

# Some Applications of Neutron Scattering to Condensed Matter Physics

Stephen E. Nagler

Chief Scientist, NSSD

Oak Ridge National Laboratory



# Outline

- I. Quick Introduction to Neutron Scattering (reminder)
- II. Neutron Diffraction - examples
  - Hydrogen, ice and related materials
  - Magnetic structures
  - In-situ processing
- III. An Advanced example: New Fe based superconductors
  - Magnetic structure
  - phonons
  - A clue? The “resonance”

# The Nobel Prize in Physics 1994



Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.



**S** Shull made use of **elastic scattering** i.e. of neutrons which change direction without losing energy when they collide with atoms.

Because of the wave nature of neutrons, a diffraction pattern can be recorded which indicates where in the sample the atoms are situated. Even the placing of light elements such as hydrogen in metallic hydrides, or hydrogen, carbon and oxygen in organic substances can be determined.

The pattern also shows how atomic dipoles are oriented in magnetic materials, since neutrons are affected by magnetic forces. Shull also made use of this phenomenon in his neutron diffraction technique.



An early crystal neutron diffractometer with rotating neutron source here used by G.D. Shull and C.G. Shull, working at Oak Ridge National Laboratory.

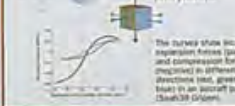
## Neutrons see more than X-rays

X-rays are scattered by electronic centers in atoms, nuclei. With X-rays it is easier to see atoms that have many electrons. Hydrogen, for example, which has only one electron, is not so easy to see. With neutrons, all kinds of atoms are visible.



## Neutrons reveal inner stresses

A hole has been punched in an important metal aircraft part. Does the part match up? Neutron diffraction can show how much the distance between the atoms has changed and hence the internal forces remaining around the hole after it has been punched.



## Neutrons show what atoms remember

Of their earlier positions when they move randomly in relation to each other in liquids and melts. Even here there is in fact some local order. The atoms cannot move infinitely close to each other. Some distances are more common than others.



Neutrons behave as particles and as waves

The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.

Bertram N. Brockhouse, McMaster University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.



**B** Brockhouse made use of **inelastic scattering** i.e. of neutrons, which change both direction and energy when they collide with atoms. They then start or cancel atomic oscillations in crystals and record movements in liquids and melts. Neutrons can also interact with spin waves in magnets.

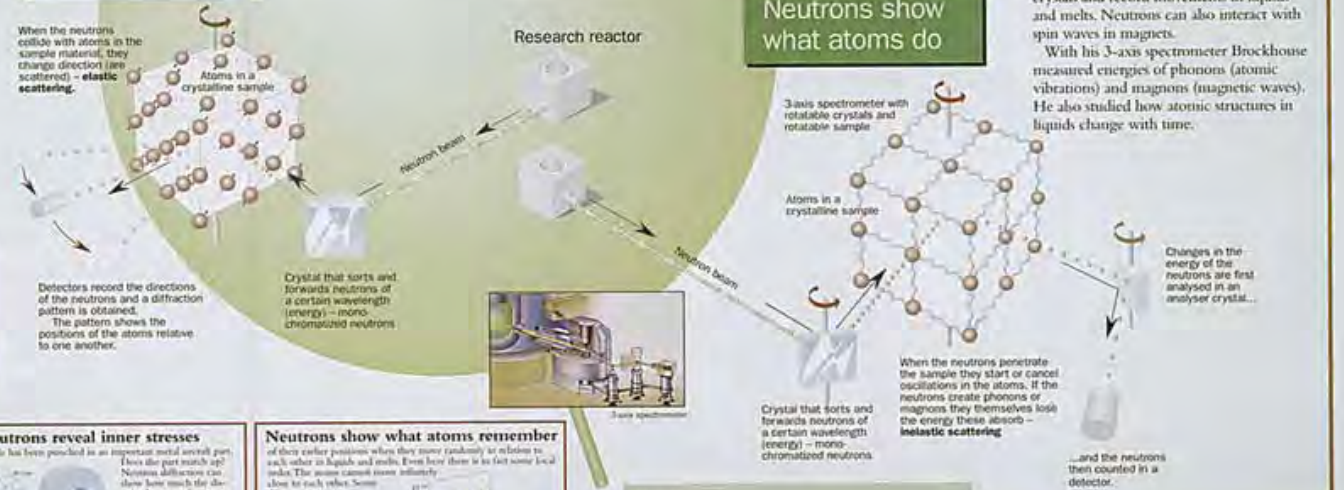
With his 3-axis spectrometer Brockhouse measured energies of phonons (atomic vibrations) and magnons (magnetic waves). He also studied how atomic structures in liquids change with time.

# Neutrons reveal structure and dynamics

Neutrons show where atoms are

Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.

Neutrons show what atoms do



**How it started**  
Brockhouse and Shull made their pioneering contributions at the first nuclear reactors in the USA and Canada back in the 1940s and 1950s. It was then that the resources of the reactors became available for peacetime research.

**...how it continues**  
Thousands of researchers are now working at the many neutron research centers throughout the world. New and very advanced neutron scattering installations have been built and more are planned in Europe, the USA and Asia. At these super-installations the researchers are studying the structure of new ceramic superconductors, molecular movements on surfaces of interest for catalytic exhaust cleaning, virus structures and the connection between the structure and the elastic properties of polymers.

KUNGLIGA VETENSKAPSAKADEMIEN  
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Information Department, Box 50006, S-171 05 Stockholm, Sweden. Tel: +46 8 73 95 80. Fax: +46 8 15 56 55. E-mail: Sekretariat@kva.se, kva@kva.se, kva@kva.se, The Royal Swedish Academy of Sciences, c/o Box 118, S-171 05 Stockholm, Sweden. Tel: +46 8 73 95 80. Fax: +46 8 15 56 55. E-mail: Sekretariat@kva.se, kva@kva.se, kva@kva.se, The Royal Swedish Academy of Sciences, c/o Box 118, S-171 05 Stockholm, Sweden. Tel: +46 8 73 95 80. Fax: +46 8 15 56 55. E-mail: Sekretariat@kva.se, kva@kva.se, kva@kva.se.

### Further reading:

- D.J. Hughes: The Nobel Prize in Physics 1994. SCIENTIFIC AMERICAN, 1994, 269(11), 74-81.
- H. Langer and J. Frenkel: The European Spallation Source. SCIENTIFIC AMERICAN, 1994, 270(1), 40-45.
- Information about the Nobel Prize in Physics 1994 (available at THE ROYAL SWEDISH ACADEMY OF SCIENCES)



# Neutrons as a probe of condensed Matter

## Compared to x-rays:

- similar wavelength: structure of materials
- weaker interactions: bulk probe
- nuclear scattering: sensitive to both light and heavy elements
- magnetic moment: sensitive to magnetic structure
- low (meV) energy: collective excitations - phonons, magnons

# Development of Neutron Diffraction



Neutron diffraction was pioneered at ORNL by Clifford Shull and Ernest Wollan, pictured above. An early version of the apparatus is shown at right. This work resulted in the award of the Nobel prize to Shull in 1994.

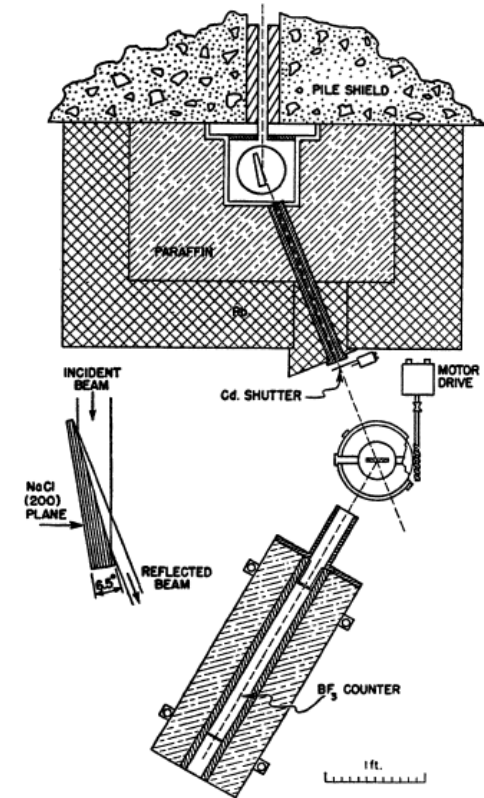


FIG. 1. Arrangement of apparatus, showing the monochromating crystal (detailed in left center) collimating slits, shielding, second spectrometer with location of powder specimen and counter.

Shull and Wollan established the rules for scattering lengths of H and D (below left), and used this to prove that Pauling's model was the correct description for the structure of water (right).

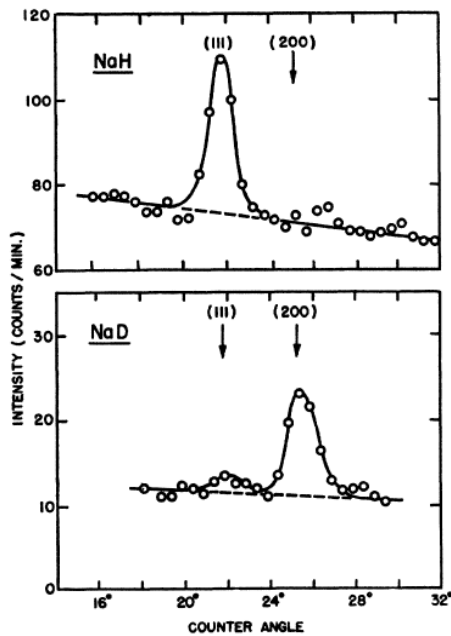


FIG. 1. Powder diffraction patterns over the (111) and (200) peaks of NaH and NaD. The diffuse scattering for NaH is seen to be much larger than that for NaD.

