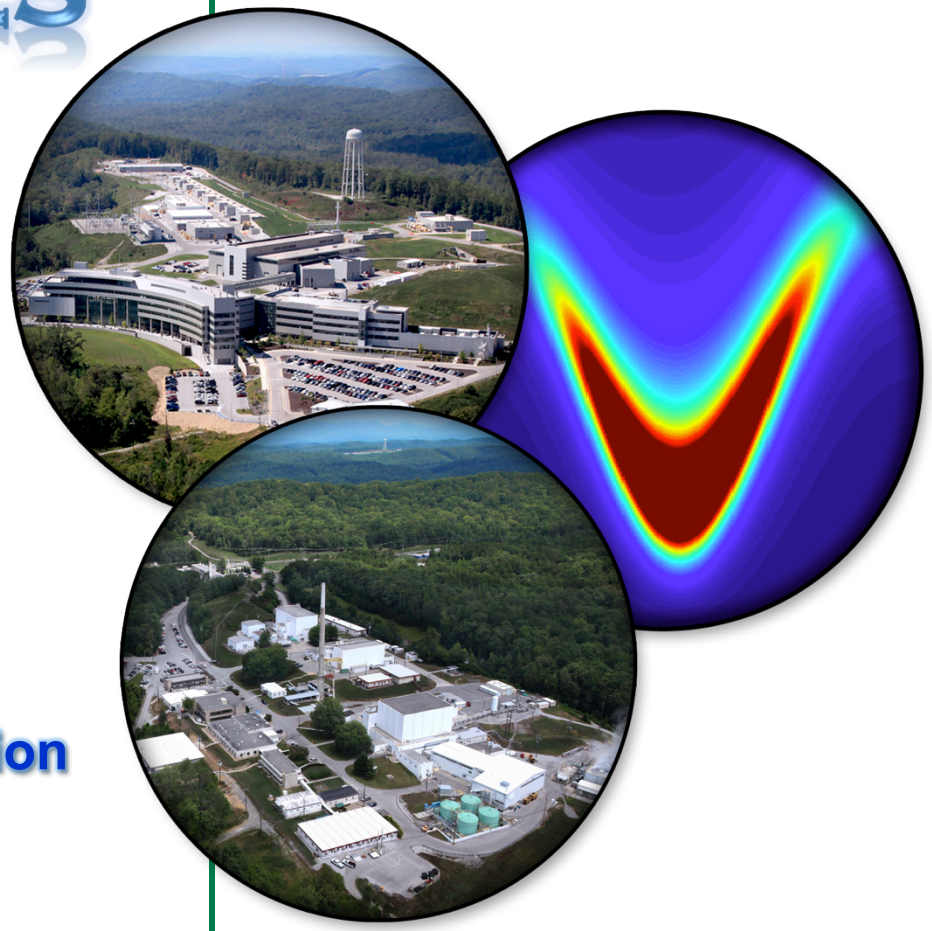
RESEARCH OPPORTUNITIES IN POWDER DIFFRACTION



Clarina R. dela Cruz

Quantum Condensed Matter Division

Neutron Sciences Directorate

Oak Ridge National Laboratory

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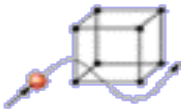
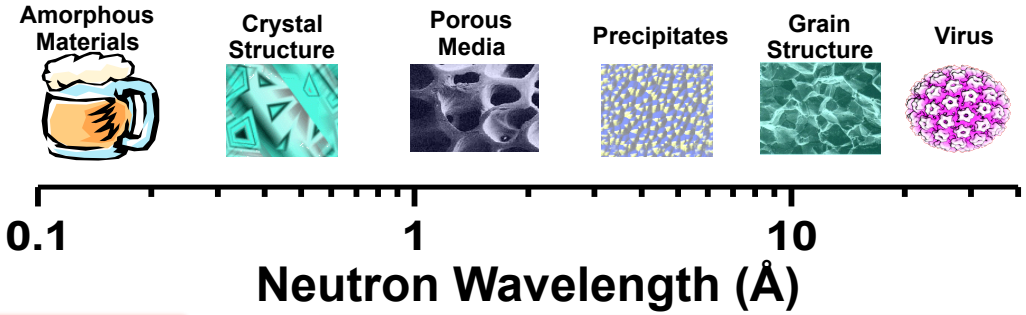
WHERE ARE THE ATOMS?

We need wavelength (λ) ~ Object size (for condensed matter that is Å)



$$q = \frac{4\pi \sin(\theta)}{\lambda} = \frac{2\pi}{d}$$

Neutron WAVELENGTHS are similar to atomic scale dimensions



X-ray

λ : 0.1 Å – 10 Å

λ[Å] = 12.398/E_{ph}[keV]

Source:

- **Lab diffractometers**
- **Synchrotron Sources**

Neutron

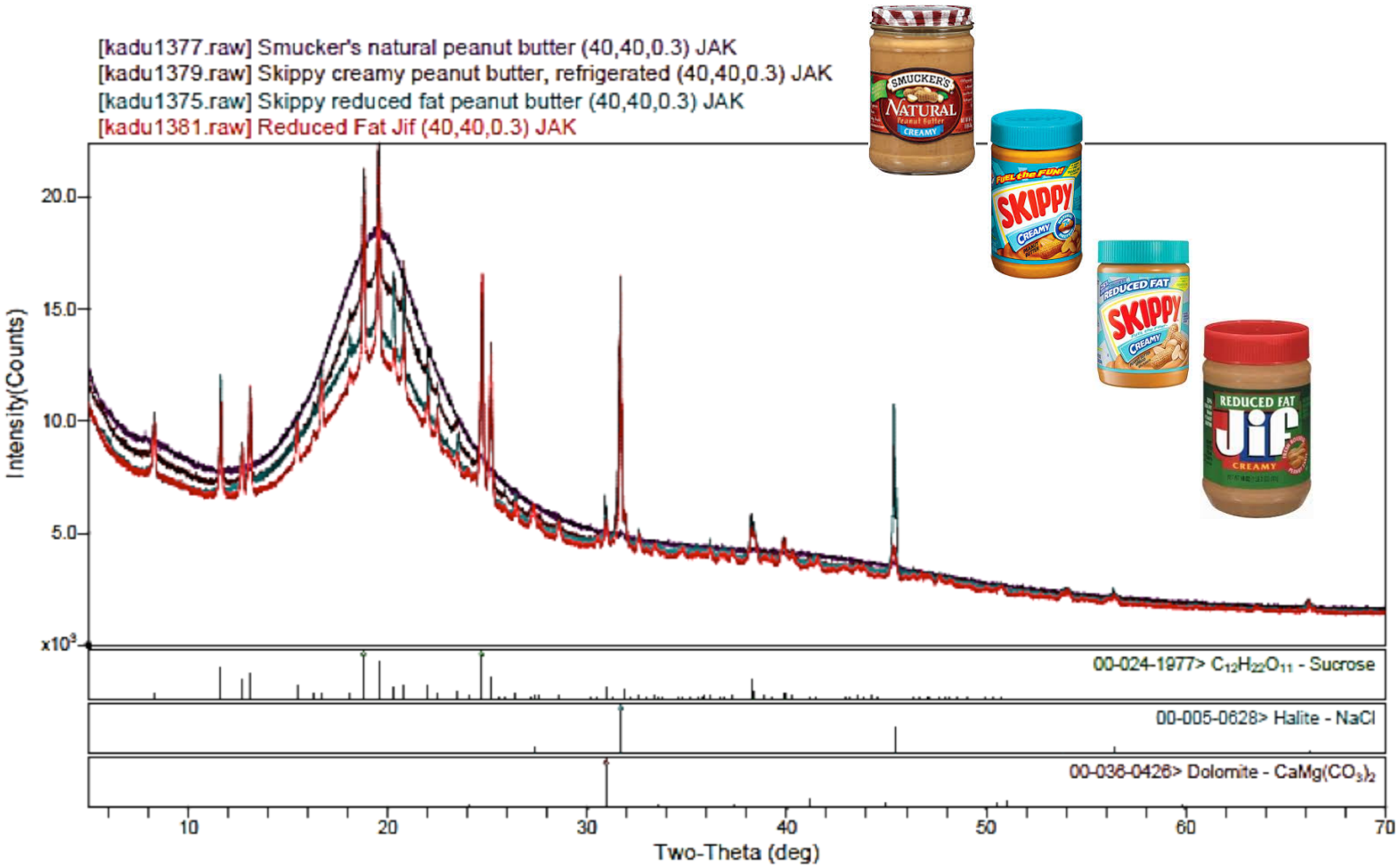
thermal λ : 1 - 4 Å

E_n[meV] =81.89/ l^2[Å]

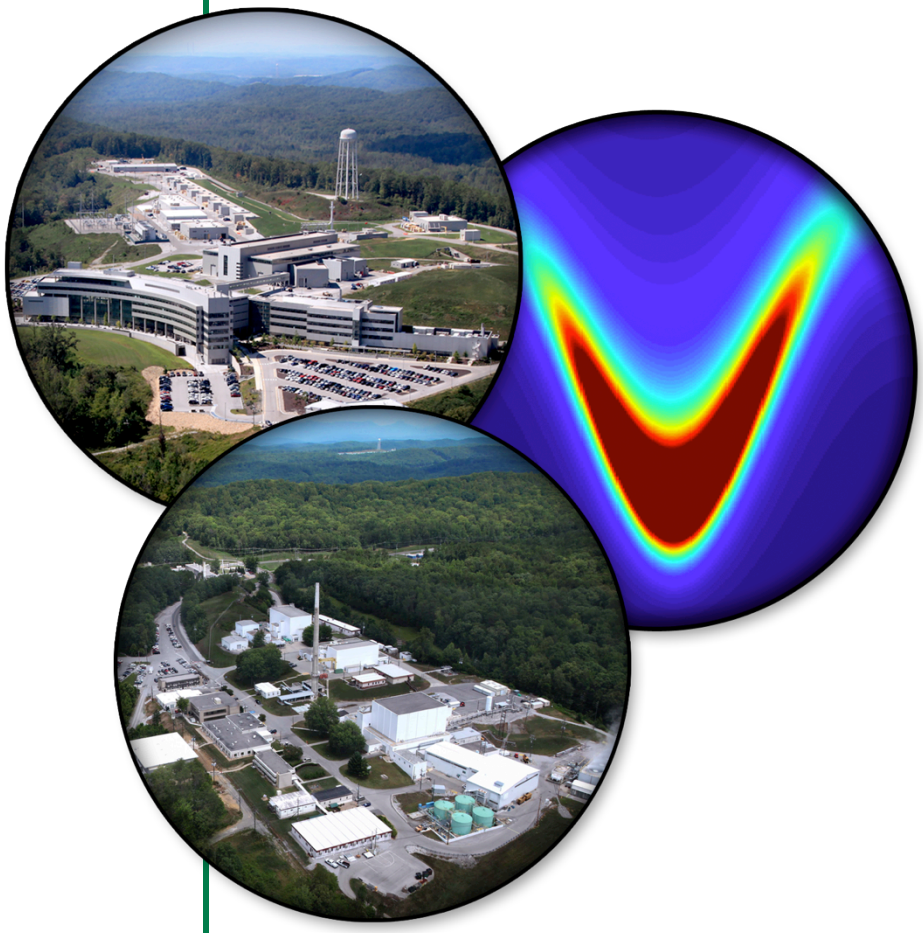
Source:

- **Reactors (fission)**
- **Spallation Source**

What is your favorite Peanut Butter?



Finger Printing and Quantitative Phase Analysis



Slides from Dr. Jim Kaduk

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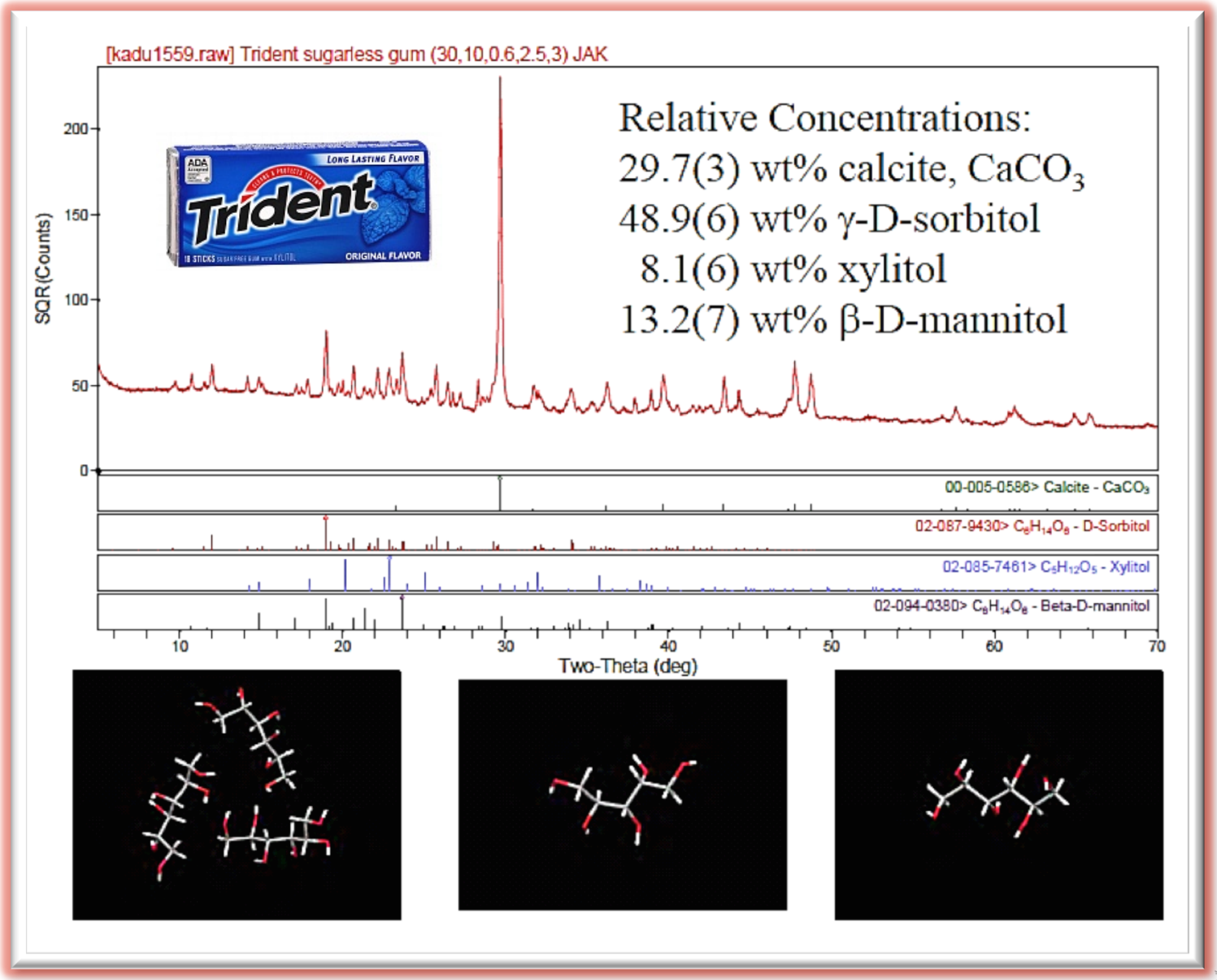
QUANTITATIVE X-RAY ANALYSIS RESULTS ON PEANUT BUTTER

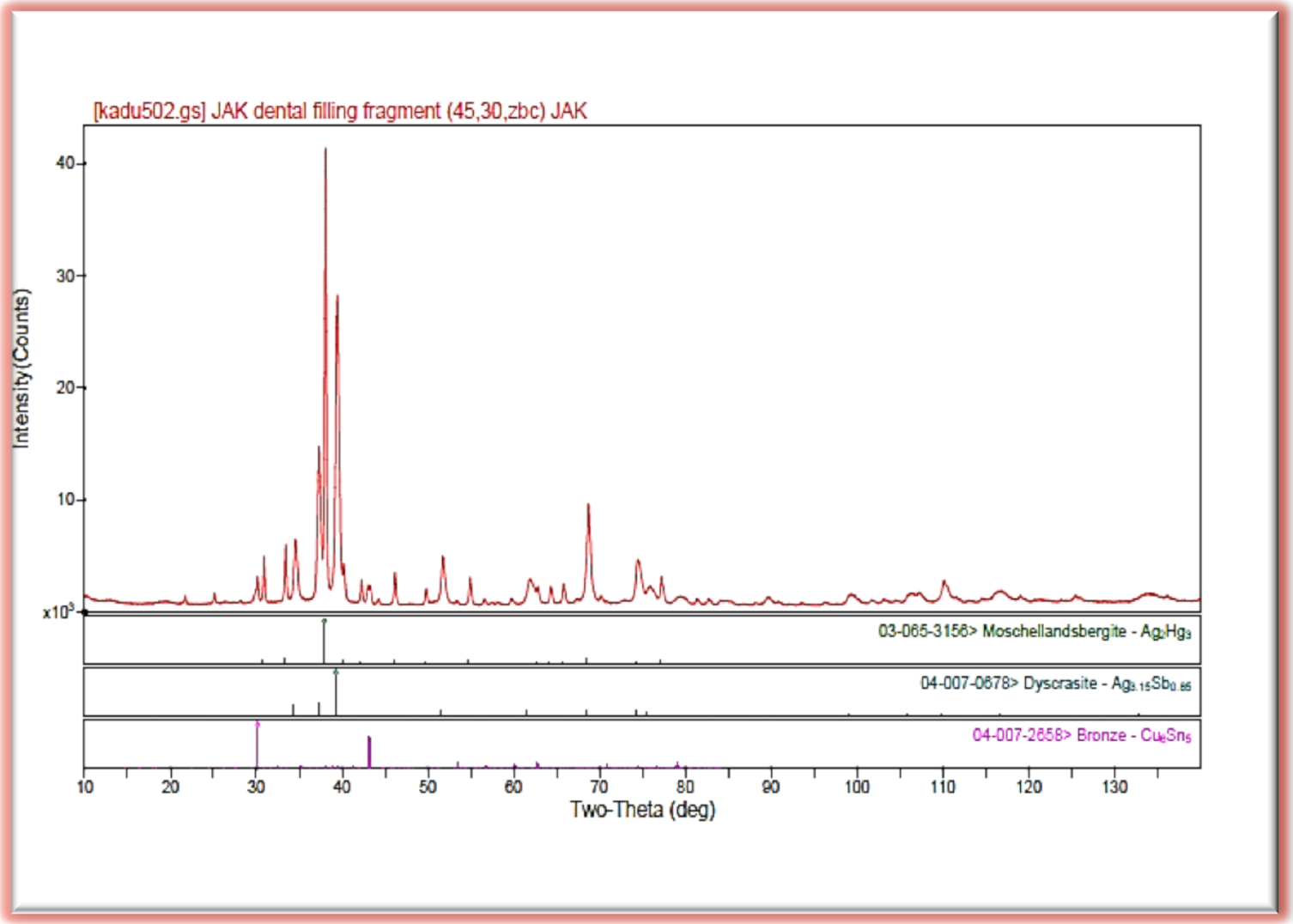
Now, which one is really your favorite?

