agrees well with theoretical calculations and molecular dynamics simulations

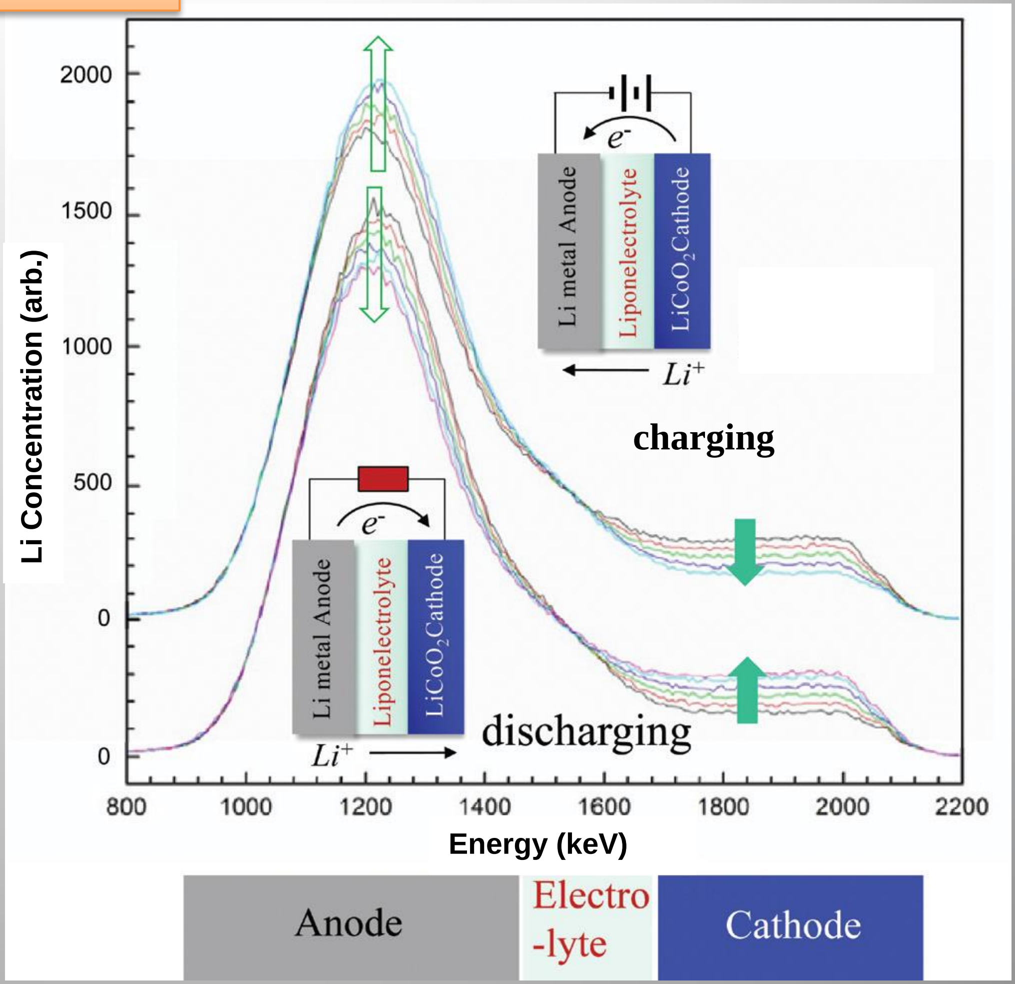


Woodka et. al., PRL 109 058102 (2012)

Lithium Battery Development

- Companies, universities and federal laboratories seek analytical techniques to assist in the development of powerful and longer lasting lithium ion batteries.