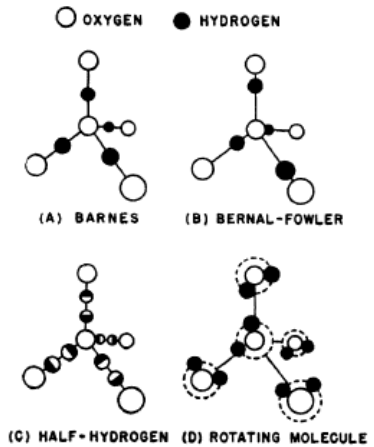


FIG. 2. Schematic diagram of four structural models which are used in calculating pattern intensities for various proposed structures of ice.

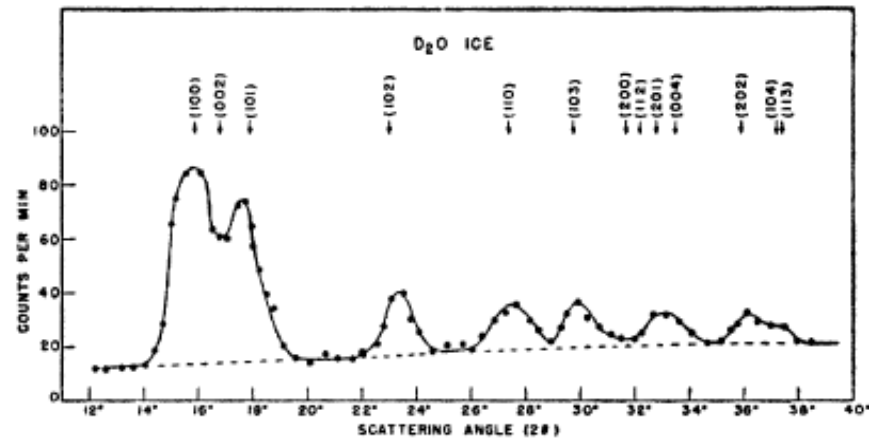
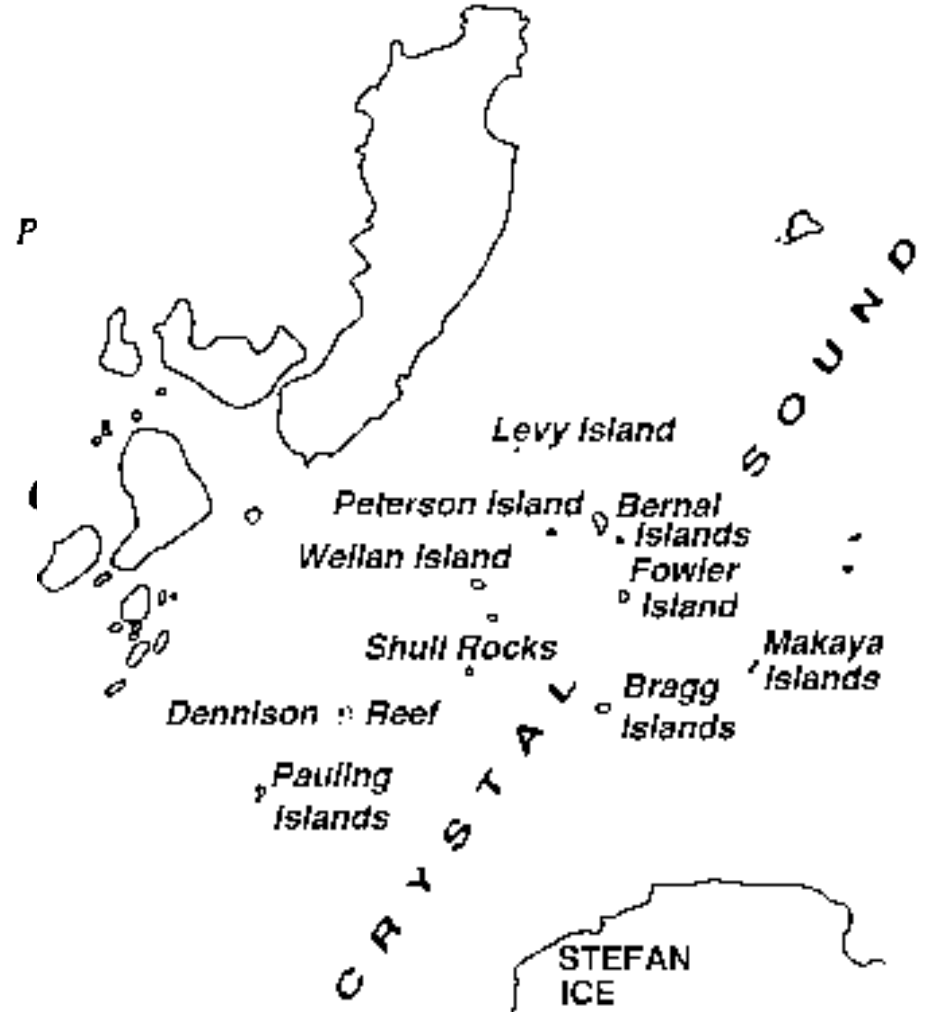
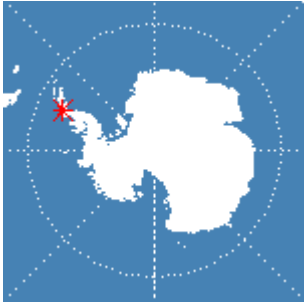


FIG. 1. Neutron diffraction powder pattern of heavy ice ( $D_2O$ ) taken at  $-90^\circ C$  with neutrons of wave-length 1.06Å.

- C. G. Shull, E. O. Wollan, G. A. Morton, and W. L. Davidson, *Neutron diffraction studies of NaH and NaD*, Phys. Rev. **73**, 842-847 (1948).
- E. O. Wollan, W. L. Davidson, and C. G. Shull, *Neutron diffraction study of the structure of ice*, Phys. Rev. **75**, 1348-1352 (1949).

# H-Bonding in Crystals & Structure of Ice

- Henri Levy, Selmer Peterson & colleagues in Chemistry Division
- Wollan & Shull



# Growth of Ferroelectric Ice Observed by Time-Resolved Neutron Diffraction

A full understanding of the properties of ice is of great interest for many branches of research, notably including earth and planetary sciences. Recent work using the WAND instrument at HFIR has shown that the stable phase of ice at low T and ambient pressure may be a ferroelectric structure known as ice XI (see figure 1, below).

If true, this may mean that ice particles in interstellar space or on remote planets might generate a spontaneous electric field. This could explain some anomalous spectra observed in interstellar space, and may also play a role in phenomena like the formation of planetary rings.

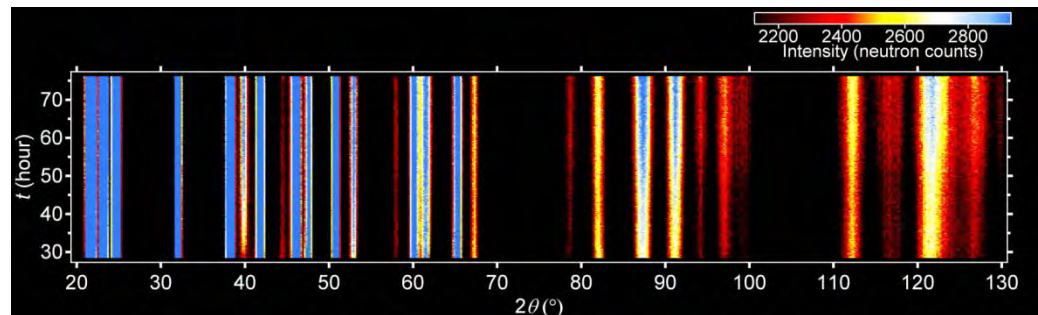


Fig. 2 Time-resolved diffraction pattern of ice measured at HFIR using the WAND

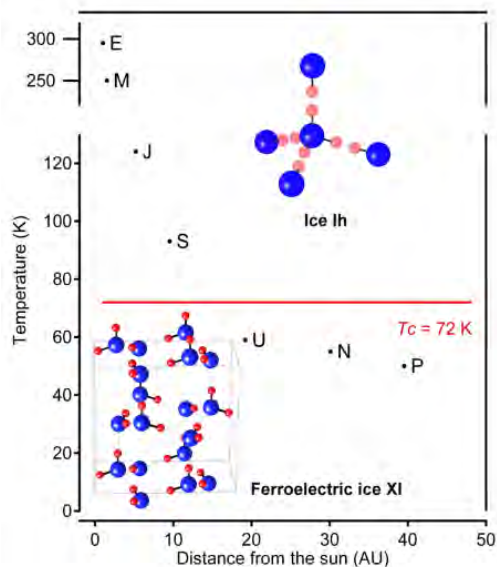


Fig. 1 Atomic structure of (top) ordinary ice and (bottom) ice XI.

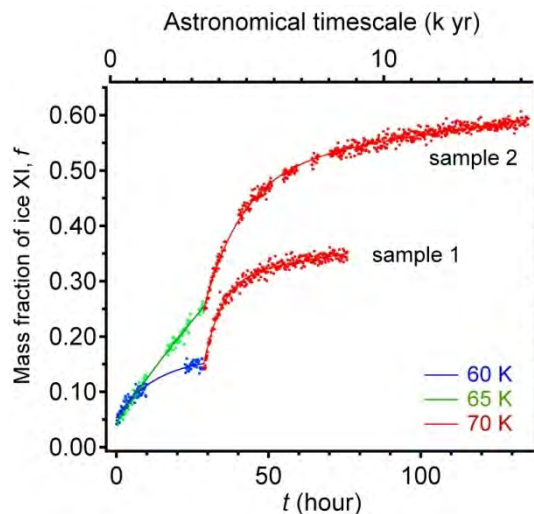
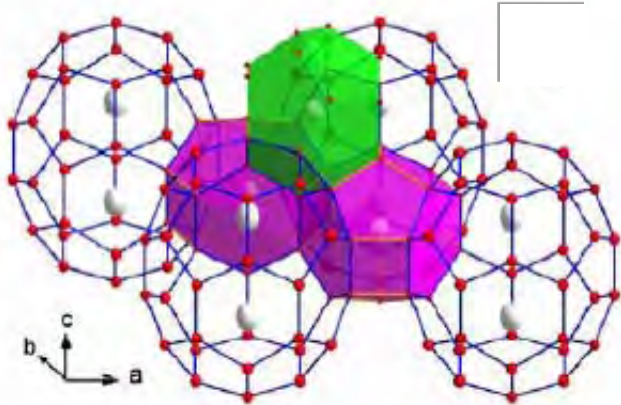


Fig. 3 Mass fraction of ice XI vs. time for deuterated ice doped with an impurity. The fraction reaches unity after approximately 28 days for temperatures around 65K.