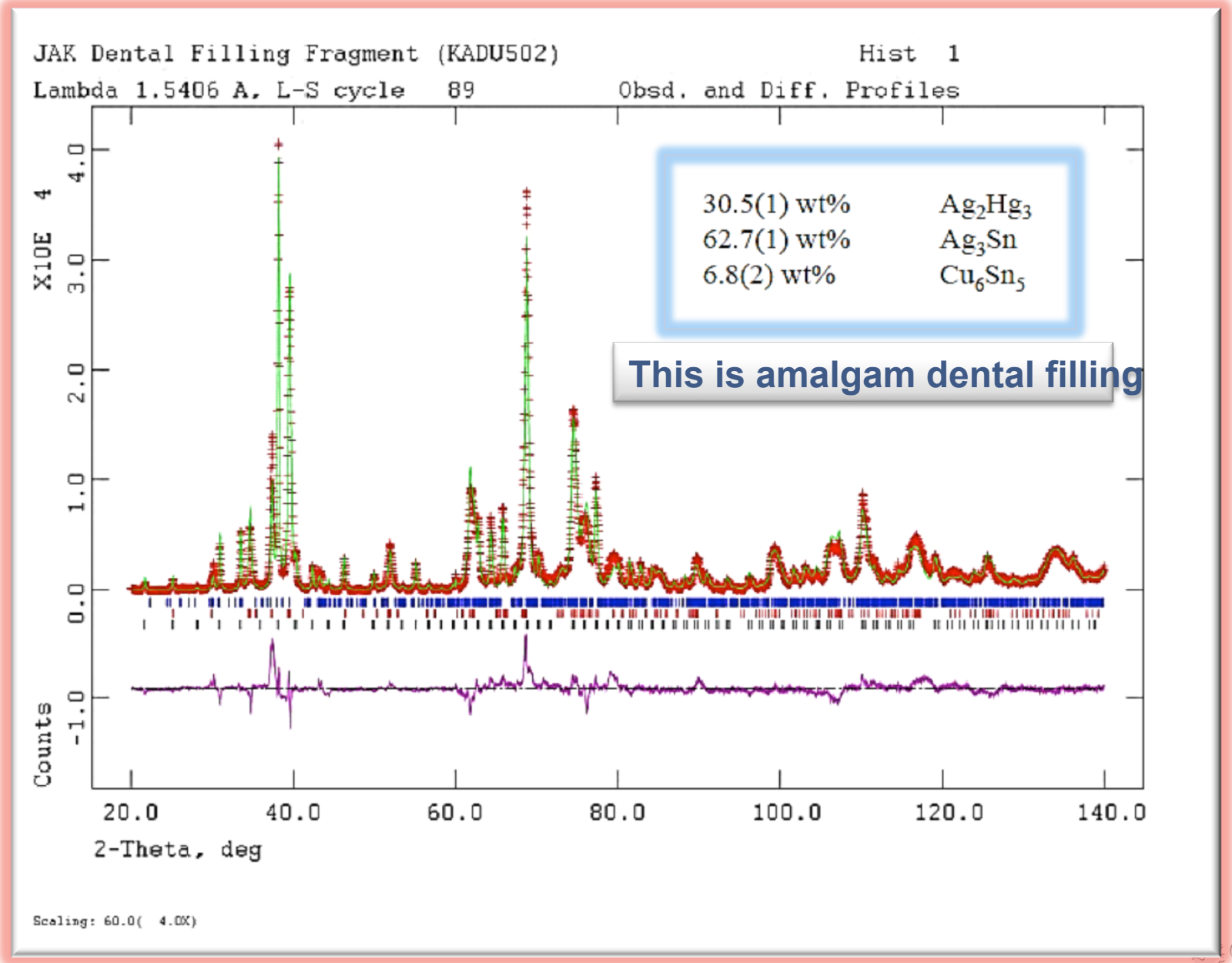
Sample	Skippy creamy	Skippy reduced fat	Jif reduced fat	Smucker's Natural
Ingredients	peanuts sugar salt hydr. veg. oils	peanuts corn syrup sol. sugar soy protein salt hydr. veg. oils mono/diglyc. minerals vitamins	peanuts corn syrup sol. sugar soy protein salt hydr. veg. oils molasses minerals vitamins	peanuts salt
sucrose, $C_{12}H_{22}O_{11}$ wt% NI sugars, wt%	 9.4 9.4	 10.0 11.4	 12.2 11.1	- 3.1
halite, NaCl wt% NI NaCl, wt%	 ~1 1.2	 ~2? 1.2	 ~1 1.6	 Small 1.0
dolomite, $CaMg(CO_3)_2$ wt%	-	0.2	-	-
β_2 fat, SSS wt%	-	-	1.4	-

Trident Sugarless Gum (Original Flavor)



Dental Filling Fragment





CRYSTALLOGRAPHIC DATABASES

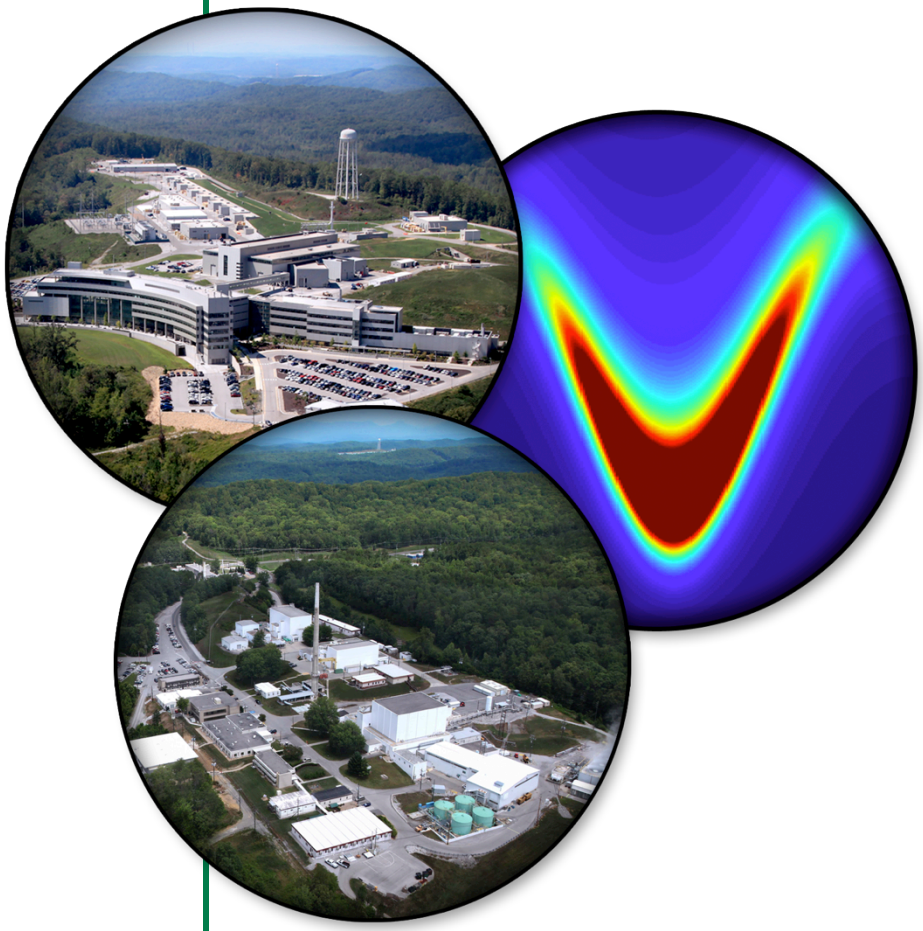
- **Powder diffraction file, maintained by ICDD**
  http://www.icdd.com/products/overview.htm

DATA ENTRY SOURCE	PDF-2 Release 2012	PDF-4+ 2012 WebPDF-4+ 2012	PDF-4/ Minerals 2012	PDF-4/ Organics 2013
Total No. of Data Sets	250,182	328,660	39,410	471,257
00- ICDD	108,711	108,711	11,548	33,727
01- FIZ	131,404	59,927*	11,094*	6,132
02- CCDC	0	0	0	431,359†
03- NIST	10,067	3,122*	208*	39
04- MPDS	0	156,900	16,560	0
New Entries	6,271	17,807‡	1,768	1,076
No. with atomic coordinates	0	171,856	19,355	39,496
No. with cross-referenced atomic coordinates	0	45,286	7,767	255

* MPDS entries, containing more data, replace duplicate reference patterns and citations from FIZ (01-ICSD) and NIST (03-NIST) entries in PDF-4+, WebPDF-4+ and PDF-4/Minerals. PDF-4+, WebPDF-4+ and PDF-4/Minerals are the only products that contain data sources from MPDS (04-LPF).
† PDF-4/Organics is the sole product that contains data sourced from the Cambridge Structural Database (CSD) published by Cambridge Crystallographic Data Centre (02-CSD).
‡ While 17,807 new entries were added to the PDF-4+ database, the product increased by a net of 12,369 entries due primarily to new entries with atomic coordinate sets replacing duplicate entries without atomic coordinates.

***CCDC (Chembridge Crystallographic database): organic structures**
***ICSD (Inorganic crystal structure database): FIZ**
***NIST & MPDS**

NEUTRON POWDER DIFFRACTION



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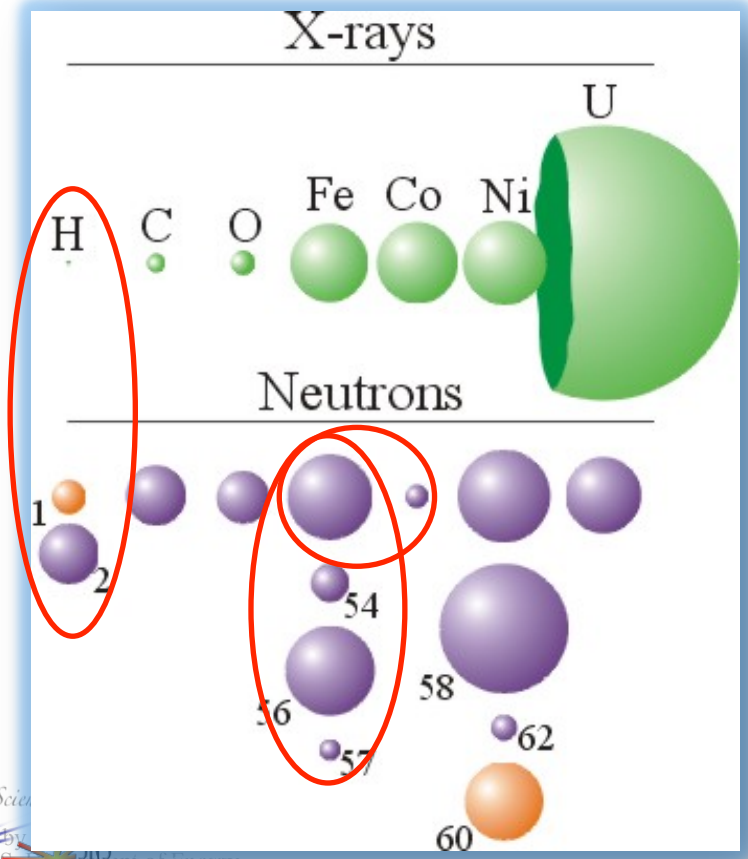
WHY USE NEUTRONS?

Neutrons "see" NUCLEI

- sensitive to light atoms
- can exploit isotopic substitution
- use contrast variation to differentiate complex structures
- Electrically neutral, allows non-destructive analysis and ease of *in-situ* experiments, e.g. T, Pr, B, chemical reaction etc.



Neutrons have a MAGNETIC moment

- determine microscopic magnetic structure
- study magnetic fluctuations

Neutrons have SPIN

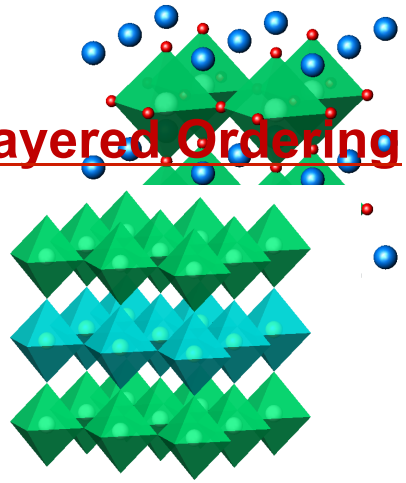
- can be formed into polarized neutron beams

OXYGEN, WHERE ART THOU?

Ba_2CuWO_6: An Ordered Tetragonal Perovskite

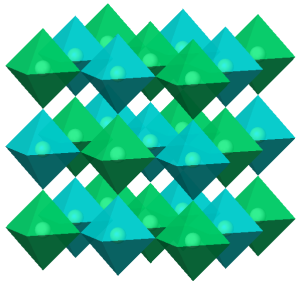
Iwanaga et. al. J. Solid State. Chem. 147, 291(1999)

Layered Ordering



Rock Salt Type Ordering

Simple cubic AMX_3 pe 3045.