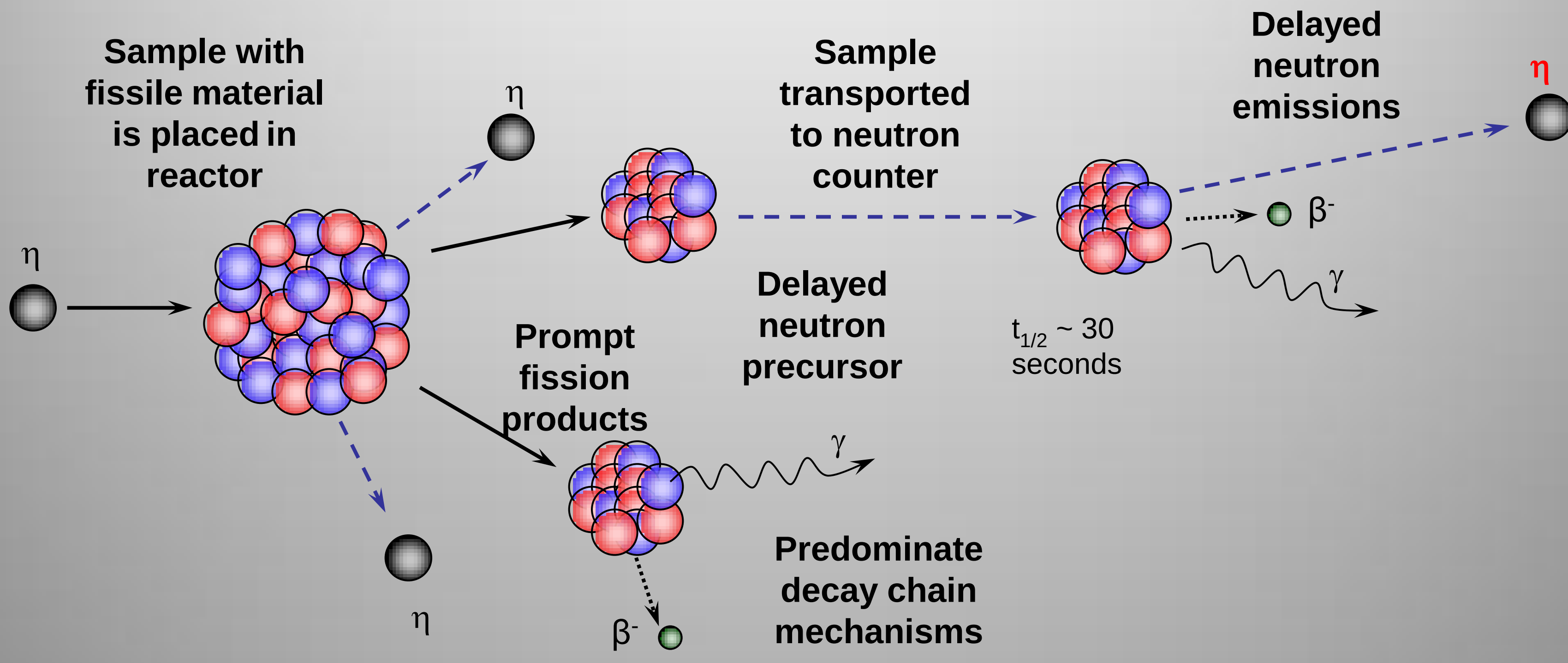
- ***Neutron Depth Profiling (NDP)***, a nondestructive analytical technique, determines the depth distribution and dynamic shift of lithium ions within the batteries while they operate.