H. Fukazawa, A. Hoshikawa, Y. Ishii, B.C. Chakoumakos, and J.A. Fernandez-Baca, "Existence of Ferroelectric Ice in the Universe." *The Astrophysical Journal*, Vol. 652, L57-L60 (2006)

## Example: Clathrates

The word clathrate is derived from the Latin Clatratus meaning with bars or a lattice; Made up of bars or railings



Gas hydrates are formed by a lattice of water molecules that encloses molecules of a trapped gas. A large amount of methane is naturally 'frozen' in this form, it has been discovered both in permafrost formations and on the ocean floor.



In-situ neutron studies of clathrate structures at high pressure are planned by C. Tulk and colleagues.

# Neutrons and Antiferromagnetic Structure

C.G. Shull, W.A. Strauser and E.O. Wollan, Phys. Rev. **83**, 333 (1951).

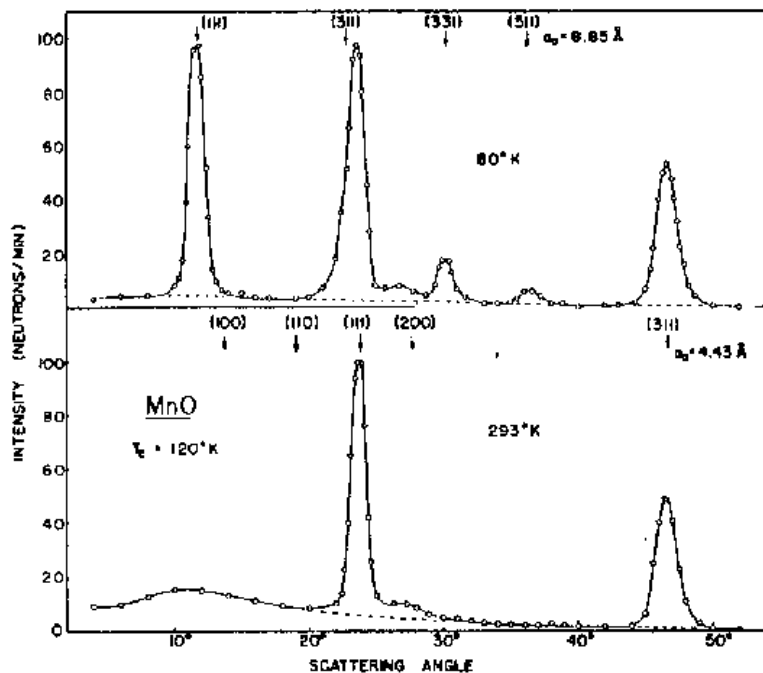


FIG. 4. Neutron diffraction patterns for MnO taken at liquid nitrogen and room temperatures. The patterns have been corrected for the various forms of extraneous, diffuse scattering mentioned in the text. Four extra antiferromagnetic reflections are to be noticed in the low temperature pattern.

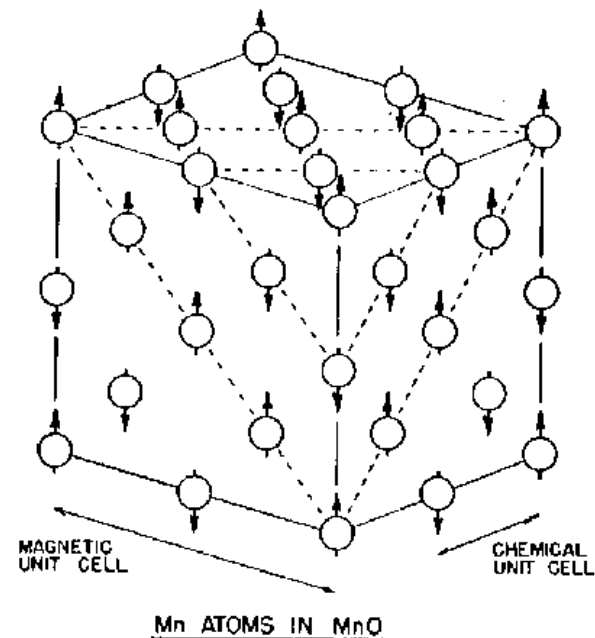
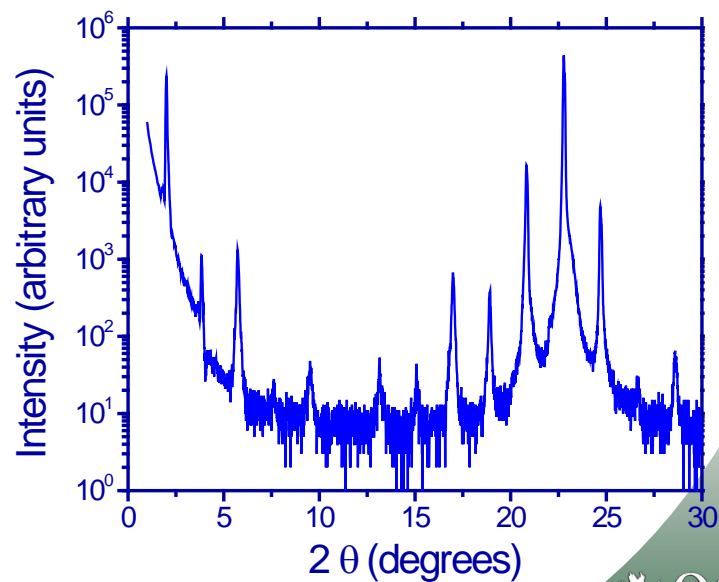
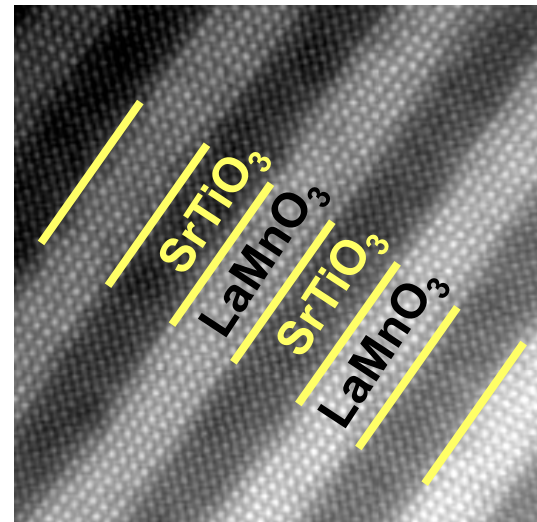
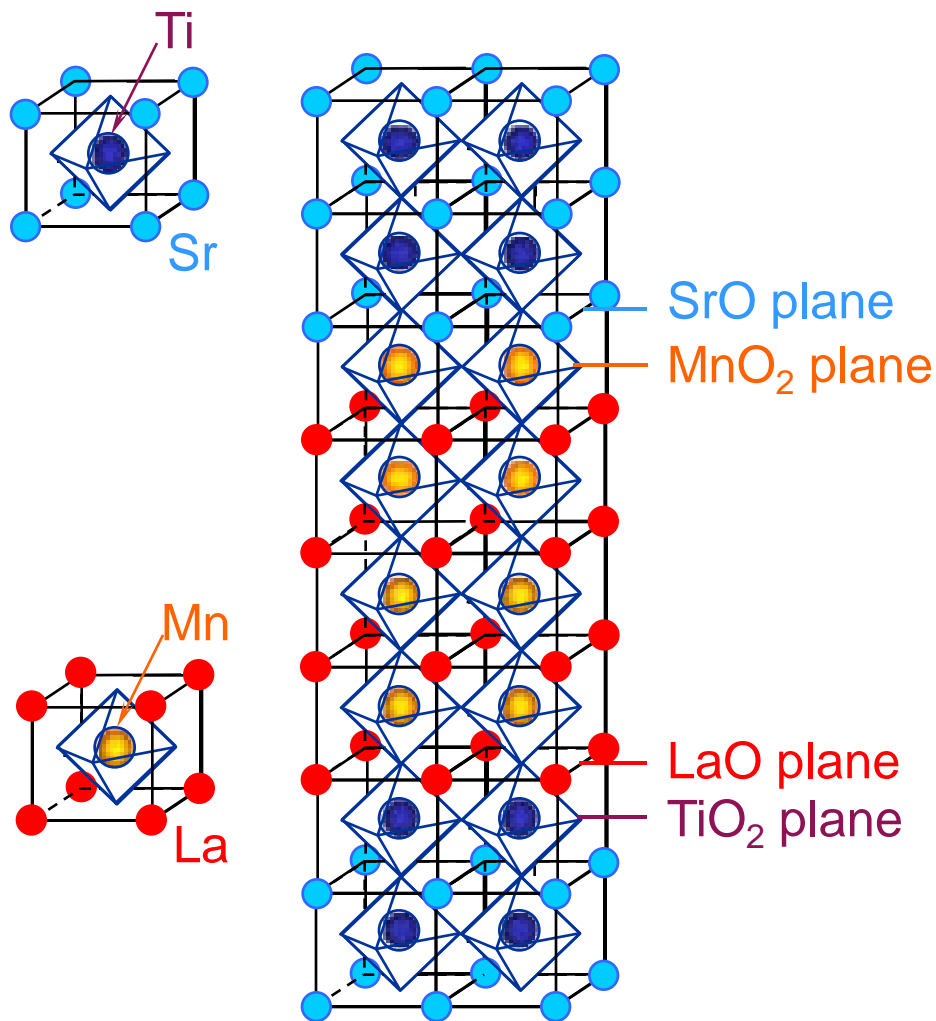


FIG. 5. Antiferromagnetic structure existing in MnO below its Curie temperature of 120°K. The magnetic unit cell has twice the linear dimensions of the chemical unit cell. Only Mn ions are shown in the diagram.