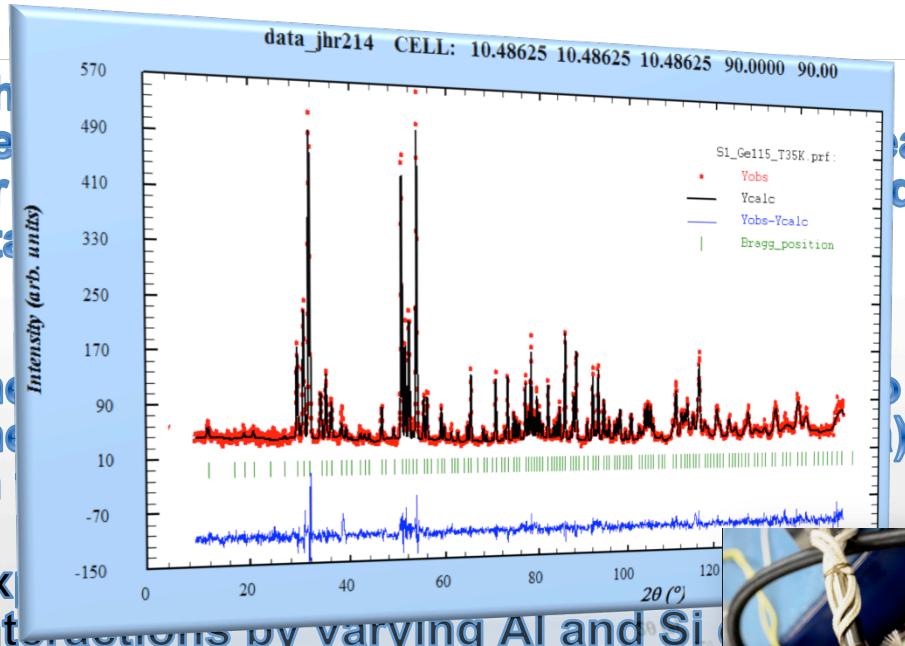
Cu^{2+} is a Jahn Teller active ion ➔ elongates CuO_6 octahedra along c-axis

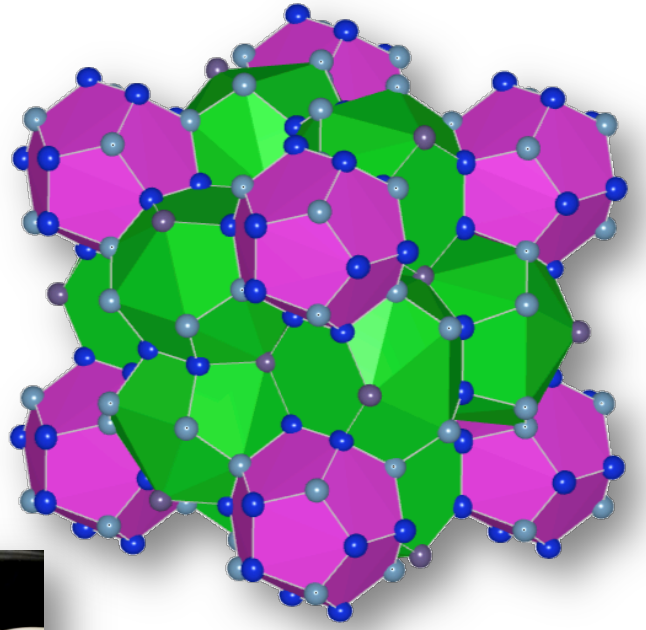
Double Perovskites $A_2MM'O_6$

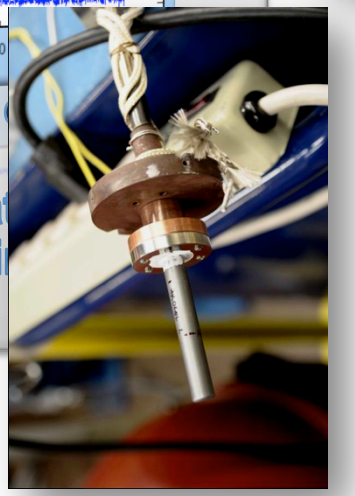
Out of 3 possible ordering only 2 observed

$Ba_8Al_xSi_{46-x}$: Tuning thermoelectric materials at the atomic level

Roudebush, J.H., C. de la Cruz, B.C. Chakoumakos, S.M. Kauzlarich, Neutron Diffraction Study of the Type-I Clathrate $Ba_8Al_xSi_{46-x}$: Site occupancies, cage volumes and the interaction between the guest and host framework. *Inorganic Chemistry*, 2011



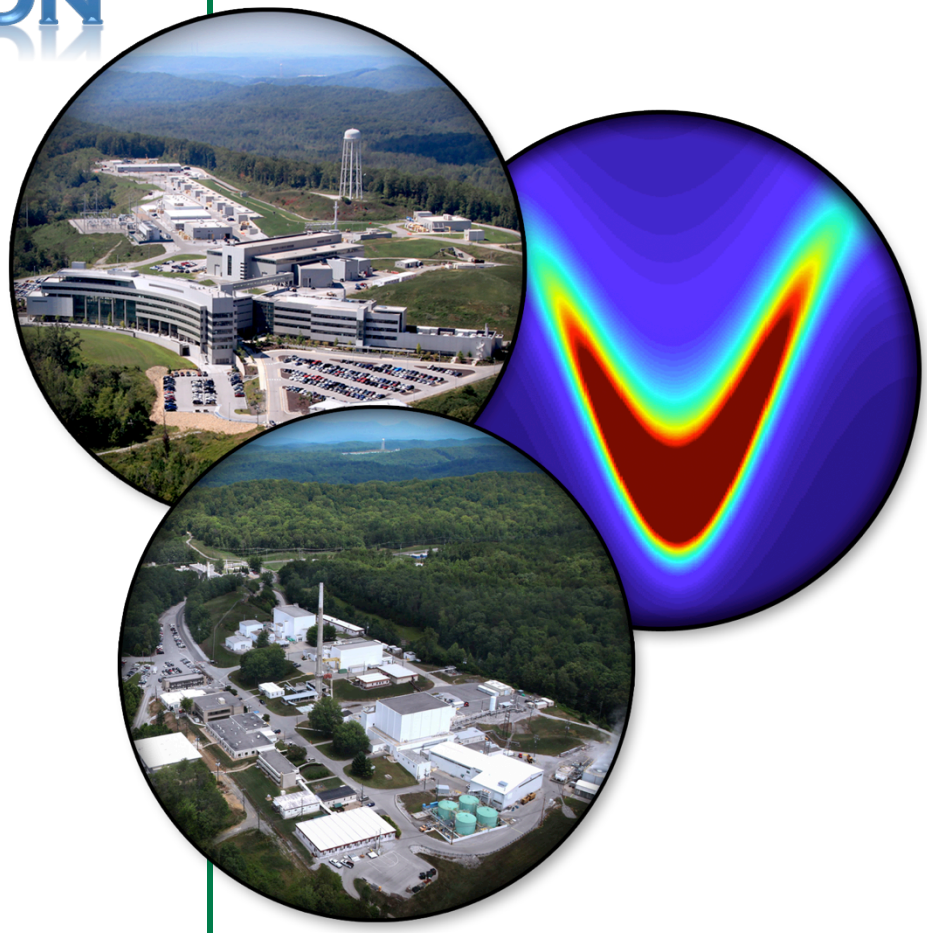




This clathrate crystal structure consists of a host framework (Al and Si polyhedral cages) enclose one Guest (Ba) atom in each.

new findings emphasize the importance of site occupancies in the framework sites NEAREST to the guest atom in the large cage.

MAGNETISM STUDIES USING POWDER DIFFRACTION



Neutrons have a **MAGNETIC** moment

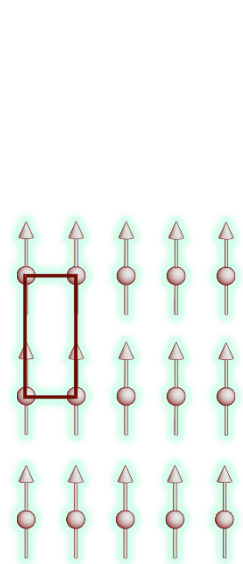
- determine microscopic magnetic structure
- study magnetic fluctuations

Neutrons have **SPIN**

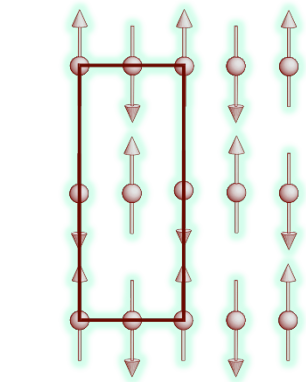
- can be formed into polarized neutron beams

MAGNETIC STRUCTURES

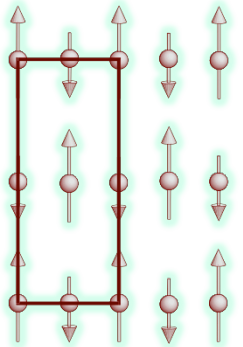
MAGNETISM → originates from orbital and spin motions of unpaired electrons and their interactions



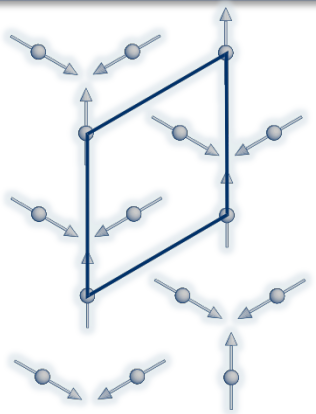
ferromagnetic



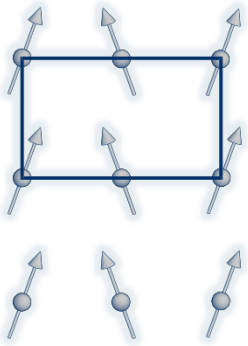
antiferromagnetic



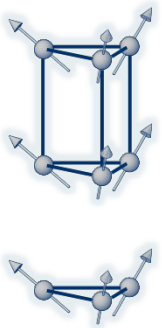
ferrimagnetic



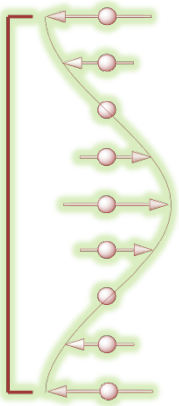
triangular



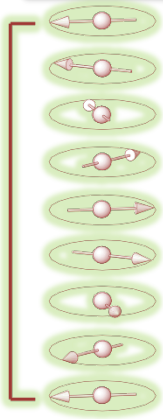
canted



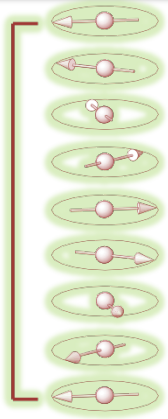
umbrella

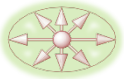


Sine or Cosine



Circular helix

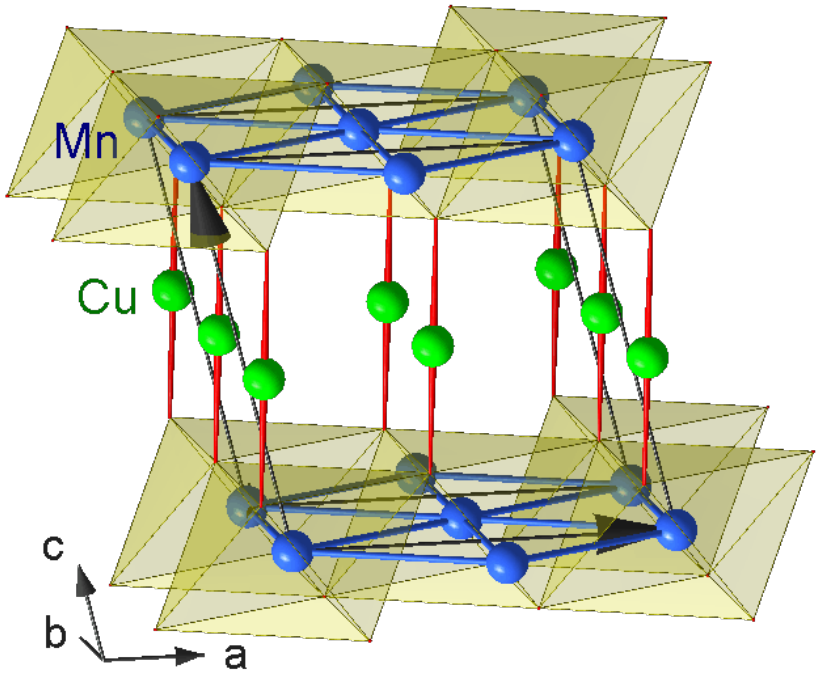




Elliptical helix

Magnetoelastic effect in the Triangular Lattice System $CuMnO_2$

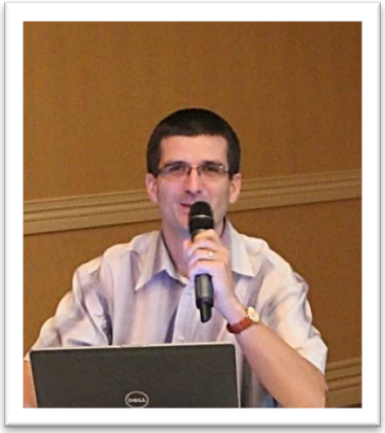
F. Damay *et al.*, PRB 80, 094410 (2009)
V. O. Garlea *et al.*, PRB 83, 172407 (2011)



Monoclinic: **C2/*m***

Jahn-Teller distortion of $Mn^{3+}O_6$ ($3d^4$)

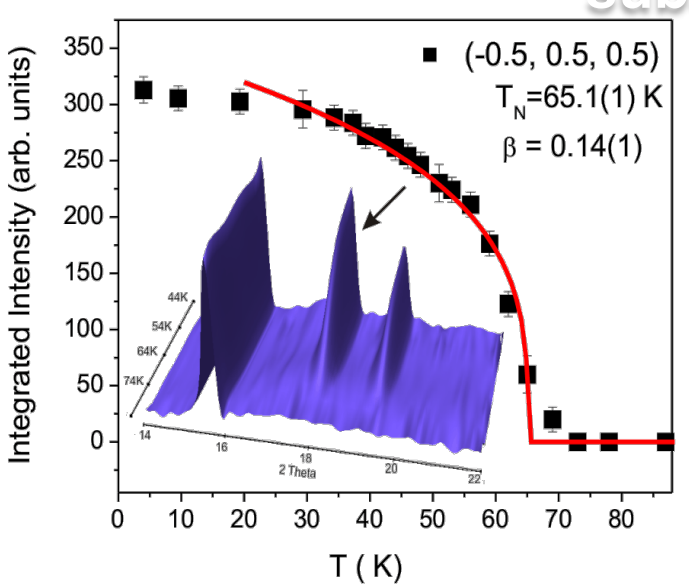
Ferro-orbital ordering $d_{3r^2-z^2}$

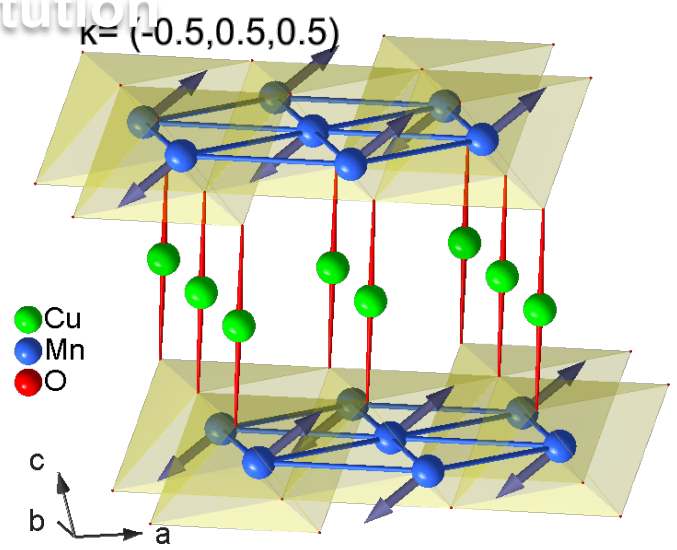


Ovi Garlea, QCMD, ORNL

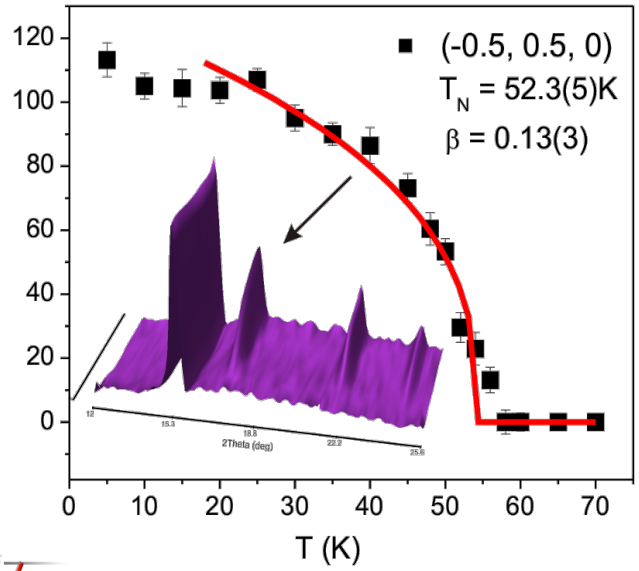
$Cu(Mn_{1-x}Cu_x)O_2$: Tuning of Magnetism by chemical substitution