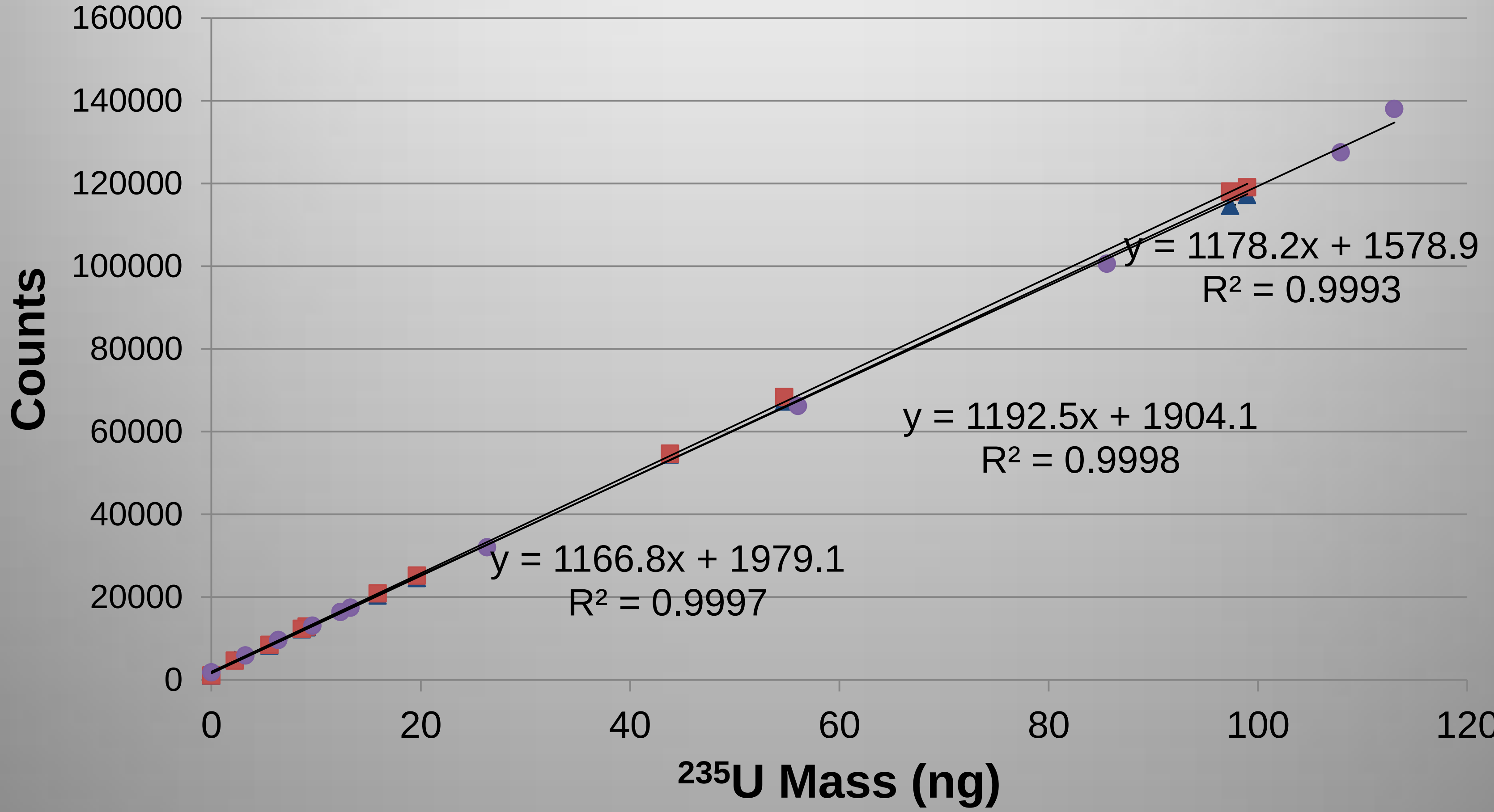
http://www.ncnr.nist.gov/AnnualReport/FY2010/AR_2010.pdf

NDP spectra show the lithium distributions in a thin film Li battery. (The discharge spectra set is offset by 500 units.) The time sequence of Li depth profiles are captured during the battery charging and discharging. Below the graph, colored strip illustrates the approximate positions of the battery components in the NDP spectra.

Delayed Neutron Activation Analysis (DNAA) Principle



Delayed Neutron Activation Analysis Linear Response (mg to pg range)



Advantages of DNAA

- Rapid
  - Approximately 5 min analysis time per sample
- Highly Selective
  - Responds only to fissile materials, e.g. ^{235}U
- Non-destructive
  - Samples can be analyzed multiple times or by alternative techniques
- Matrix-independent
  - Ceramics, raw materials, polymers, adhesives, etc.
- Sensitive
  - Potential for measuring sub-nanogram levels in up to 30 mL of material

Key Points to Take Away

- Neutron techniques compliment other metrological techniques
- Nondestructive multi-dimensional probe of electron spin, chemical composition, magnetics structure, crystal structure, lattice stress – even man-made nano devices
- Relatively inexpensive, but beam time is limited
- Proprietary research & measurements
- The number and quality of neutron instruments are in constant development – world wide.

The Uniqueness and Impact of Using Neutrons to

Characterize Semiconductor Materials

Presented 27 March 2013

Frontiers of Characterization and Metrology for Nanoelectronics
NIST, Gaithersburg, MD