# Interfacial magnetism in $\text{LaMnO}_3 / \text{SrTiO}_3$ superlattices

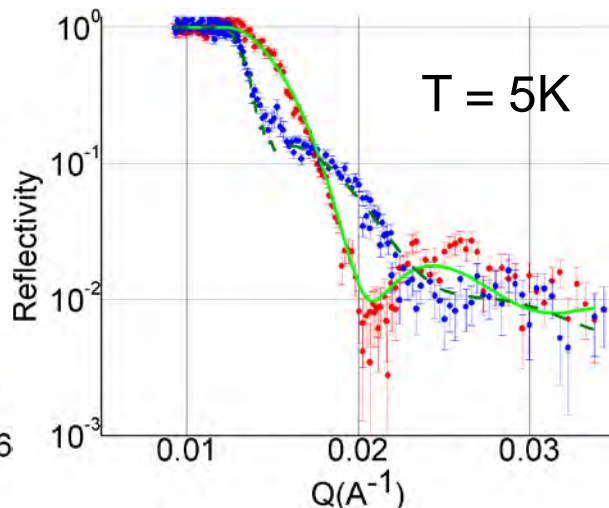
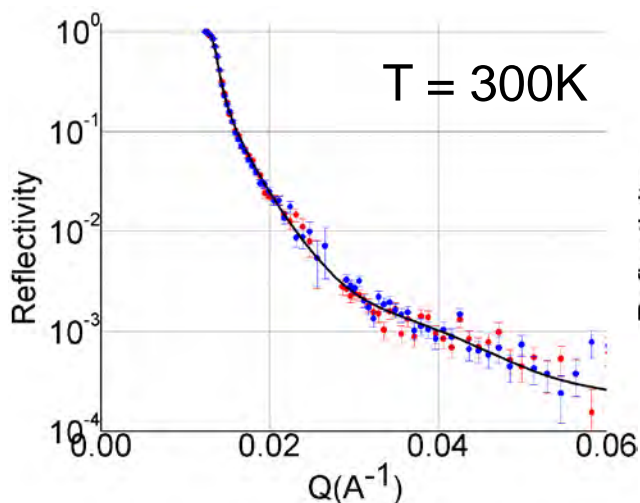
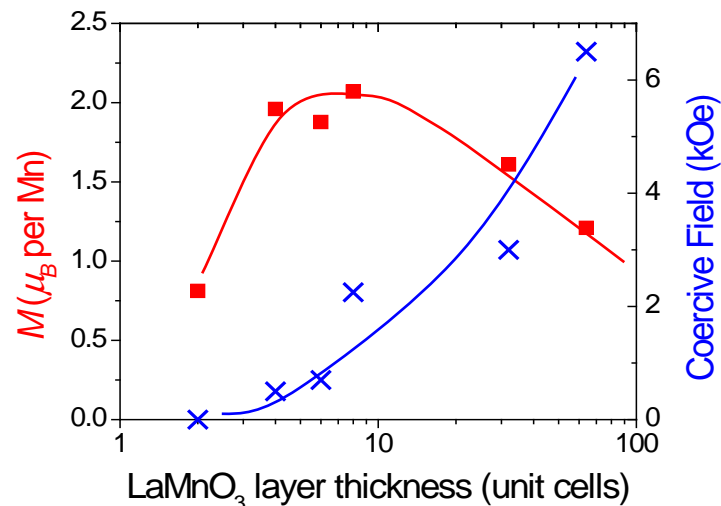
Hans Christen, V. Lauter & colleagues

Two dissimilar interfaces:  
 $\text{SrO}/\text{MnO}_2$  and  $\text{LaO}/\text{TiO}_2$



# Interfacial magnetism in $\text{LaMnO}_3 / \text{SrTiO}_3$ superlattices

- $\text{LaMnO}_3/\text{SrTiO}_3$  superlattices have a higher magnetization (per Mn) than  $\text{LaMnO}_3$  films.
- Macroscopic magnetometry measurements cannot distinguish between the two types of interfaces.
- Polarized neutron reflectometry is used to determine the magnetization depth profile.

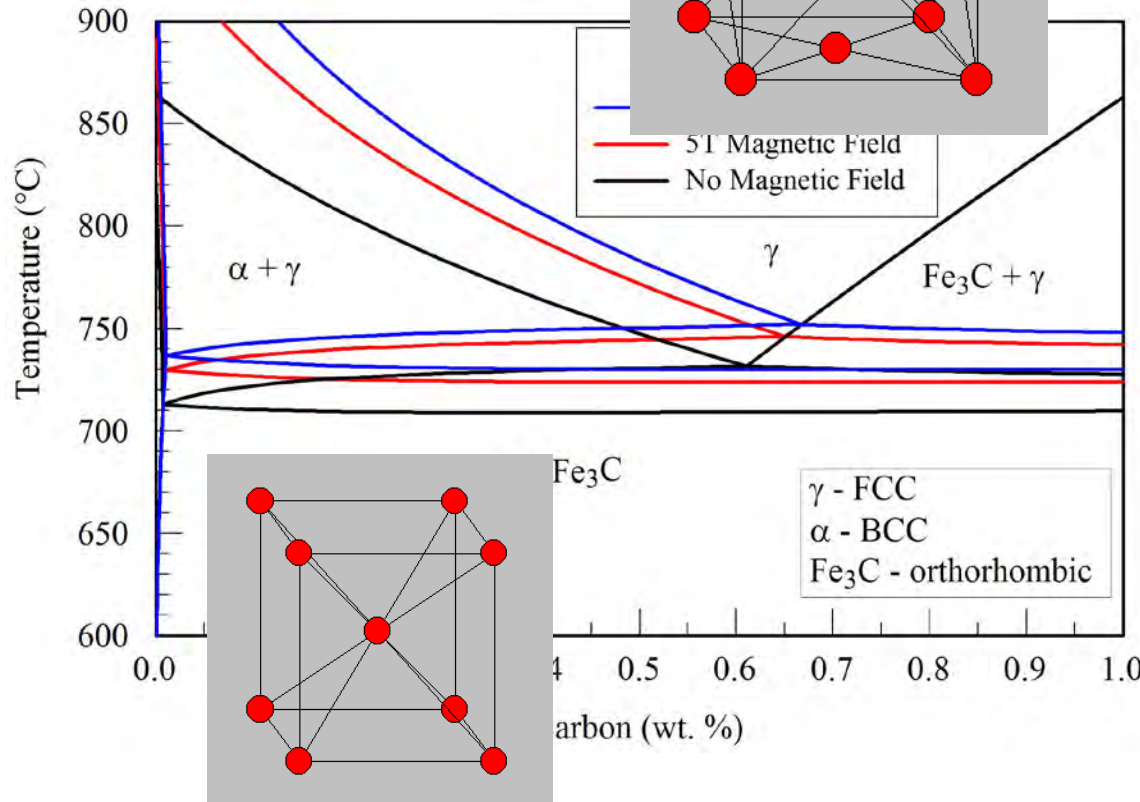
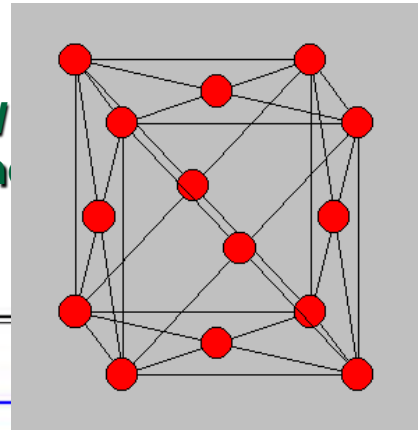


Neutron reflectivity profiles  $R+$  (red) and  $R-$  (blue) at  $H = 1\text{ T}$  in the plane of the film. Solid lines correspond to a model fit to the data with a depth-dependent scattering length density.