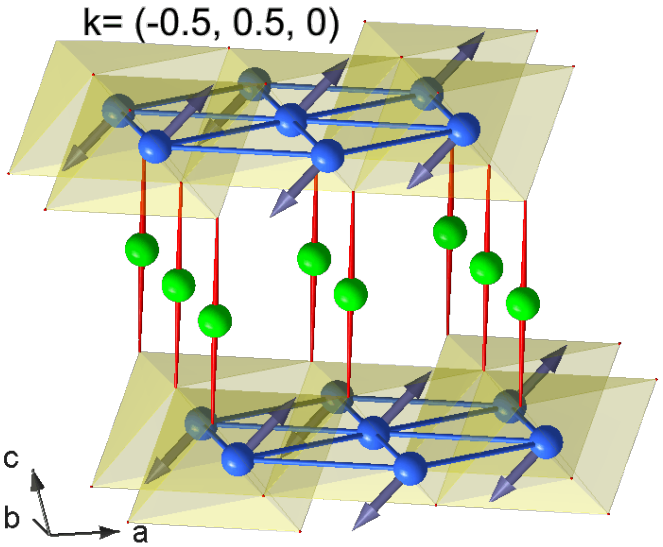
$CuMnO_2$





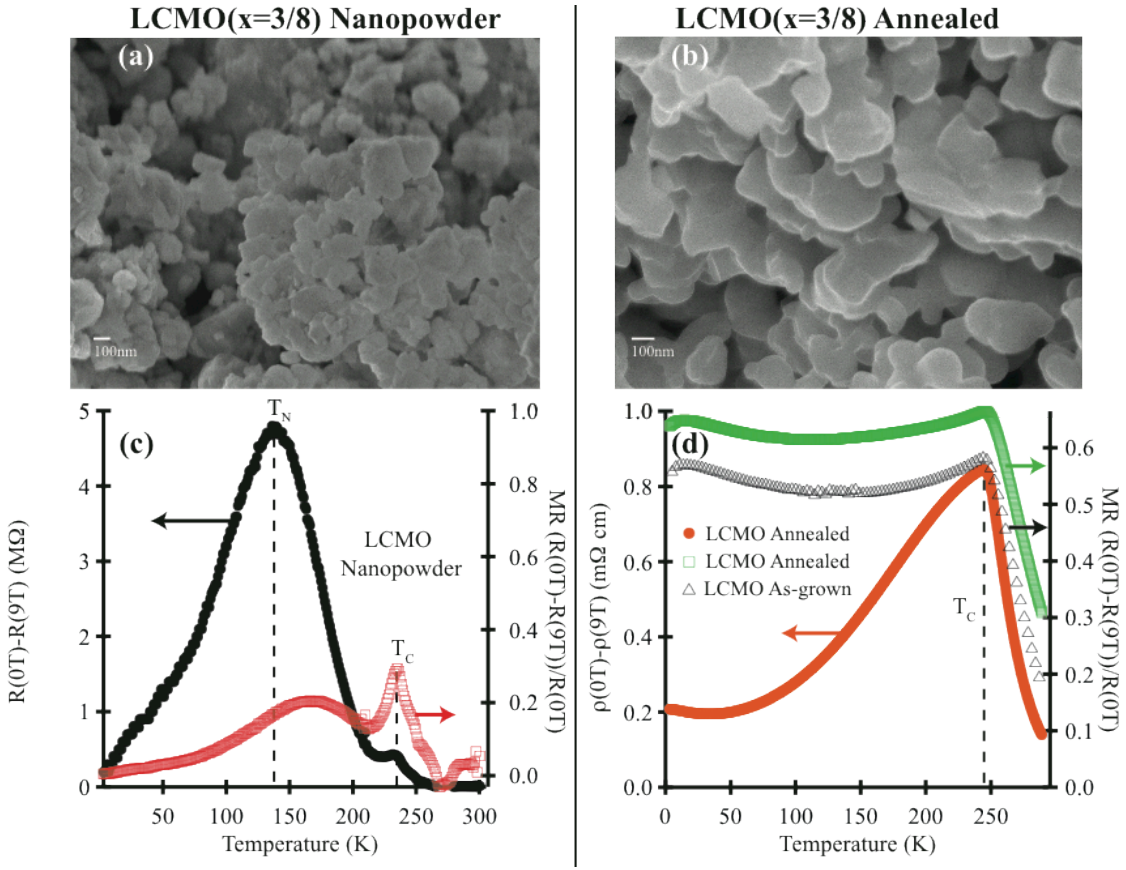
$Cu(Mn_{0.93}Cu_{0.07})O_2$





Neutron scattering study of nanocrystalline powders

Phase separation in nanocrystalline $La_{5/8}Ca_{3/8}MnO3$, *C. Dhital et al.*, Phys. Rev. B 84, 144401 (2011)



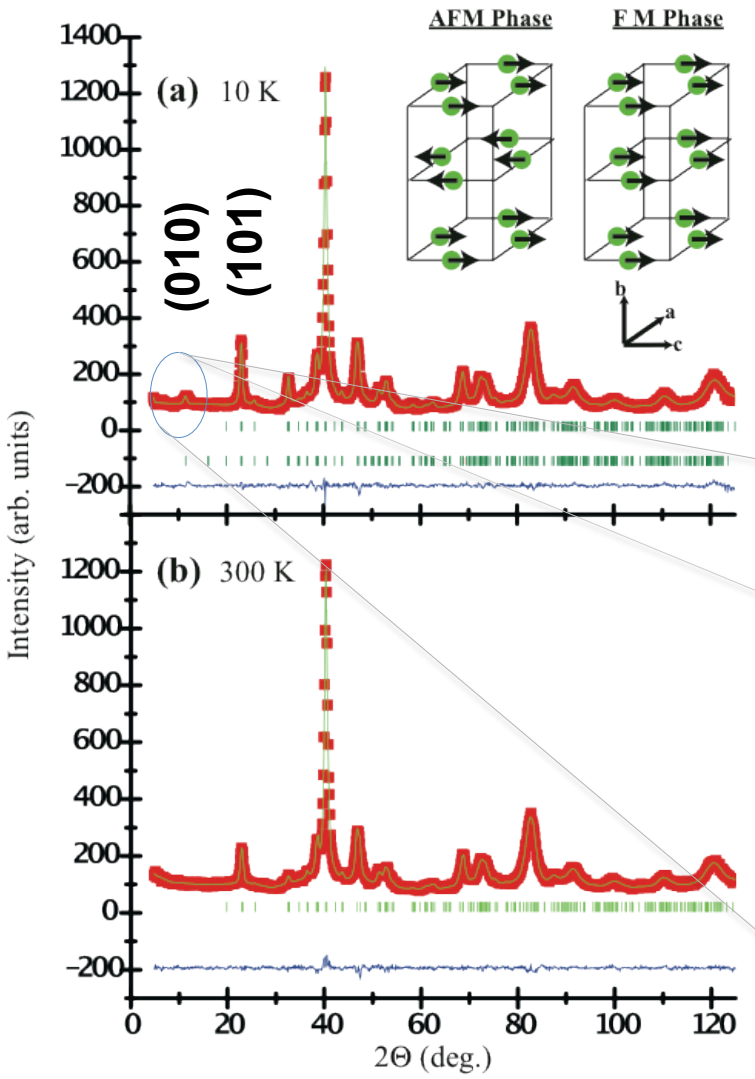
NANOSCALE MATERIALS

→ magnetic proprieties influenced by grain boundaries, surface strain effects, etc.

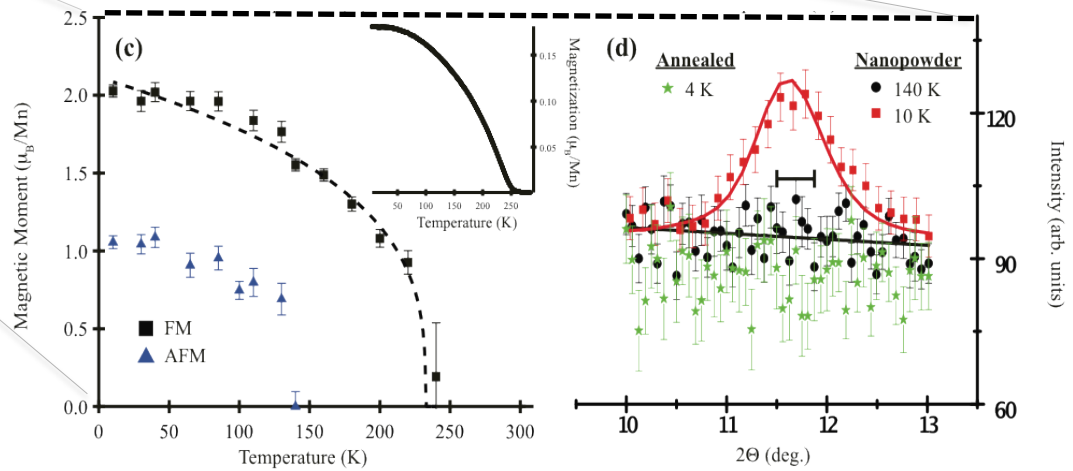
LCMO : Additional Magnetoresistance (MR) feature appears in ball milled nanopowder

Magnetic phase separation in the nanoregime?

LCMO nanopowder: Emergence of coexisting AF order



- **Phase separated A-type AF order in nanopowder, due to an anomalous enhancement of strain in the nanopowder**
- AF order reversibly annealed out of sample
- **T_N coincides with second MR feature in nanopowder**



Sample environments

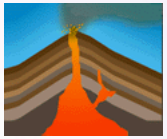
key to forefront experiments in condensed matter science and beyond

Neutrons are **NEUTRAL** particles
- are highly penetrating
- non-destructive probes
- study samples in extreme environments

Extremes of Temperature

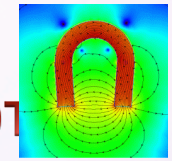
Low (cryostats)
- conventional closed cycle refrigerators (3.2 K – 700 K)
- ^{4}He cryostats (1.2 K – 4 K) and ^{3}He - ^{4}He dilution (50 mK)

High (furnaces)
- Conventional (up to 1200 °C)
- Special purpose (up to 3000 °C)



High Magnetic Fields

Superconducting magnets
typical - 8T; special - 16T; pulsed 30T



High Pressure

Fluid/gas cells (He or liquid) [to 1 GPa]

Clamp cells [to 2GPa]

Anvil presses (to 100 GPa)

Other Specialized Environments

Load frames, sheer cell, friction stir welder, etc.

FERROELECTRIC ORDER

MAGNETIC ORDER

MULTIFERROICS

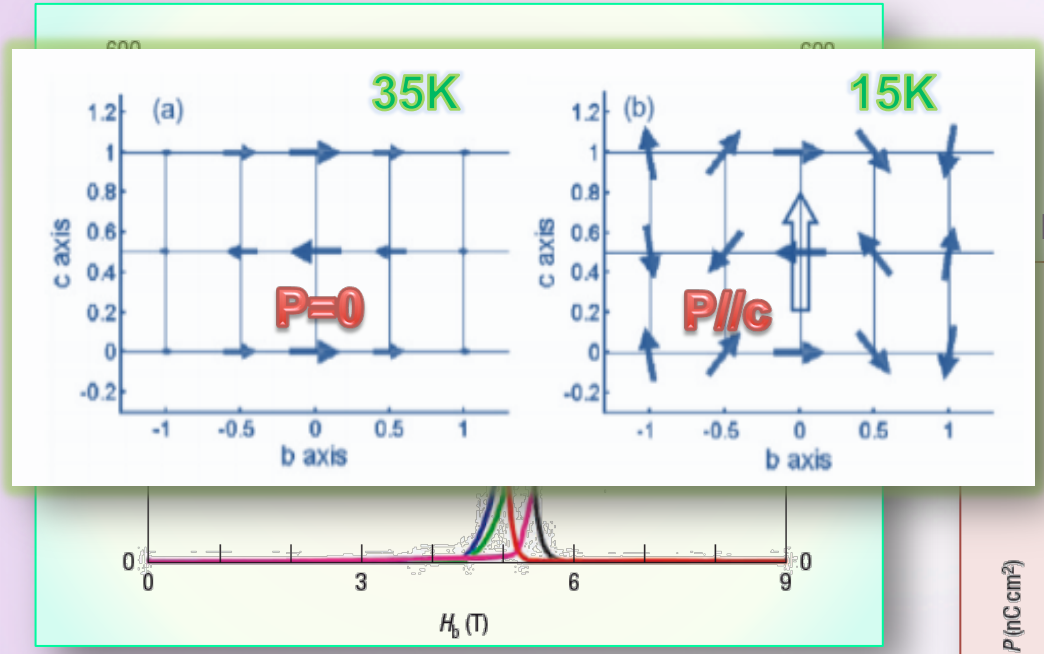
$P_i = P_i^s + \varepsilon_o \varepsilon_{ij} E_j + \alpha_{ij} H_j + \ldots$

$M_i = M_i^s + \mu_o \mu_{ij} H_j + \alpha_{ij} E_j + \ldots$

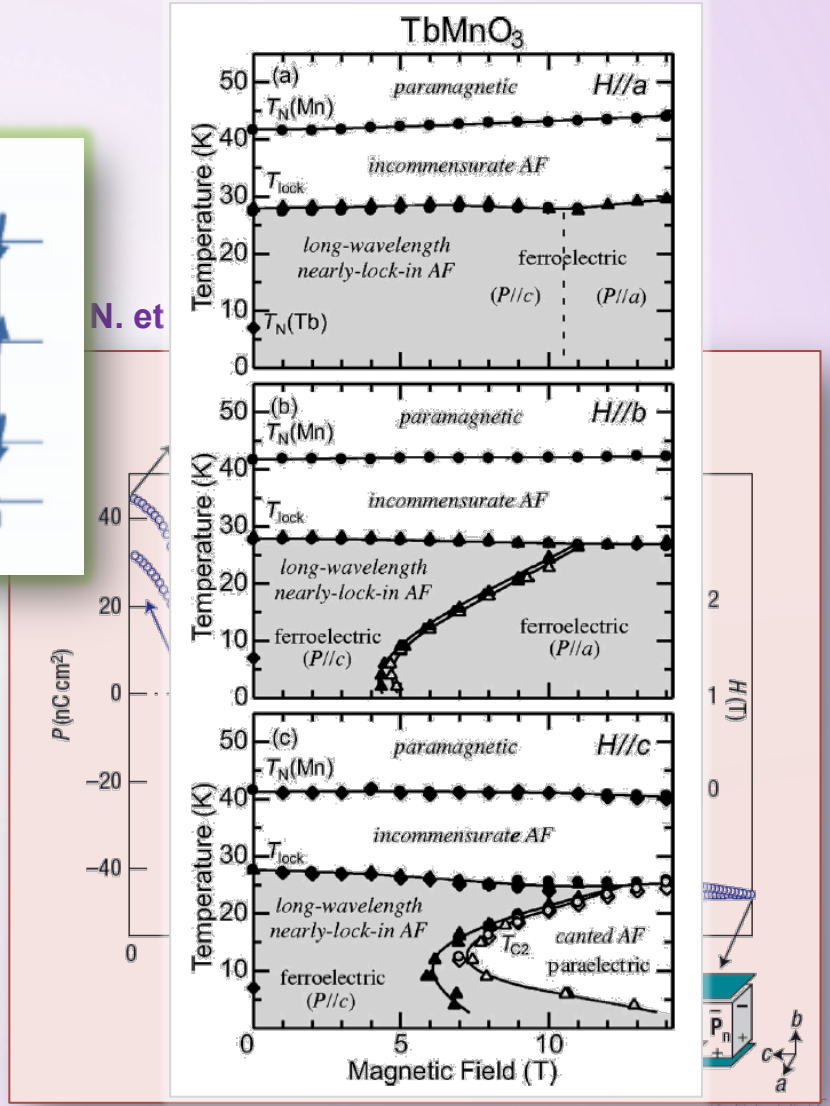
FERROELASTICITY

$$F(E,H) = F_o - P_i^s E_i - M_i^s H_i - \tfrac{1}{2} \varepsilon_o \varepsilon_{ij} E_i E_j - \tfrac{1}{2} \mu_o \mu_{ij} H_i H_j - \alpha_{ij} E_j H_j - \tfrac{1}{2} \beta_{ijk} E_i H_j H_k - \tfrac{1}{2} \gamma_{ijk} H_i E_j E_k \ldots$$

Tunability of Multiferroics by Applied Magnetic Field



Kimura, T. et al., **Nature 426, 55–58 (2003).**

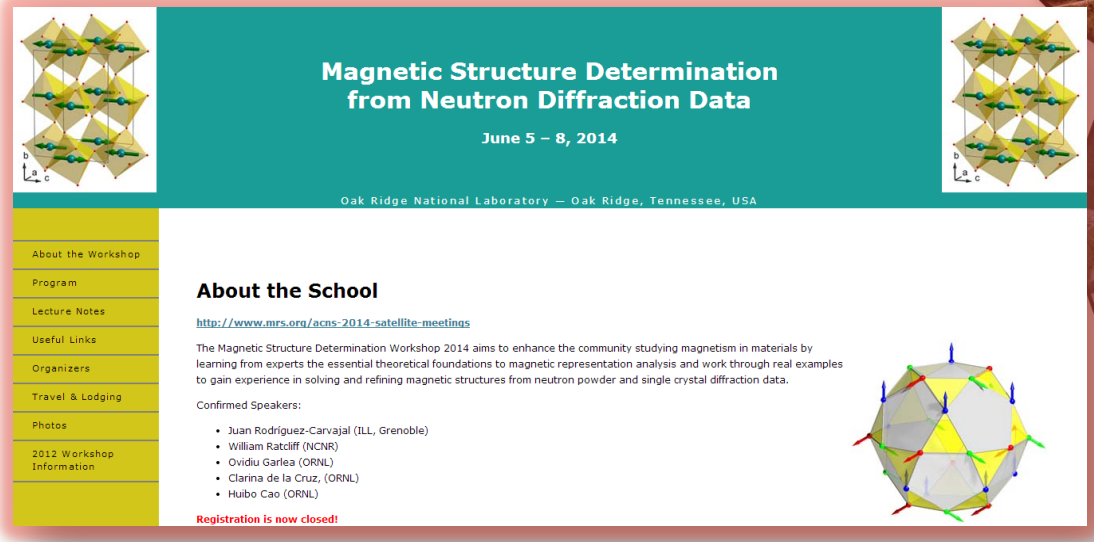


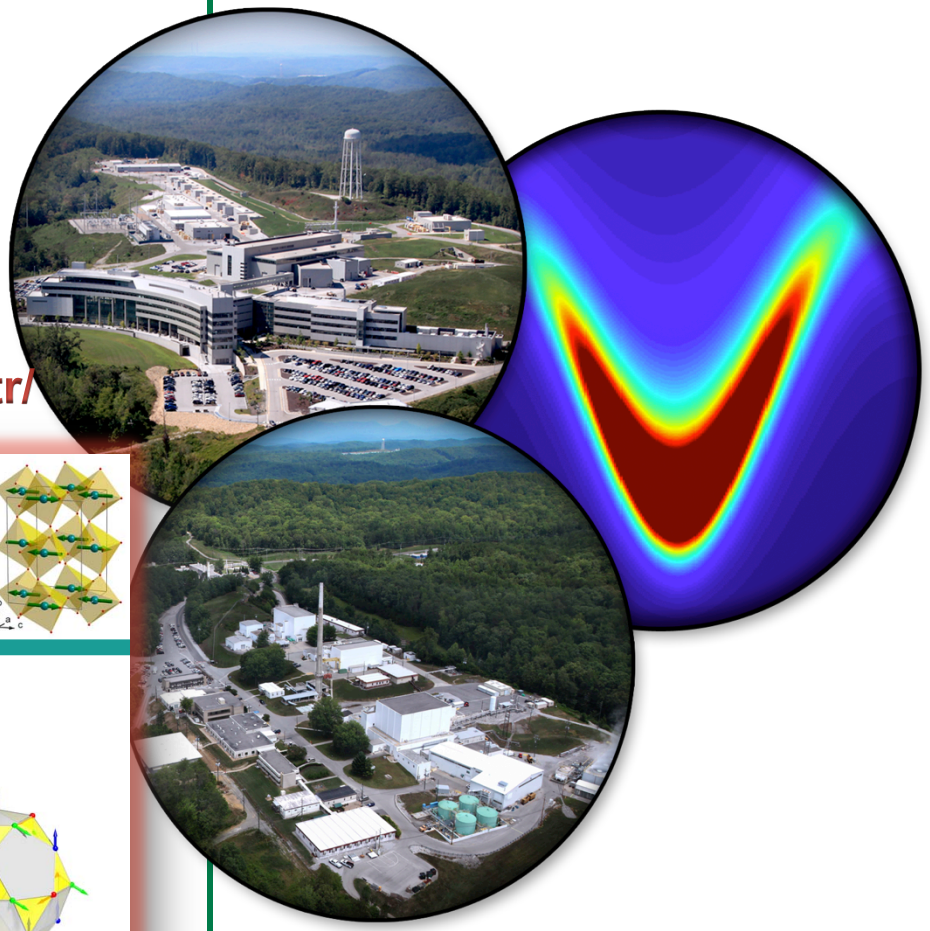
Kimura, T. et al., **Phys. Rev. B 71, 224425 (2005)**

MAGNETIC STRUCTURE DETERMINATION FROM NEUTRON DIFFRACTION DATA

Biennial workshop with NCNR

http://neutrons.ornl.gov/conf/2014/magstr/





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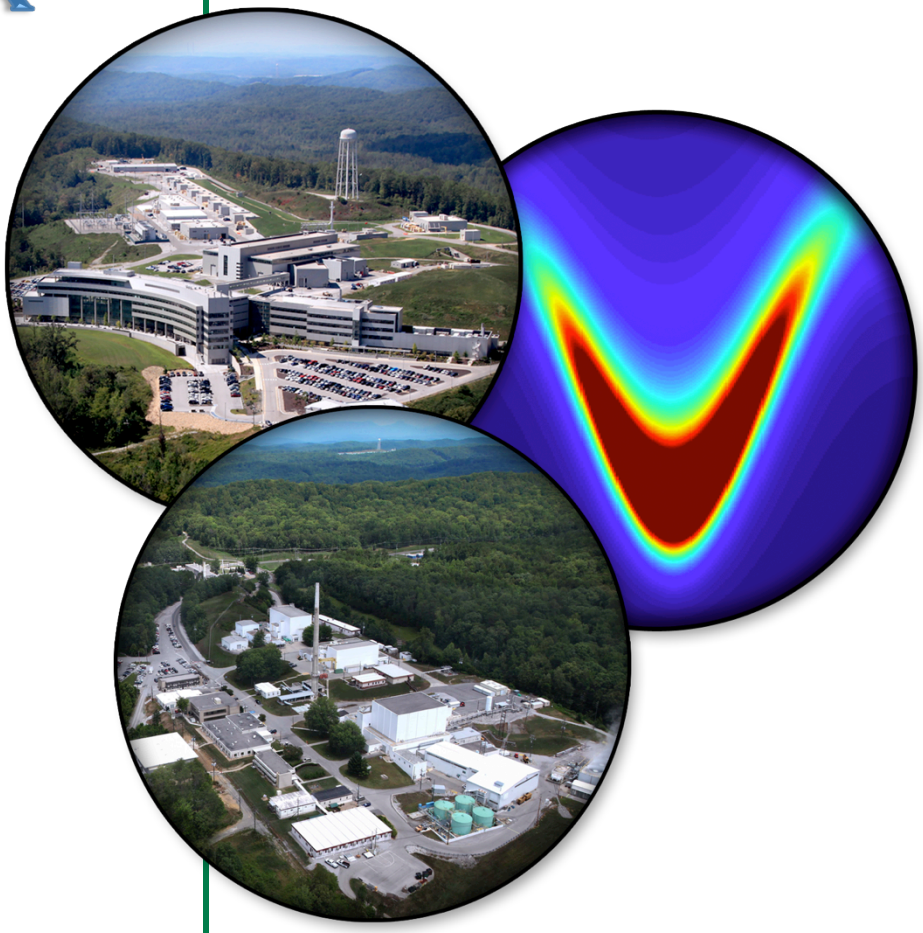
X-RAY AND NEUTRON POWDER DIFFRACTION AS COMPLIMENTARY TECHNIQUES

Ashfia Huq, CEMD, ORNL



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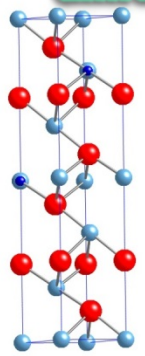
Neutrons and X-ray are complementary tools in Battery Research

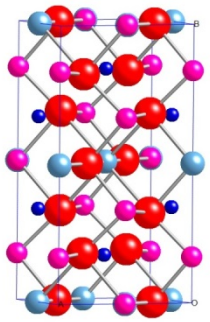
- ✓ Develop/design materials to increase performance of electrodes and electrolytes in batteries
- ✓ Structural information is crucial to understand the electrochemical properties and motion of Li in the system.

Detailed structural analysis using combined neutron and X-ray powder diffraction

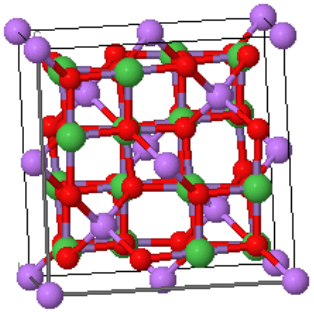
Elements	Neutron scattering length : *b*	Atomic Number : *Z*
Li (natural)	**-1.9**	**3**
Mn	-3.73	25
Co	2.49	27
Ni	10.3	28



Space Group : R -3 m
a = 2.85, c = 14.28
$Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$



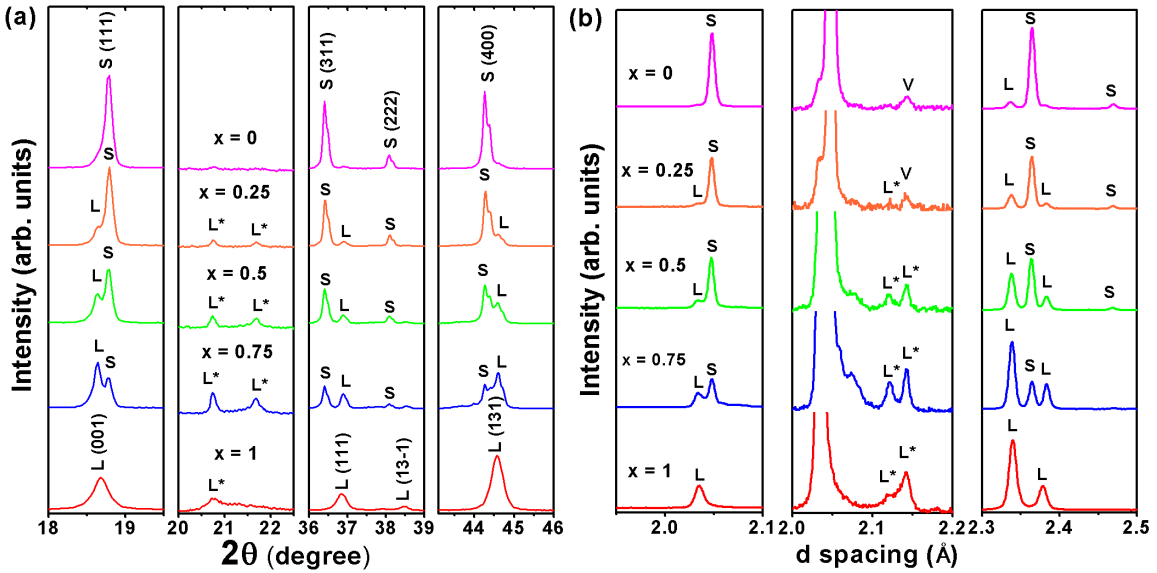
Space Group : C 2/m
a=4.94,b=8.55, c = 5.04, b =109.3
$Li(Li_{0.2}Ni_{0.17}Mn_{0.6}Co_{0.03})O_2$



Space Group : F d 3 m
a = 8.17
$Li(Ni_{0.425}Mn_{1.5}Co_{0.075})O_4$

Neutrons reveal higher Li concentration in TM layer for x=0.5 and 0.75, improving cycle life for these compositions.

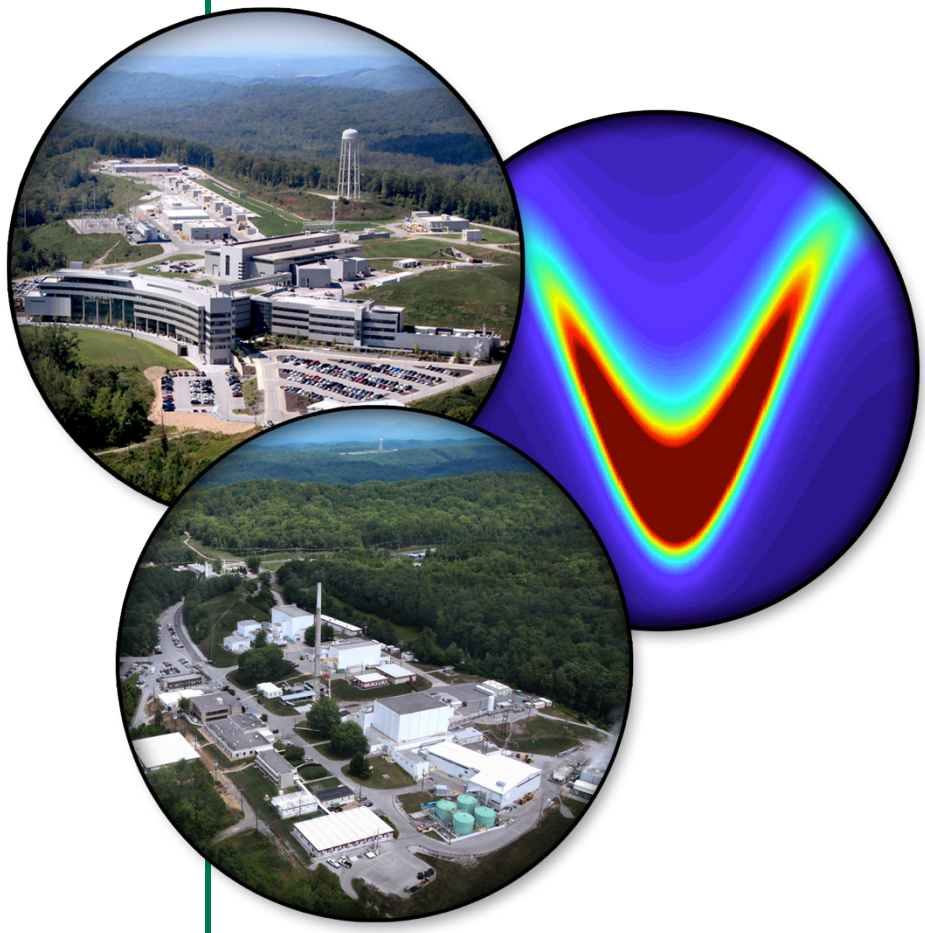
X-RAY



NEUTRON

- ✓ No TM ordering in the spinel phase.
- ✓ Li and TM ordering converts the nominally layered (R3m) phase to form a monoclinic phase (C2/m) where superstructure reflections are observed.
- ✓ Impurity cubic phase is identified as Ni_6MnO_8, instead of the traditional cubic $Li_xNi_{1-x}O_y$.
- ✓ Ex-situ XRD reveals entire layered phase (C2/m) transforms irreversibly into cubic spinel (Fd-3m with 3V plateau) in the composite cathodes during extended cycling.
- ✓ Higher Li occupancy in the transition metal layer of the layered phase appears to be the driving force for this facile structural transformation that improves the cycle life of the cathode.

IN SITU STUDIES OF SOLID OXIDE FUEL CELL MATERIALS



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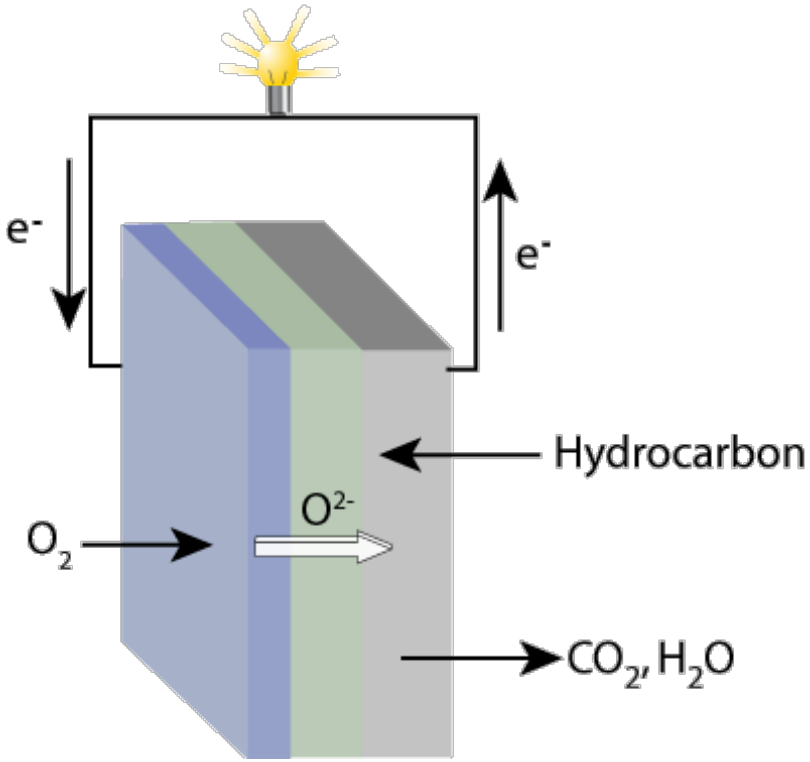
Solid Oxide Fuel Cell (SOFC)



- Cathode - Porous, 2-phase composite
- Electrolyte - Dense, single phase
- Anode - Porous, Multi-phase composite

- Oxygen from the air is reduced at the cathode.

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

- Oxidation of fuel at the anode.

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

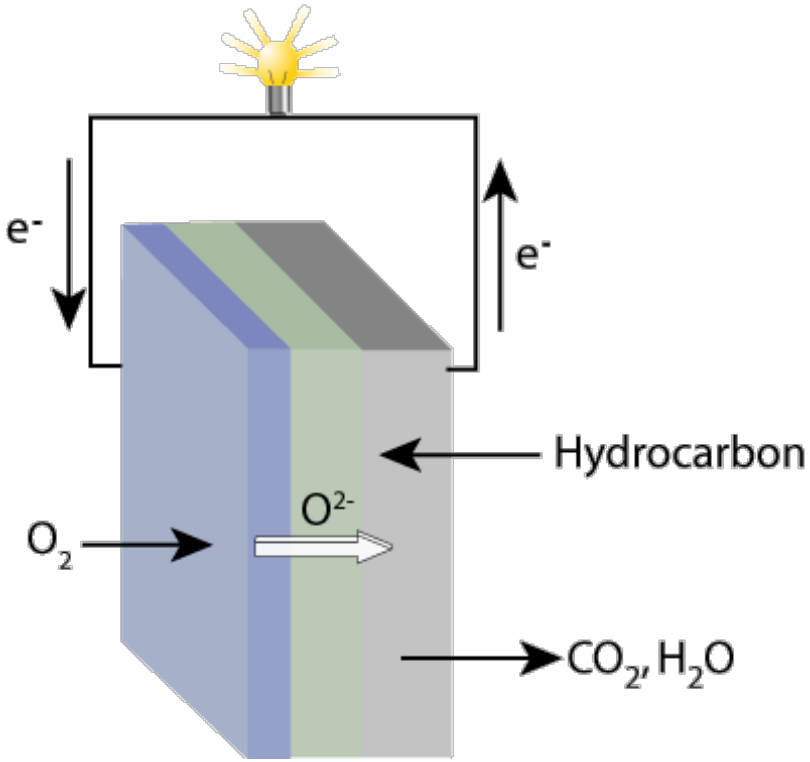
- Current cells have a reformer to generate CO/H_2 fuels from hydrocarbons.