# Magnetic Field Processing of Steel

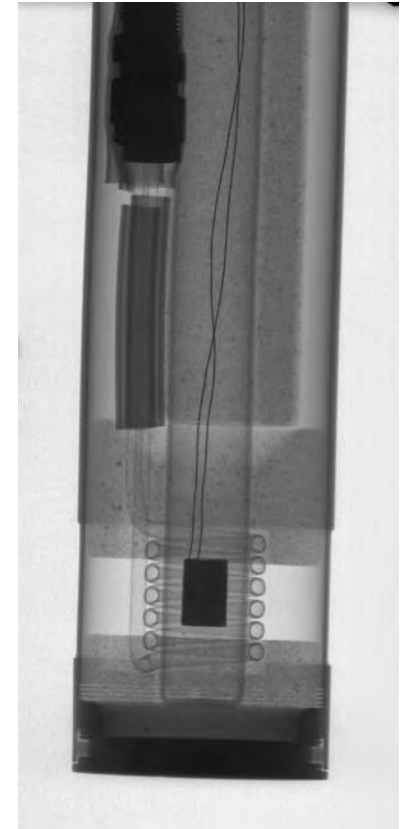
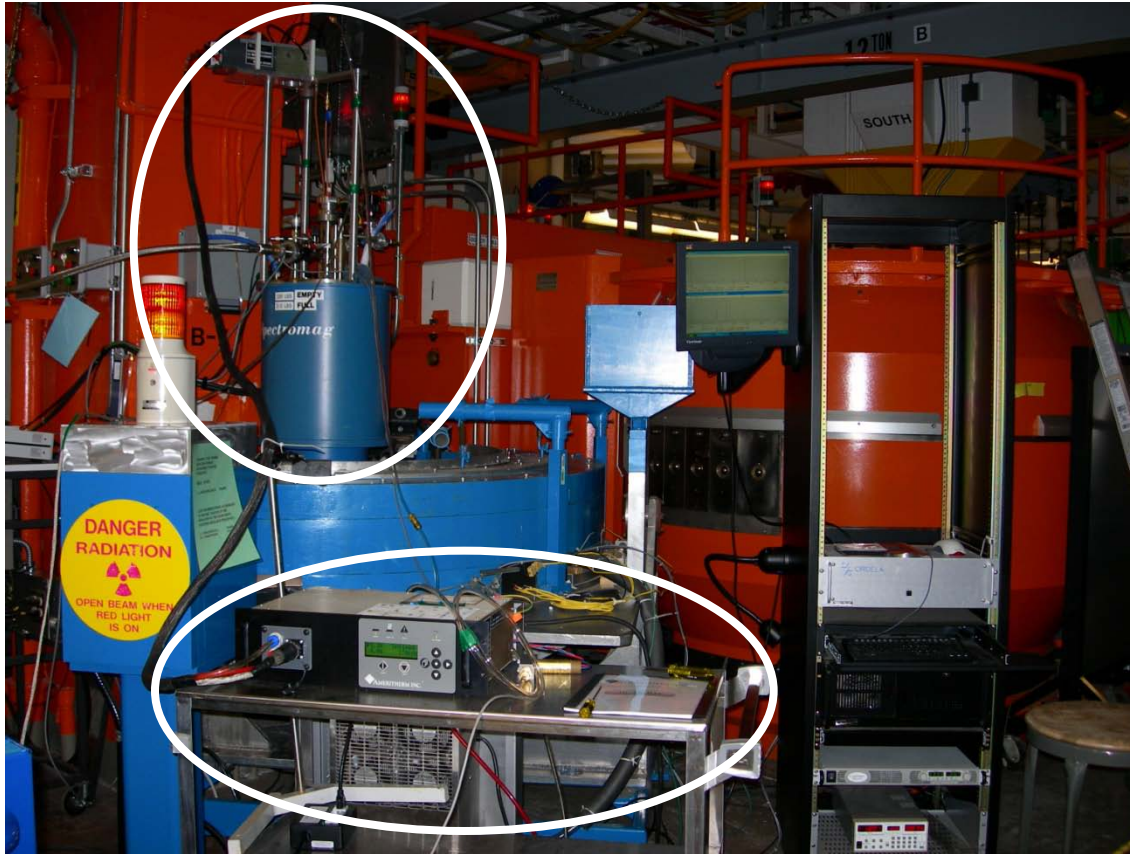
G. M. Ludtka, G. Mackiewicz-Ludtka, C. R. Hubbard  
 Materials Science & Technology Division  
 J. B. Wilgen, R. A. Kisner  
 Engineering Science & Technology Division  
 J. A. Fernandez-Baca  
 Neutron Scattering Science Division

**Magnetic Field Processing (red term) Alters the Free Energy and Allows a 3-D Continuum of Diagrams!!!**



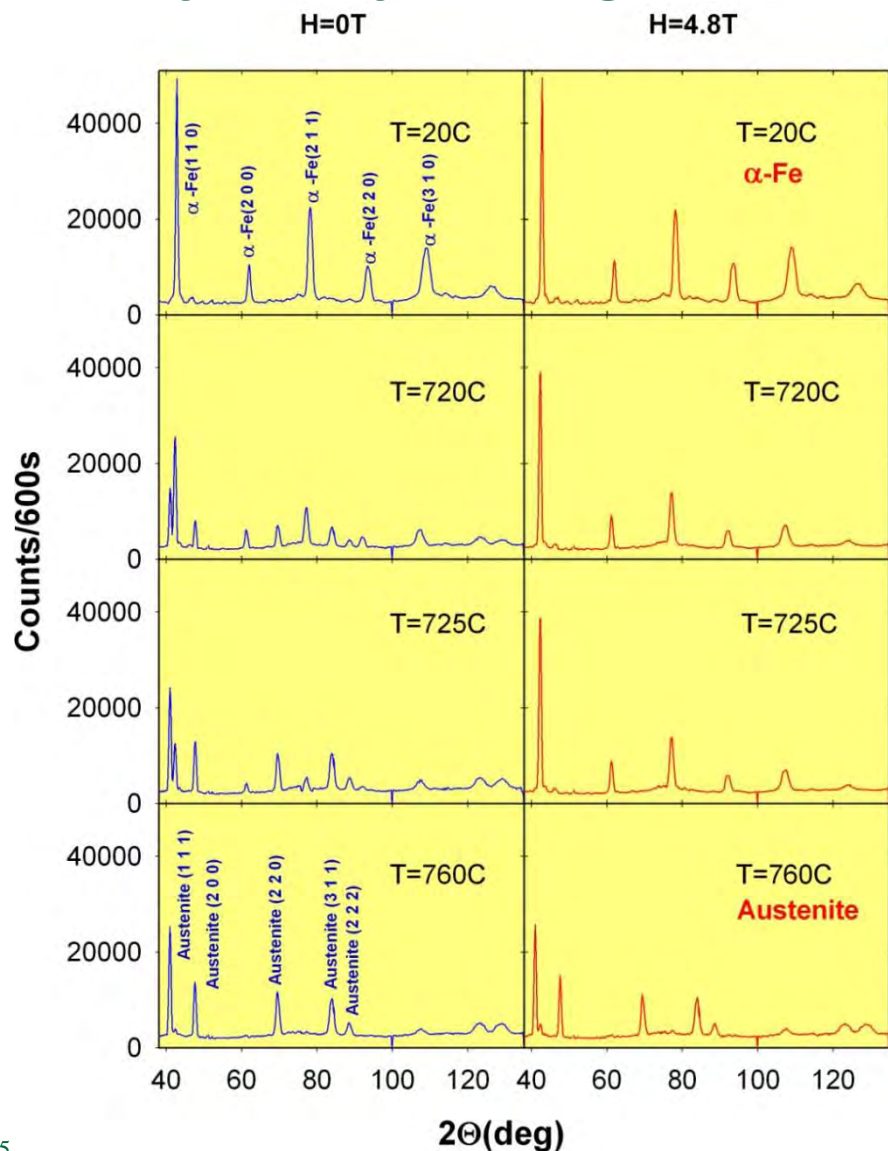
Magnetic fields shift phase transformation temperatures upward and increase solubility limits (ThermoCalc simulation) for a 1045 steel exposed to 5T (red) and 7T (blue) magnetic fields.

# Thermal magnetic system at the WAND



- Built induction heater insert for a 5T magnet
- T up to 1200 deg C and H-5T !!

# Demonstration of In-situ WAND Neutron Diffraction Measurements on a Ultra-High Purity Fe-0.75wt.%C Binary Alloy Using the Thermal Magnetic Insert



Temperature (°C)	Phase(s) present for H=0	Phase(s) present for H=4.8T
25	$\alpha$	$\alpha$
720	$\alpha + \gamma$	$\alpha$
725	$\alpha + \gamma$	$\alpha$
760	$\gamma$	$\gamma$

# Neutron Scattering Investigations of New Fe Based Superconductors

## Collaborators

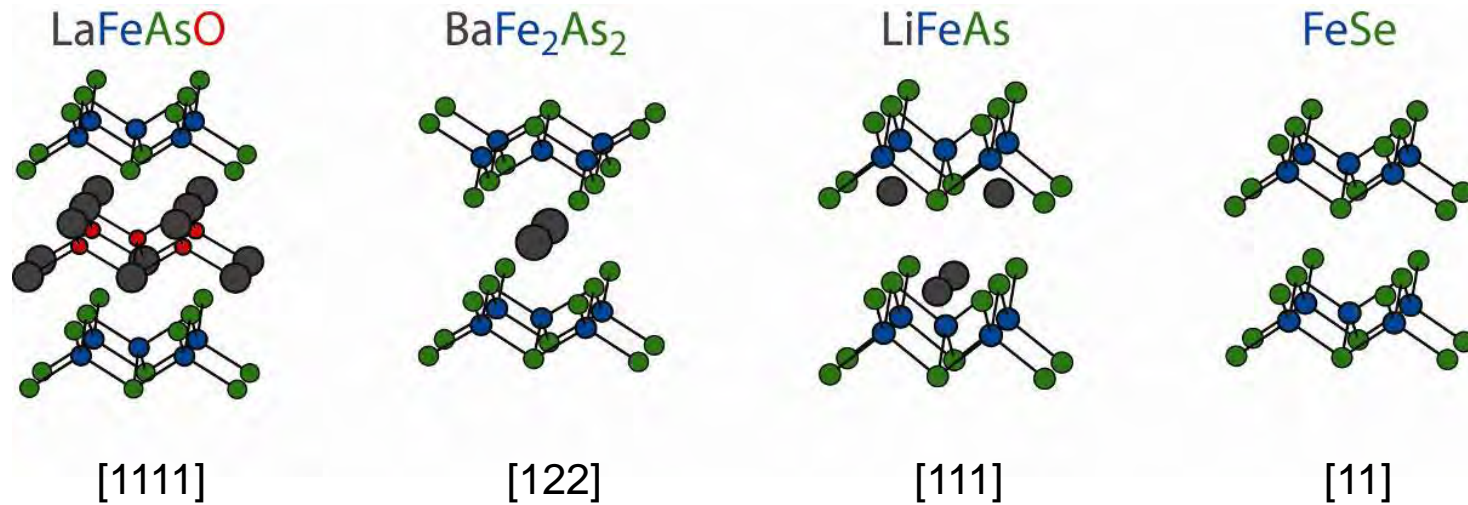
- **A. Christianson, M. Lumsden**, G. MacDougall, H. Mook
- D. Abernathy, M. Stone
- T. Egami, K. Lokshin, D. Parshall
- E. Goremychkin, R. Osborn
- M. McGuire, A. Sefat, R. Jin, B. Sales, D. Mandrus