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

- Ideally we can utilize hydrocarbons directly:

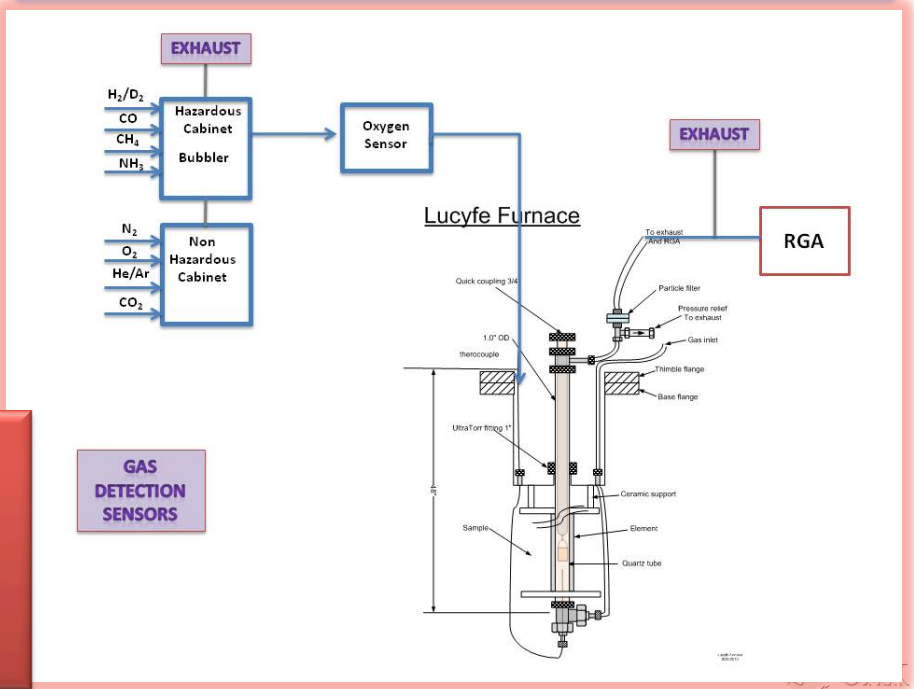
$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$

In situ Neutron powder diffraction of SOFC materials



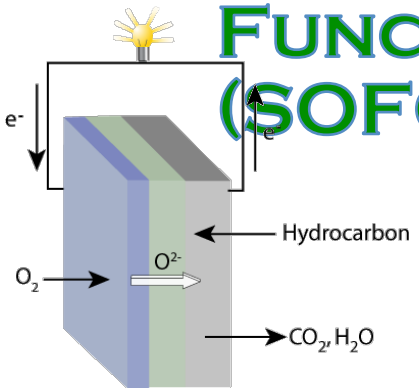
Understanding the structure-function relationship between crystal structure and composition on oxygen ion transport to optimize the performance of SOFC materials

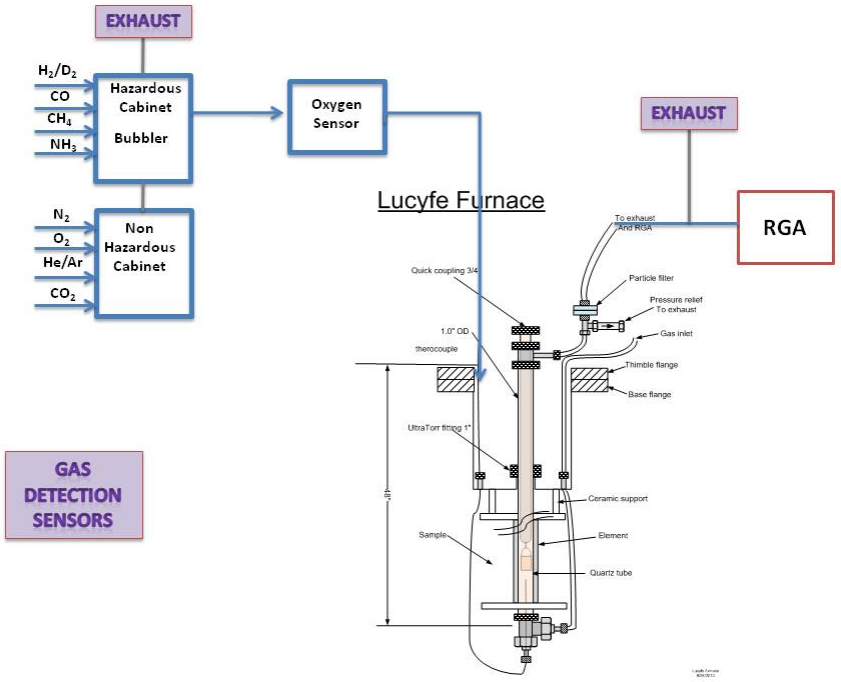
Structural information must be obtained under operational condition (IN-SITU)



An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) make experiments possible under operational condition.

Understanding Structure and Function in Solid Oxide Fuel Cell (SOFC)





Challenge

A basic understanding of the structure-function relationship that describes the influence of crystal structure and composition on oxygen ion transport is needed to fully optimize the performance of these materials.

This valuable structural information must be obtained under operational condition.

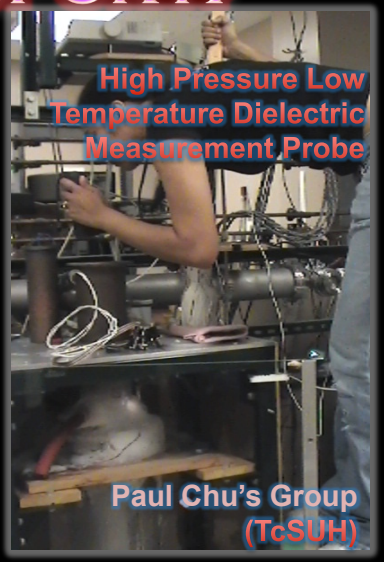
- Cathode - Porous, 2-phase composite
- Electrolyte - Dense, single phase
- Anode - Porous, Multi-phase composite

An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) make experiments possible under operational condition.

A Neutron Scattering experiment is NOT the first step…

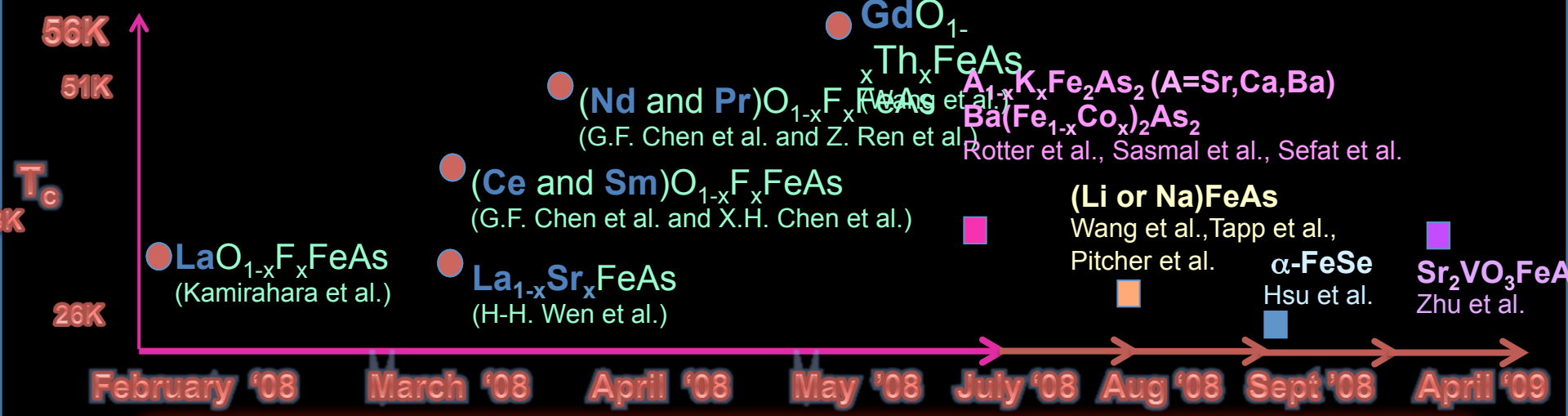
HOT Materials discovery

Bulk thermodynamic/transport/ dielectric properties



The Story of Fe-based superconductors: A Neutron Scatterer's perspective

FeAs-based Superconductors



J|A|C|S
COMMUNICATIONS

Published on Web 02/23/2008

NON-Cu based high temperature Superconductors!

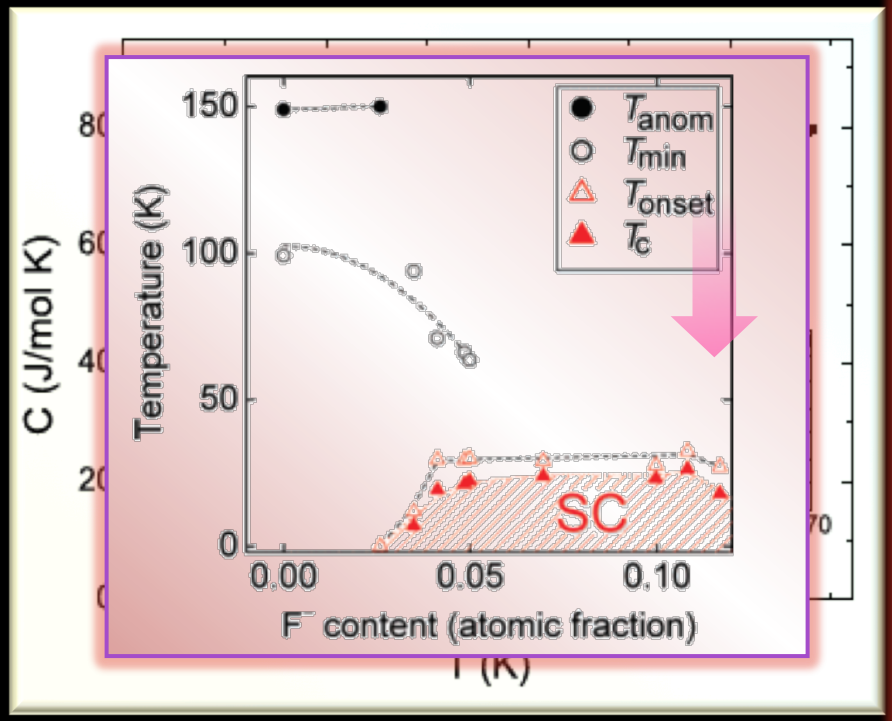
Iron-Based Layered Superconductor $La[O_{1-x}F_x]FeAs$ (x = 0.05−0.12) with T_c = 26 K

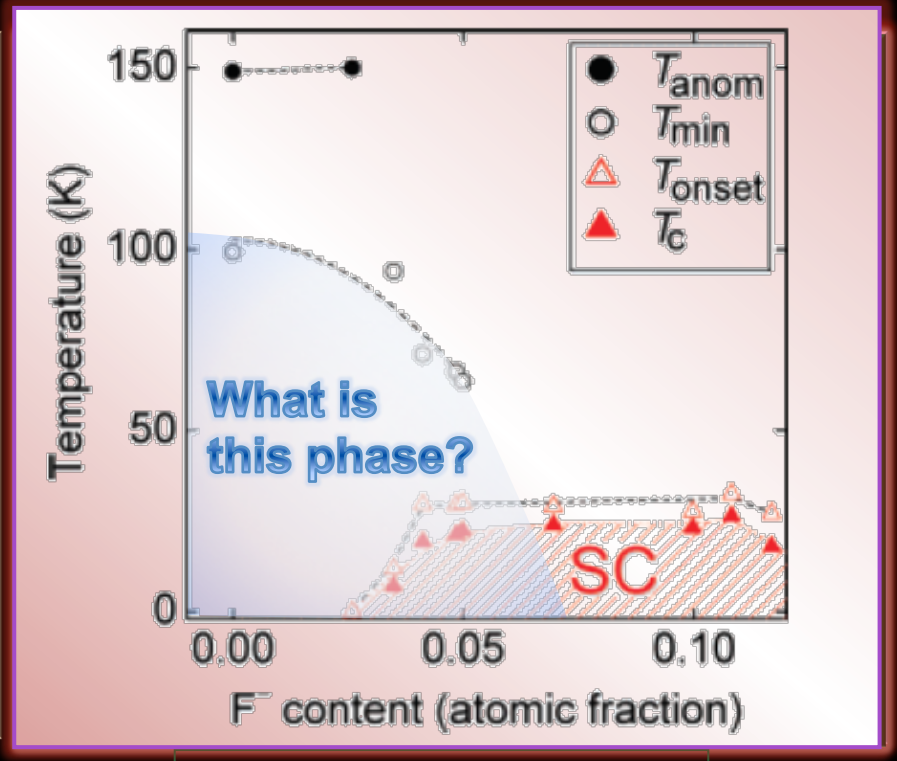
Yoichi Kamihara,*,† Takumi Watanabe,‡ Masahiro Hirano,†,§ and Hideo Hosono†,‡,§

ERATO-SORST, JST, Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-1, and Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received January 9, 2008; E-mail: hosono@msl.titech.ac.jp

Undoped $LaO_{1-x}F_xFeAs$ Parent compounds



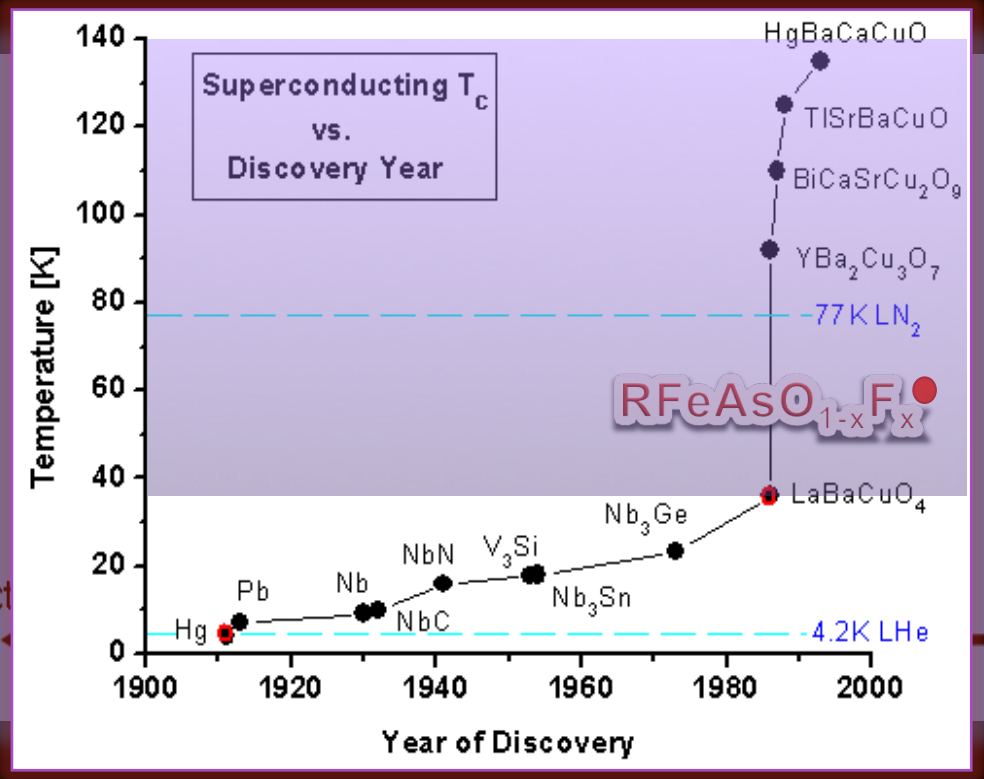


K. Prokhnenko et al. (2008)

Anomalies in the physical properties at T_{anom}~150K

The Cuprates HTSC era

Over 25 years of studying unconventional superconductivity in the Cuprates



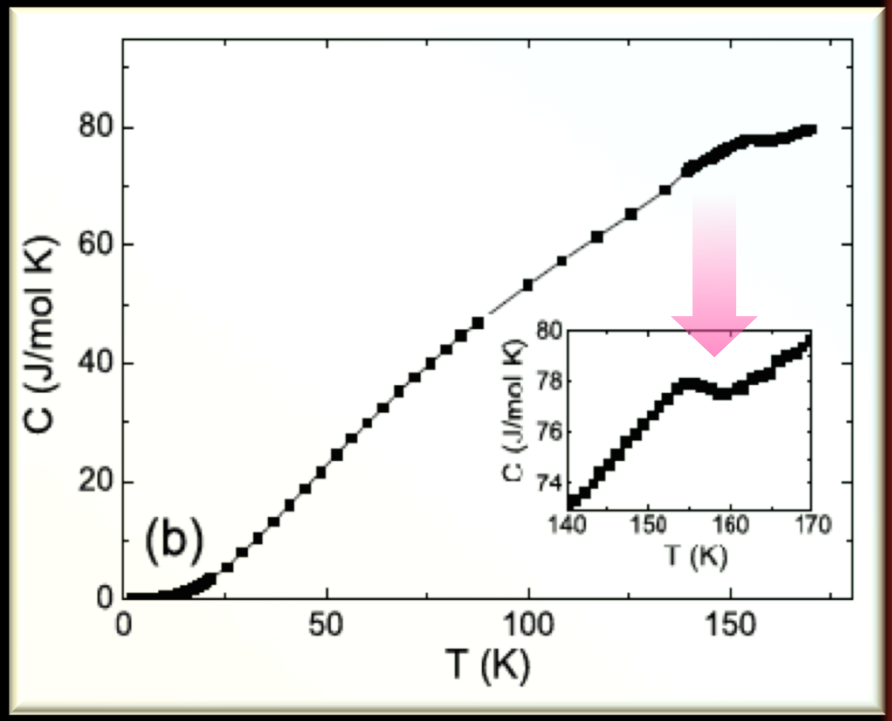
➔ general belief that SC in cuprates is derived from AFM parent compound

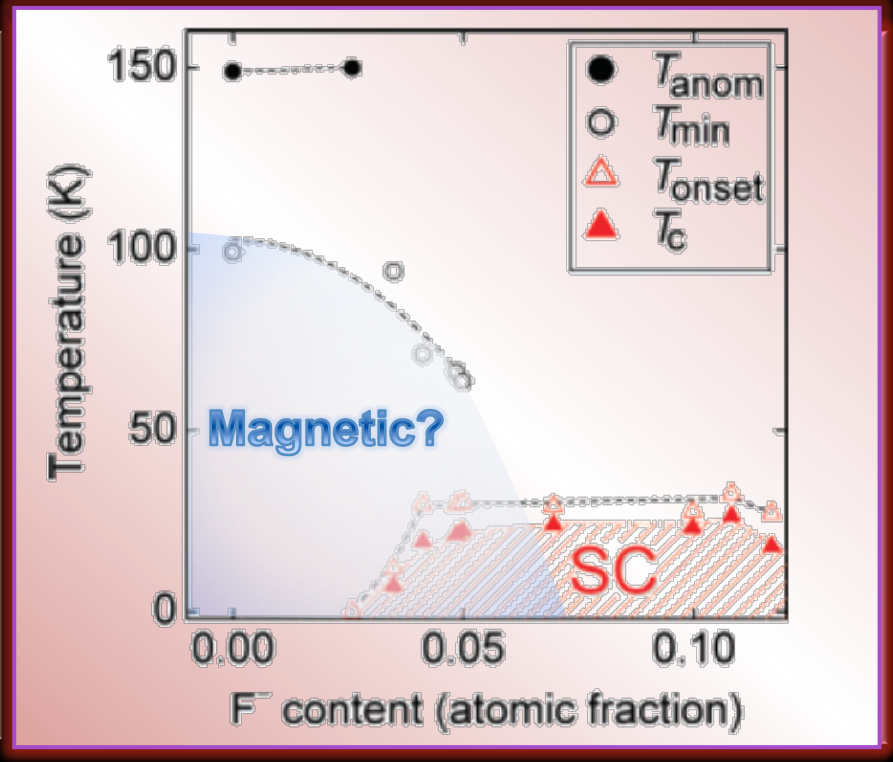
MAGNETISM is key in understanding the mechanism of High temperature superconductivity

At these high Tc's, the conventional phonon based BCS theory of superconductivity does not work.

NEUTRONS ideal and powerful probe to use in studying unconventional superconductivity

Undoped LaOFeAs Parent compound

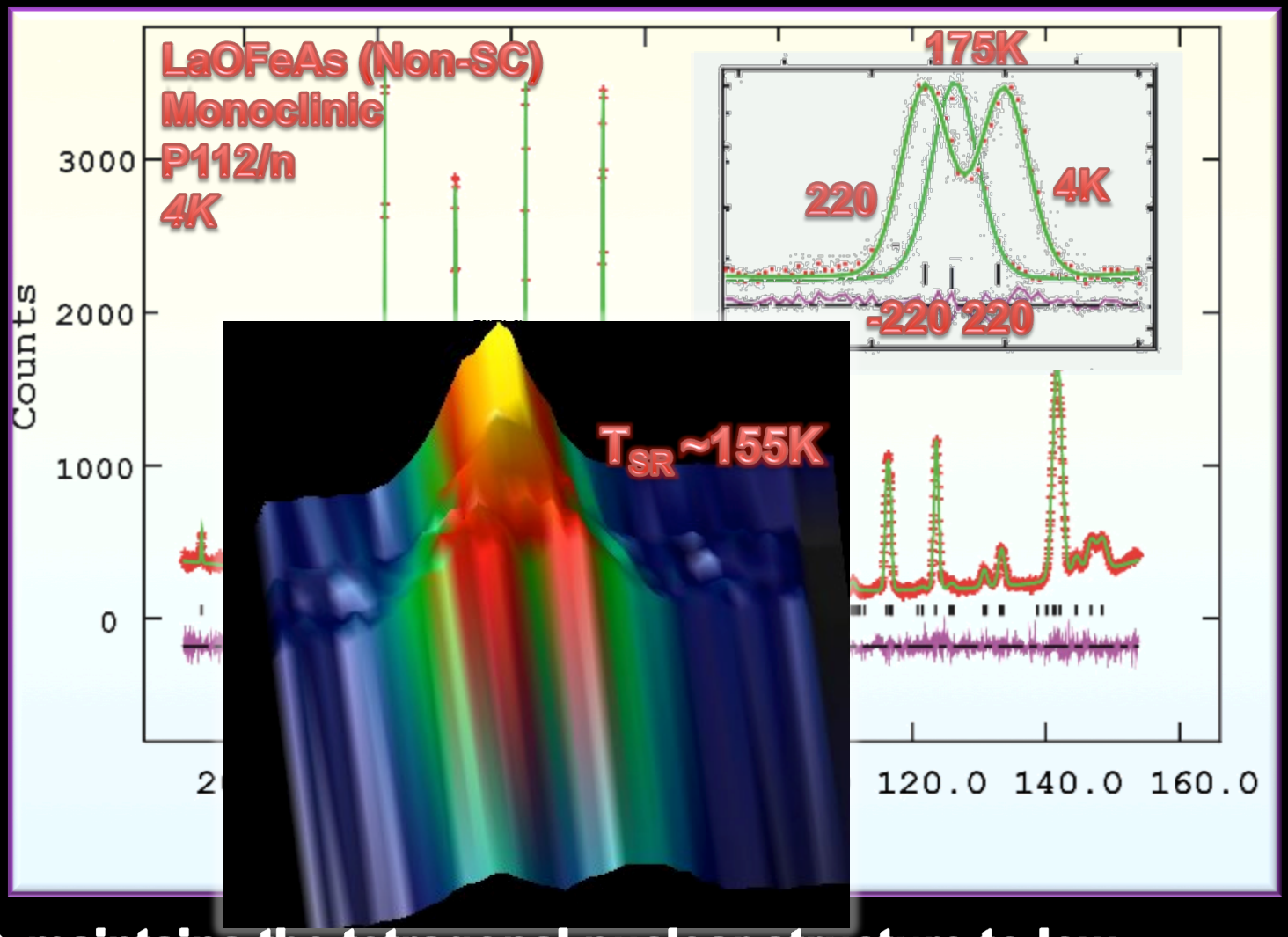




Dong et al. (2008)

Anomalies in the physical properties at T_{anom}~150K

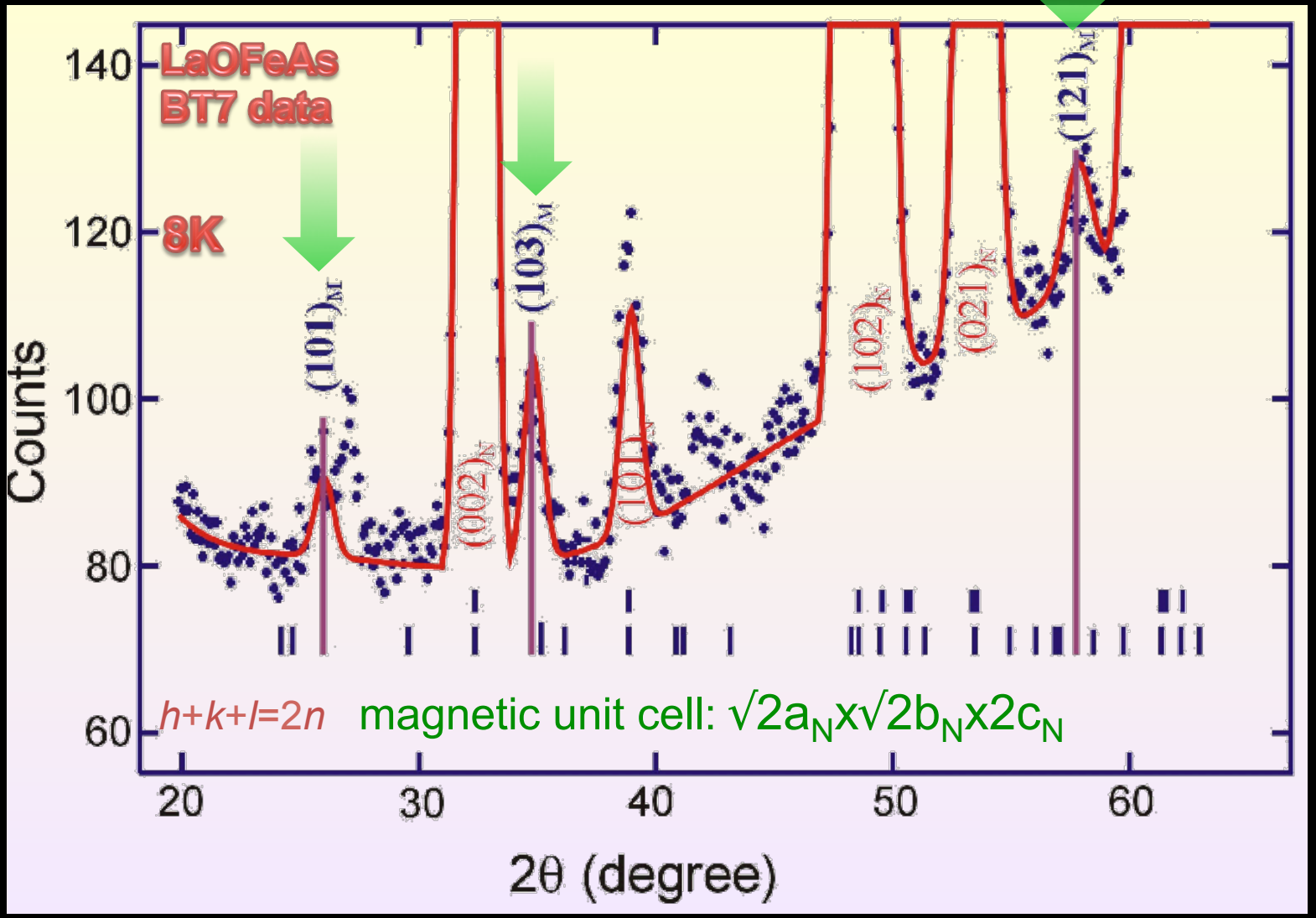
Neutron Powder Diffraction



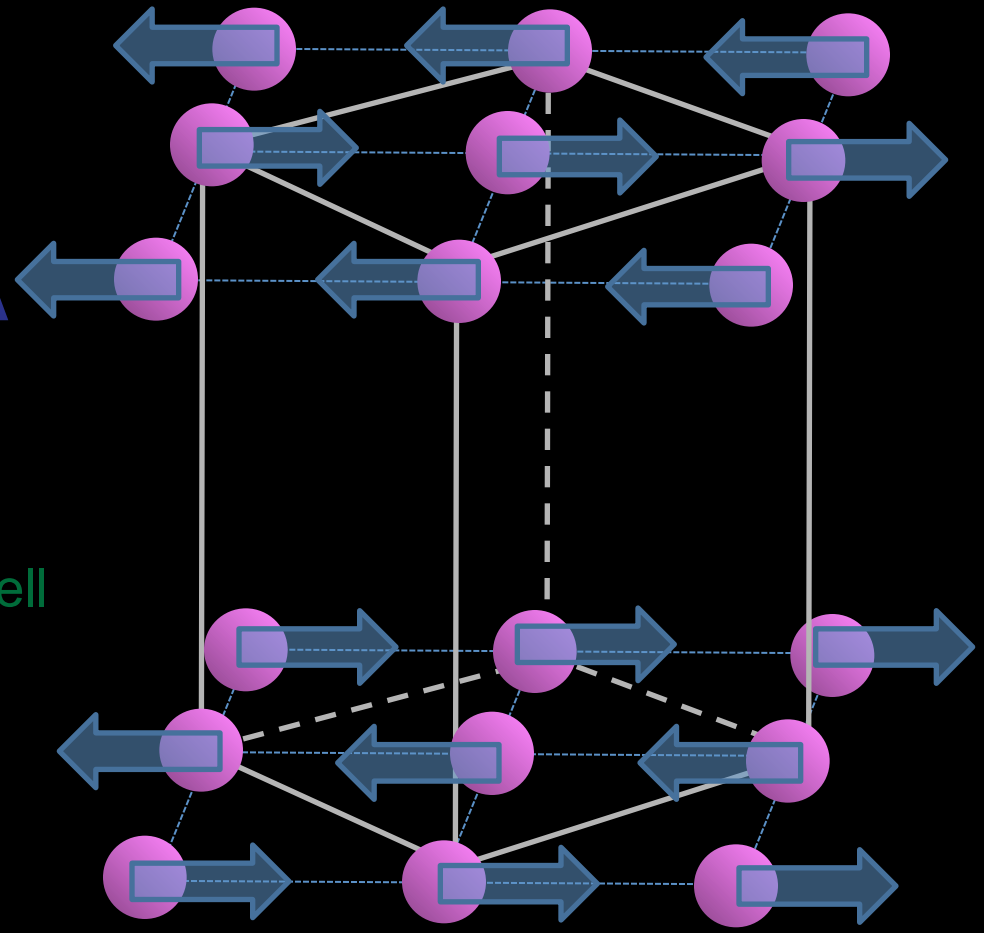
➔ maintains the tetragonal nuclear structure to low Temperatures

➔ Nuclear structure changes upon lowering the Temperature

AFM Order of Fe spins at Low-T



AFM Order of Fe spins at Low-T



c

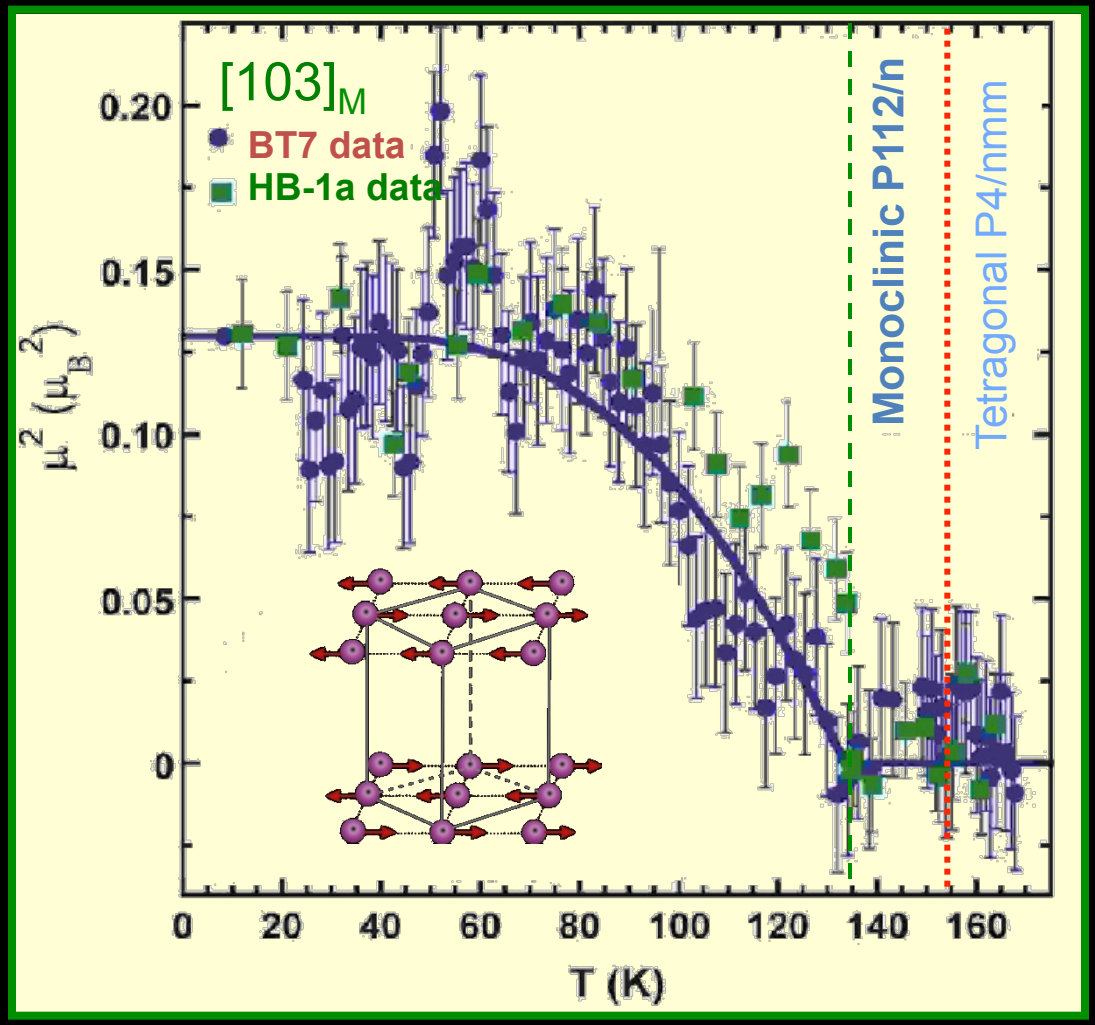
nuclear cell
$a_N x b_N x c_N$
P112/n

- Fe spins lie in the ab plane
- cannot determine unambigously the direction in-plane
- stripe type AFM order in-plane
- AFM interaction along the c-axis
- m=0.36(5) μ_B/Fe at 8K

magnetic unit cell: $\sqrt{2}a_N x \sqrt{2}b_N x 2c_N$

Magnetic Transition at T_N~137K

- solid line is a simple fit to mean field theory which gives T_N = 137 K
- the lattice is distorted at 155 K, preceding the long-range static AFM order of the Fe spins