## Acknowledgements

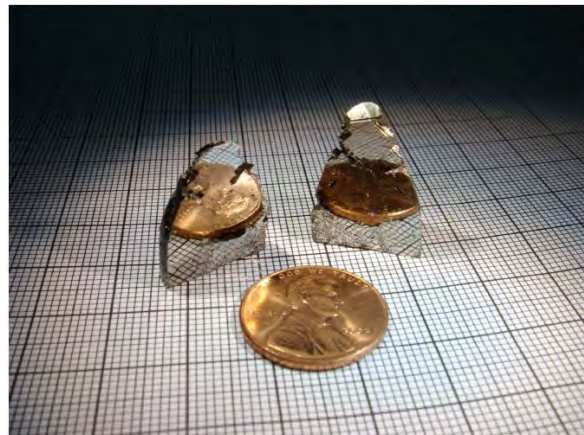
- A. Christianson, D. Mandrus, B. Sales
- P. Dai, C. dela Cruz et al.
- D. Singh



# “Parent” structures

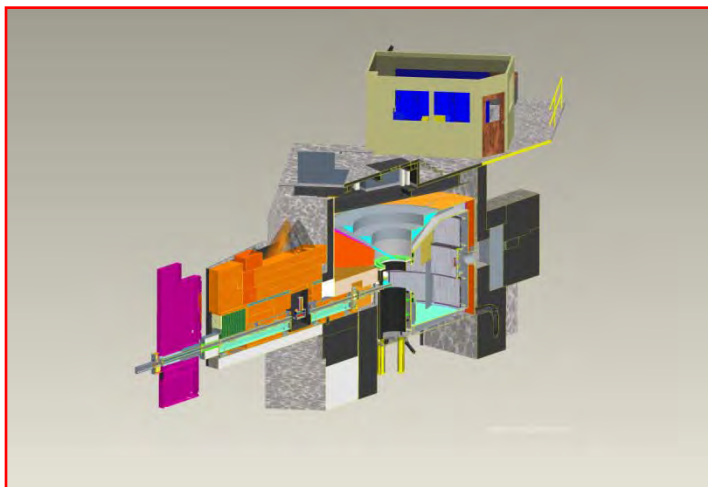
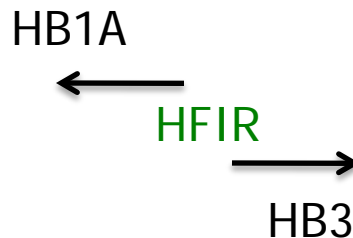


Square planar nets of Fe atoms in a tetrahedral environment is the common feature of all four superconducting structure types



Single crystals of [11] type grown by Brian Sales, ORNL

# Neutron Scattering Instruments



- **The combination of reactor and spallation source instruments is very powerful**

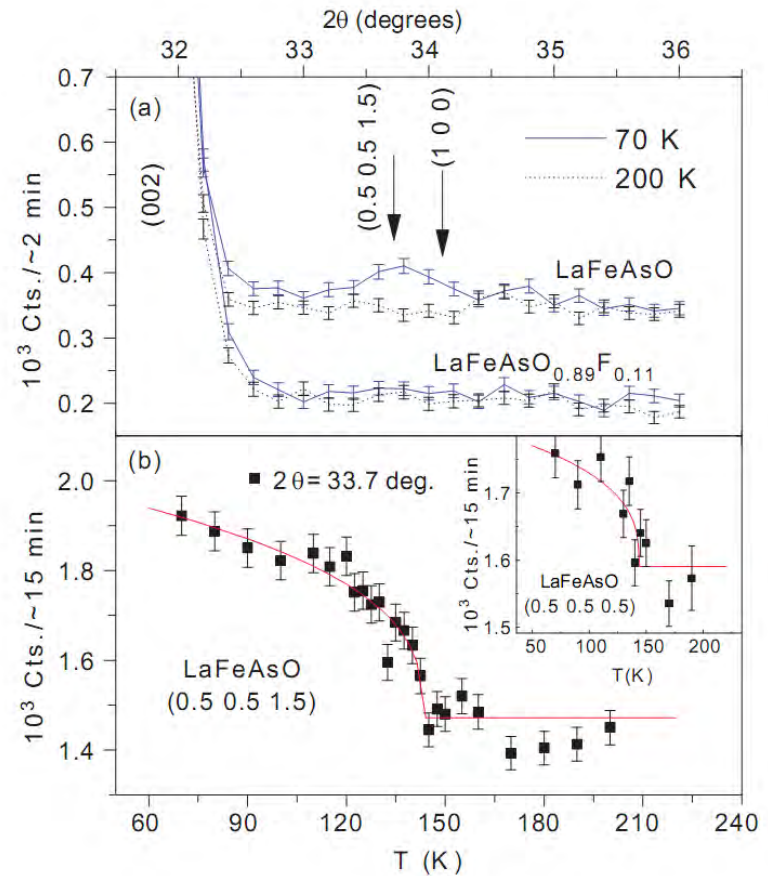
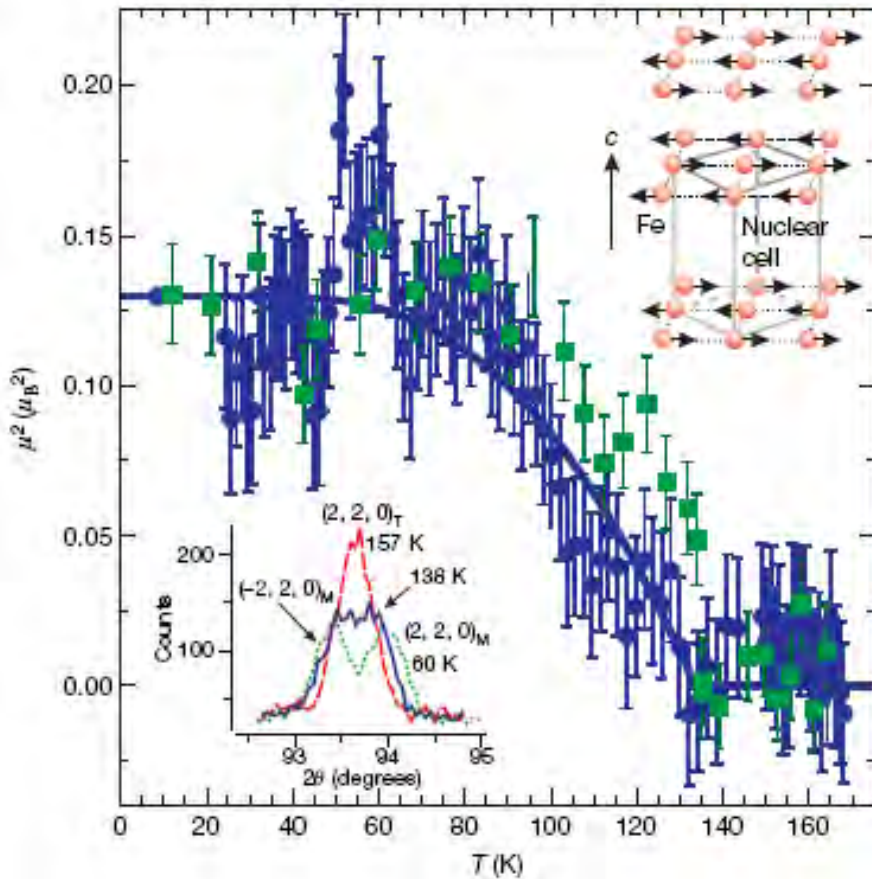
# Neutron Scattering – Magnetism & Structure

## LaFeAsO:

Ordered  $m(\text{Fe}) = 0.36 \mu_B$

(other compounds so far are between 0.3 and 1  $\mu_B$ )

C. de la Cruz et al., *Nature* **453**, 899 (2008), M. A. McGuire et al., *PRB* **78**, 094517 (2008).



# The Nobel Prize in Physics 1994



Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.



**S** Shull made use of **elastic scattering** i.e. of neutrons which change direction without losing energy when they collide with atoms.

Because of the wave nature of neutrons, a diffraction pattern can be recorded which indicates where in the sample the atoms are situated. Even the placing of light elements such as hydrogen in metallic hydrides, or hydrogen, carbon and oxygen in organic substances can be determined.

The pattern also shows how atomic dipoles are oriented in magnetic materials, since neutrons are affected by magnetic forces. Shull also made use of this phenomenon in his neutron diffraction technique.



An early (1940s) neutron diffraction experiment with ferromagnetic neutron filter used by E.J. Wollan and C.G. Shull operating at Oak Ridge National Laboratory.

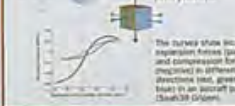
## Neutrons see more than X-rays

X-rays are scattered by electronic moments by atomic nuclei. With X-rays it is easier to see atoms that have many electrons. Hydrogen, for example, which has only one electron, is not so easy to see. With neutrons, all kinds of atoms are visible.



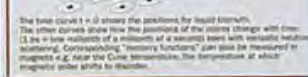
## Neutrons reveal inner stresses

A hole has been punched in an important metal aircraft part. Does the part match up? Neutron diffraction can show how much the distance between the atoms has changed and hence the internal forces remaining around the hole after it has been punched.



## Neutrons show what atoms remember

Of their earlier positions when they move randomly in relation to each other in liquids and melts. Even here there is in fact some local order. The atoms cannot move infinitely close to each other. Some distances are more common than others.



Neutrons behave as particles and as waves

The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.

Bertram N. Brockhouse, McMaster University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.



**B** Brockhouse made use of **inelastic scattering** i.e. of neutrons, which change both direction and energy when they collide with atoms. They then start or cancel atomic oscillations in crystals and record movements in liquids and melts. Neutrons can also interact with spin waves in magnets.

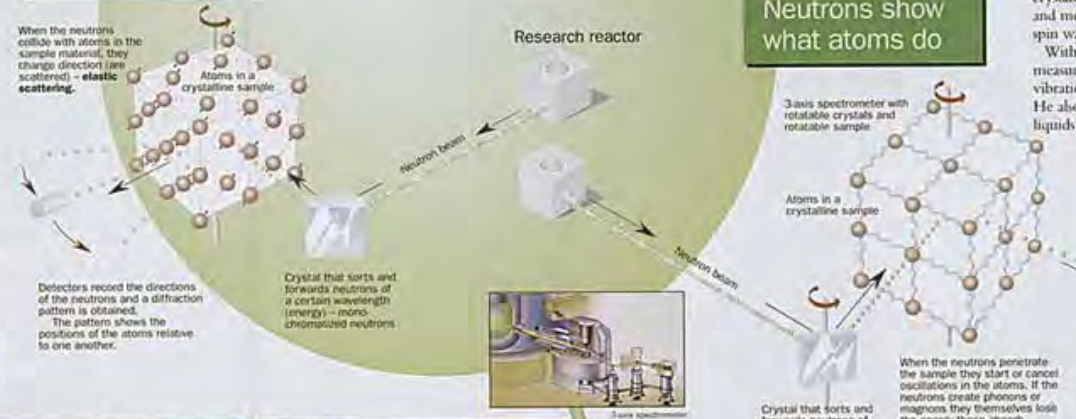
With his 3-axis spectrometer Brockhouse measured energies of phonons (atomic vibrations) and magnons (magnetic waves). He also studied how atomic structures in liquids change with time.

# Neutrons reveal structure and dynamics

Neutrons show where atoms are

Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.

Neutrons show what atoms do



**How it started**  
Brockhouse and Shull made their pioneering contributions at the first nuclear reactors in the USA and Canada back in the 1940s and 1950s. It was then that the resources of the reactors became available for peacetime research.

**...how it continues**  
Thousands of researchers are now working at the many neutron research centers throughout the world. New and very advanced neutron scattering installations have been built and more are planned in Europe, the USA and Asia. At these super-installations the researchers are studying the structure of new ceramic superconductors, molecular movements on surfaces of interest for catalytic exhaust cleaning, virus structures and the connection between the structure and the elastic properties of polymers.

**KUNGLIGA VETENSKAPSAKADEMIEN**  
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Information Department, Box 50006, S-171 05 Stockholm, Sweden. Tel: +46 8 73 95 80. Fax: +46 8 15 56 55. E-mail: Sekretariat@kva.se, kva@kva.se  
The Royal Swedish Academy of Sciences, Address: Professor Erik 8 Bergman and Professor Carl Norberg, Department of Physics, Institute University, Member of the Nobel Committee for Physics, Svalof and Haldensborg, 40131 Ludvig, Engestr. 40. Printed by: Tryckcentralen, 1324.

### Further reading:

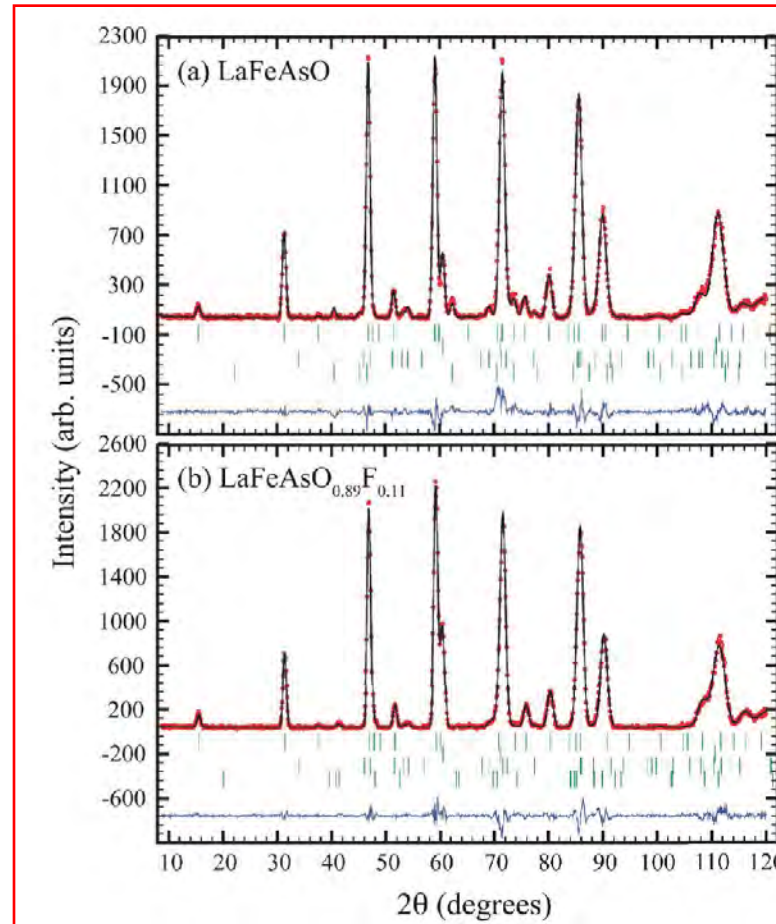
- D.J. Hughes: The Nobel Prize in Physics. SCIENTIFIC AMERICAN, 1994, 1995, 1996, 1997, 1998, 1999.
- H. Langer and J.J. Preiner: The European Space Agency. SCIENTIFIC AMERICAN, 1994, 1995, 1996, 1997, 1998, 1999.
- Information about the Nobel Prize in Physics 1994 (available at THE ROYAL SWEDISH ACADEMY OF SCIENCES)



# Phonon Density of States in [1111]

A.D. Christianson et al., Phonon Density of States of LaFeAsO<sub>1-x</sub>F<sub>x</sub>, Phys. Rev. Lett. **101**, 157004, (2008).

- Samples were synthesized independently by Oak Ridge and Ames Laboratory
- Samples were checked by neutron powder diffraction
- $T_c = 27$  (S2) and 23 K (S3)



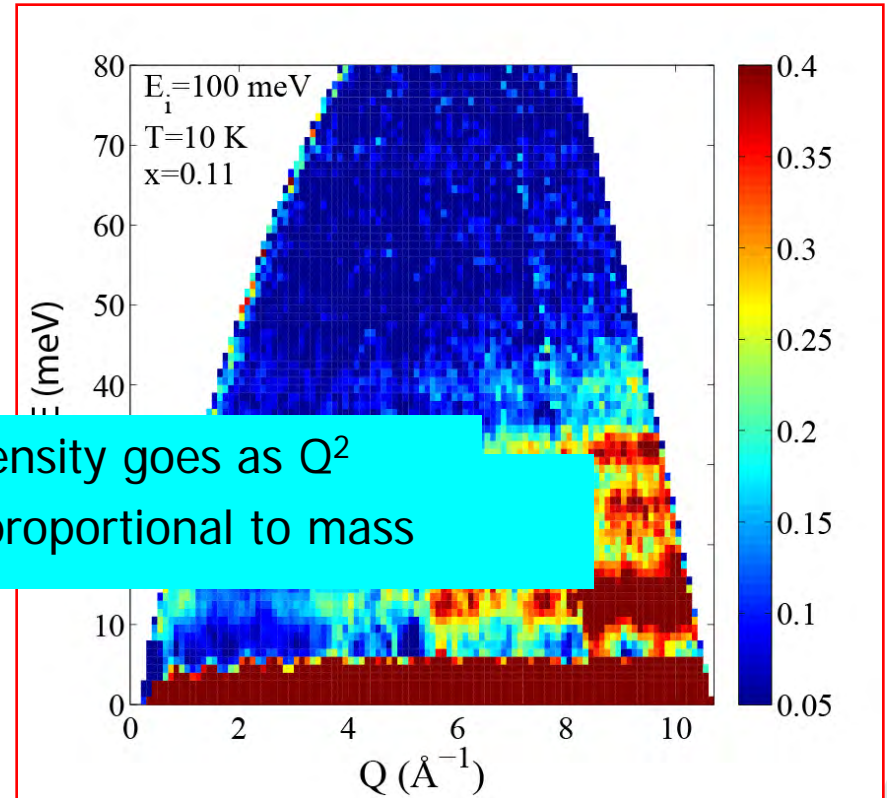
# Inelastic Scattering (ARCS)

- Only empty holder subtracted
- Clear Phonon Signal

$$S(Q, \omega) = \sum_i \sigma_i \frac{\hbar Q^2}{2m_i} \exp(-2W_i) \frac{G_i(\omega)}{\omega} [n(\omega) + 1], \quad (1)$$

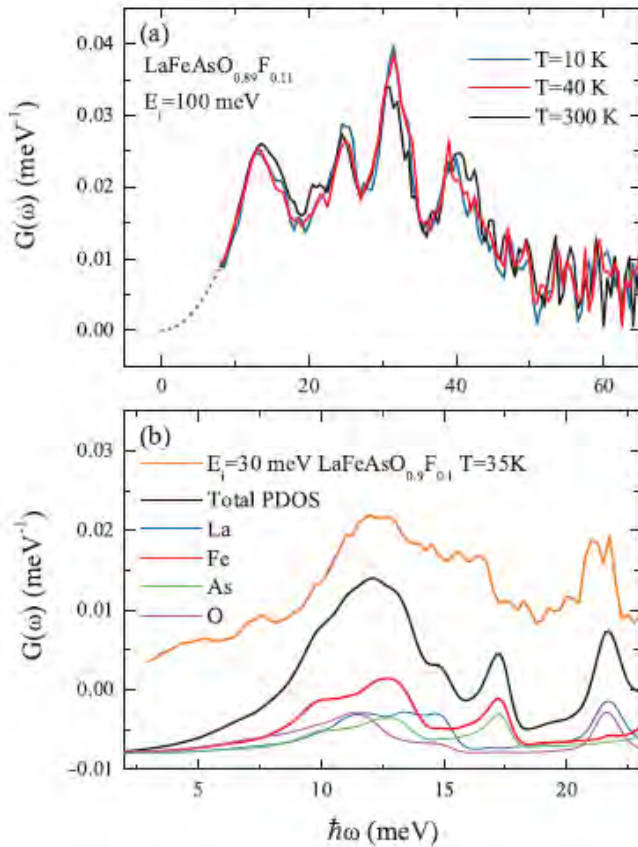
$$G_i(\omega) = \frac{1}{3N} \sum_{j\mathbf{q}} |\mathbf{e}_i(j, \mathbf{q})|^2 \delta[\omega - \omega(j, \mathbf{q})]$$

Phonon intensity goes as  $Q^2$   
 Inversely proportional to mass



Inelastic neutron scattering determines the weighted Phonon Density of States (PDOS)

# Phonon Density of States



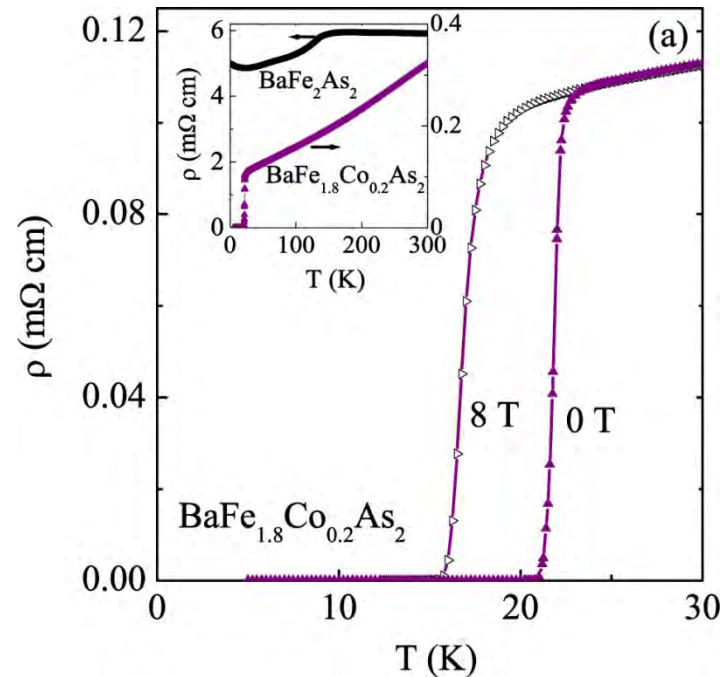
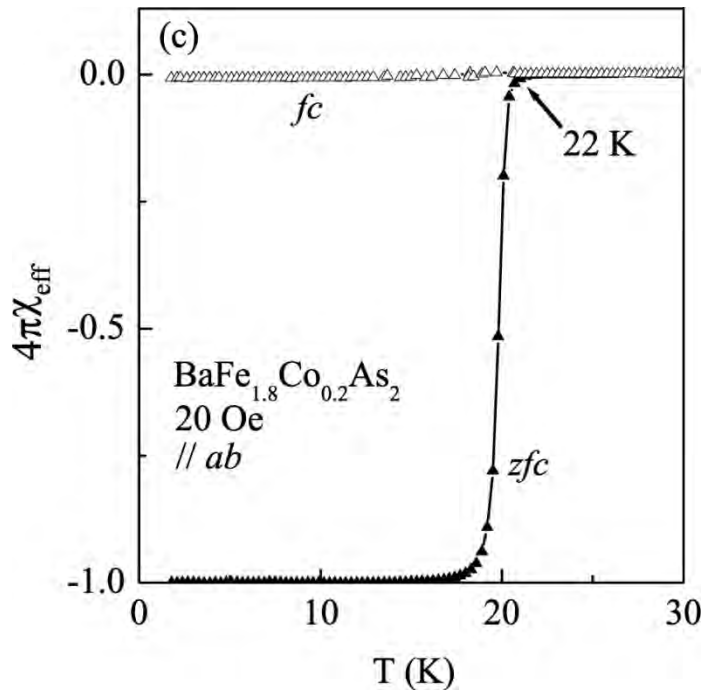
- The phonon spectrum agrees with that predicted from abinitio calculations.
- In turn, one can use the PDOS to estimate bounds on the superconducting transition temperature  $T_C$  if the electron pairing arises from phonons.
- Superconductivity does not appear to be explained by a conventional phonon mechanism in the Fe-arsenides.
- This contrasts with other materials including  $\text{MgB}_2$ ,

# “Resonant” Magnetic Excitation in [122] single crystals

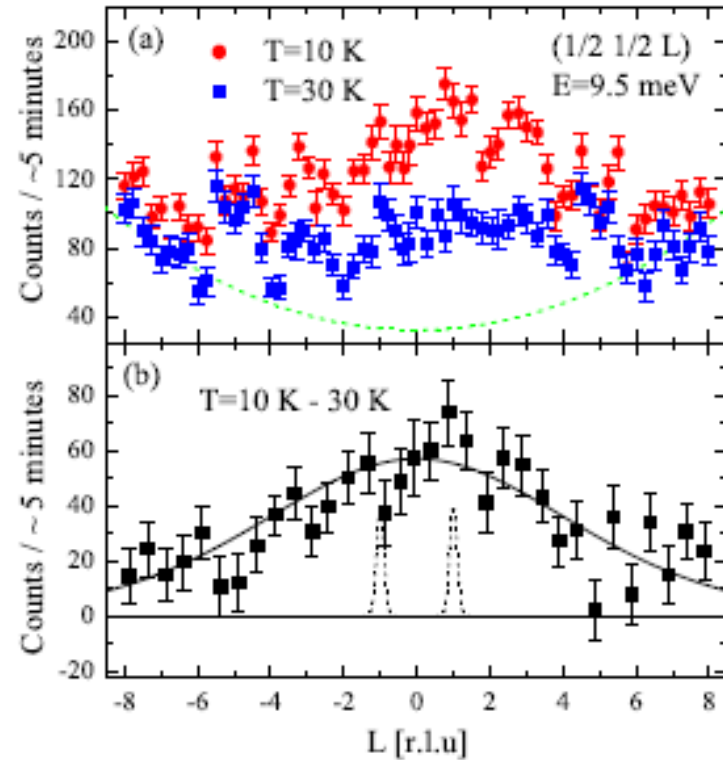
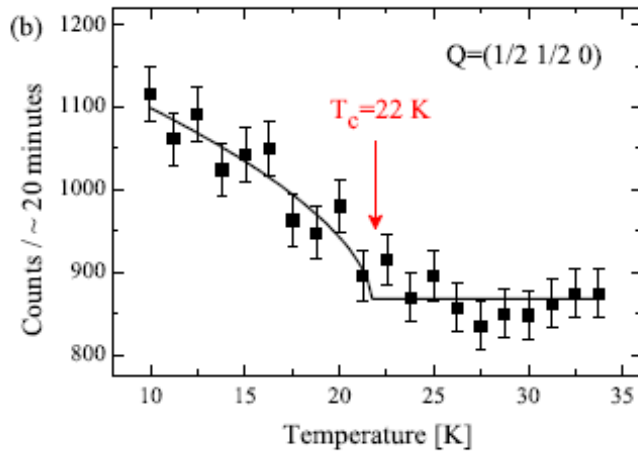
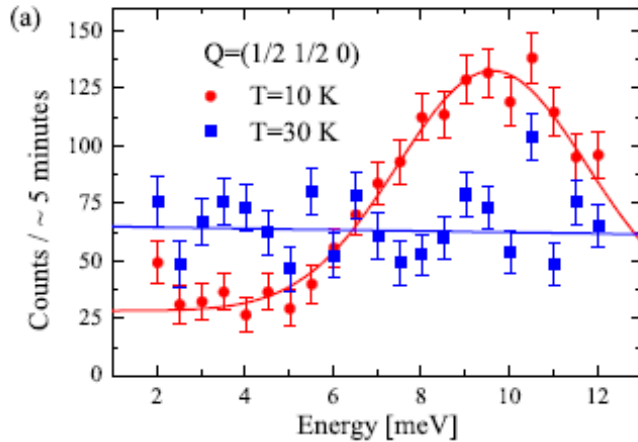
Doping Co Into Fe Planes Results in Robust Superconductivity:

$\text{LaFe}_{.89}\text{Co}_{.11}\text{AsO}$ ,  $T_c \approx 15$  K (Sefat et al PRB in press)

$\text{BaFe}_{1.84}\text{Co}_{0.16}\text{As}_2$ ,  $T_c = 22$  K (Sefat et al. PRL, in press)



# Resonance in Single Crystal $\text{BaCo}_{0.16}\text{Fe}_{1.84}\text{As}_2$



M. D. Lumsden et al., Two-dimensional resonant magnetic excitation in  $\text{BaFe}_{1.84}\text{Co}_{0.16}\text{As}_2$ , To be published in Phys. Rev. Lett., arXiv:0811.4755 (2008).

- “Resonance” found at  $(\frac{1}{2} \frac{1}{2} 0)$  in optimally doped  $\text{BaCo}_{0.16}\text{Fe}_{1.84}\text{As}_2$
- This is the square lattice  $(\pi 0)$  point
- Energy scale relative to  $T_C$  is similar to that found in cuprate materials and other [122] Fe-As compounds.
- Strong 2-dimensional character
- Suggestive of so-called “S+” superconductivity
- This could be a clue to the mechanism for the superconductivity