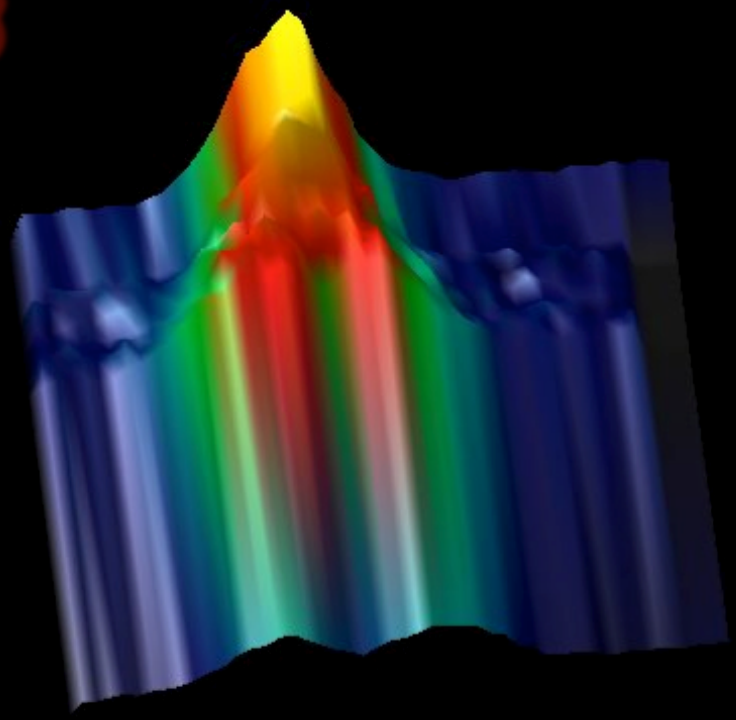


Temperature dependence of the order parameter at Q = 1.53 Å^{-1}

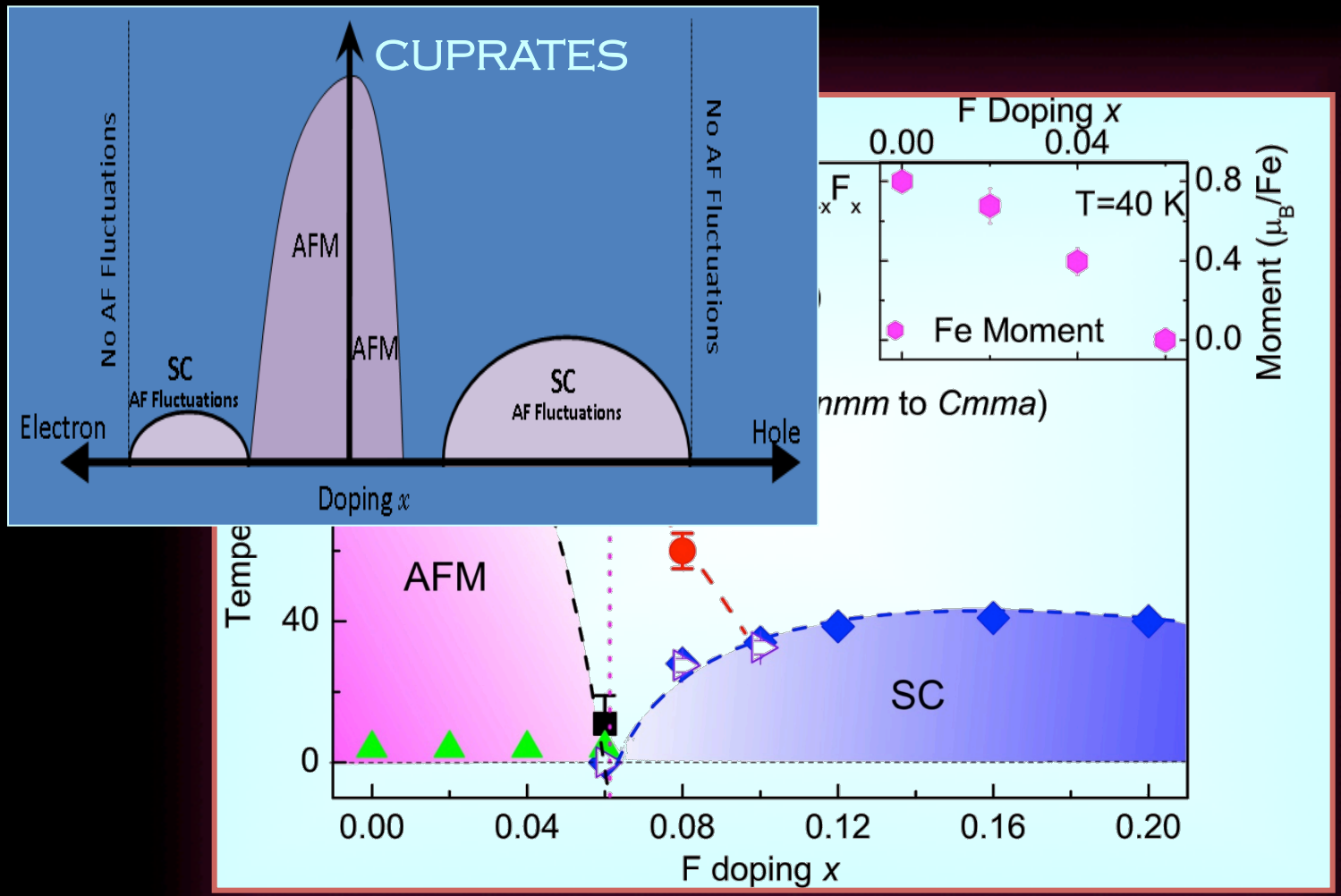
MAGNETIC ORDER VERSUS SUPERCONDUCTIVITY IN IRON-BASED LAYERED $LA(O_{1-x}F_x)FEAS$ SYSTEMS

C. dela Cruz , Q. Huang, J. W. Lynn, Jiying Li, W. Ratcliff II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, P. Dai,

Nature 453, 899-902 (12 June 2008)



Phase diagrams of FeAs superconductors



J. Zhao, Q. Huang, C. de la Cruz, S. Li, J. W. Lynn, Y. Chen, M. A. Green, G. F. Chen, G. Li, Z. C. Li, J. L. Luo, N. L. Wang, and P. Dai, Nature materials (2008)

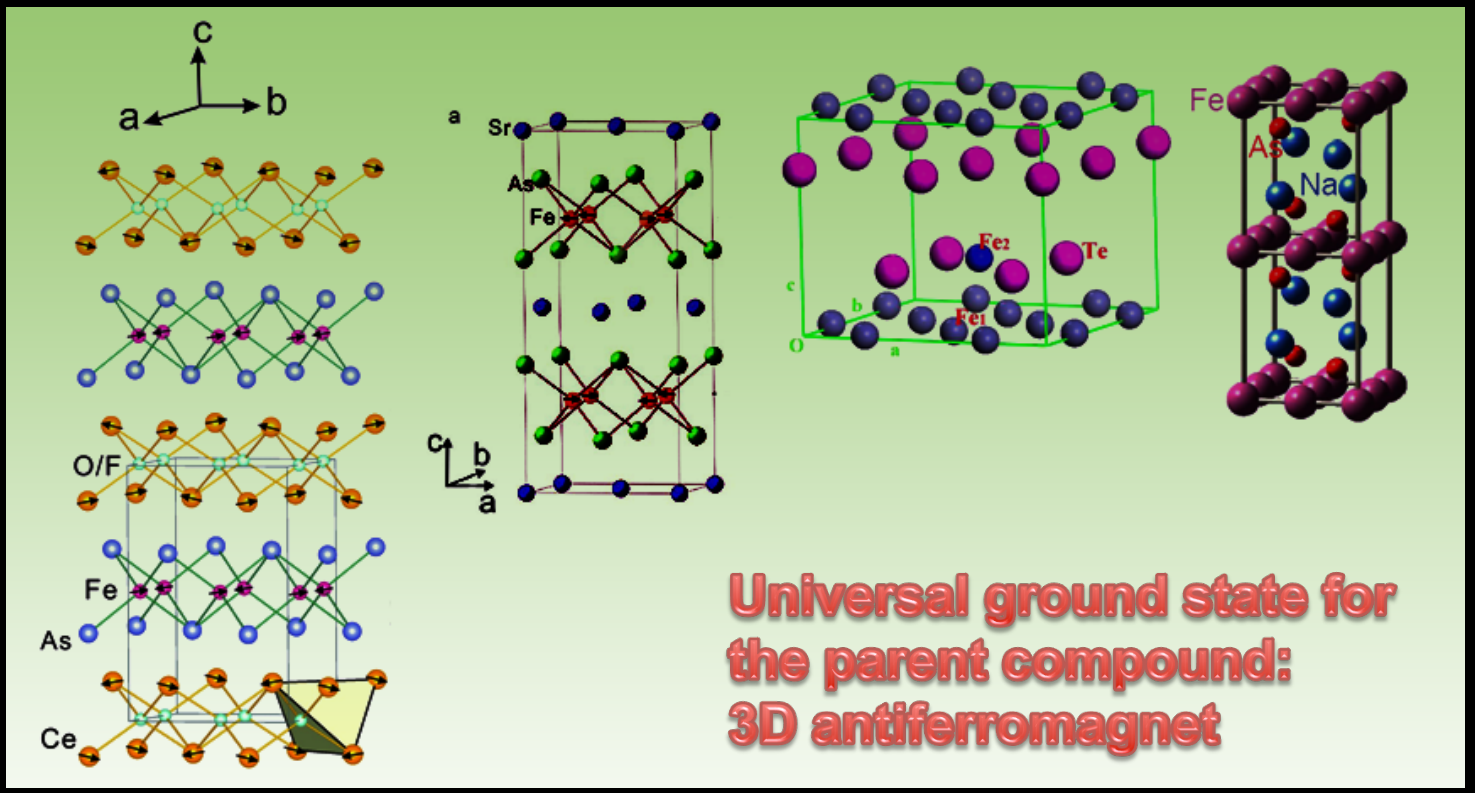
Classes of discovered Fe-based superconductors

$RFeAsO_{1-x}F_x$ "1111"

MFe_2As_2 (M=Ca,Sr) "122"

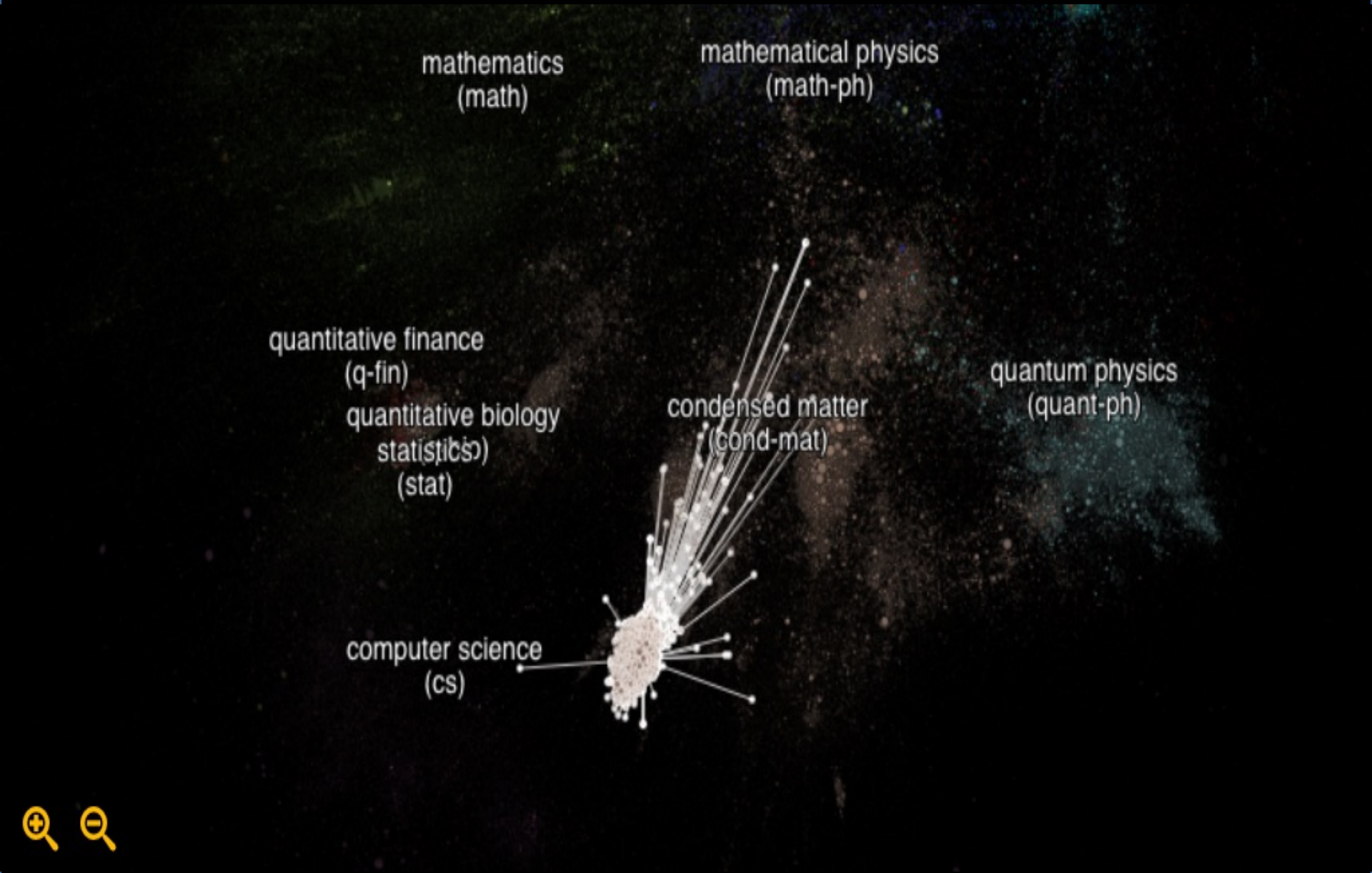
$FeTe_xSe_{1-x}$ "FeSe" or "pnictide free"

$KFeAs$ (K=Na,Li) "111"

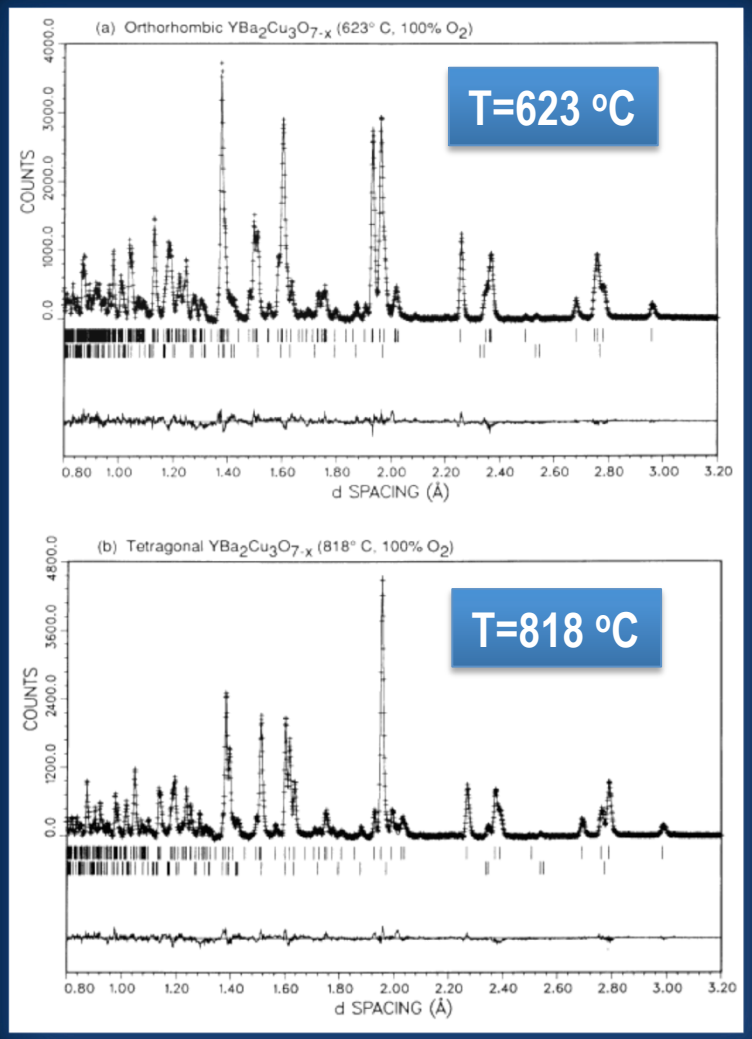


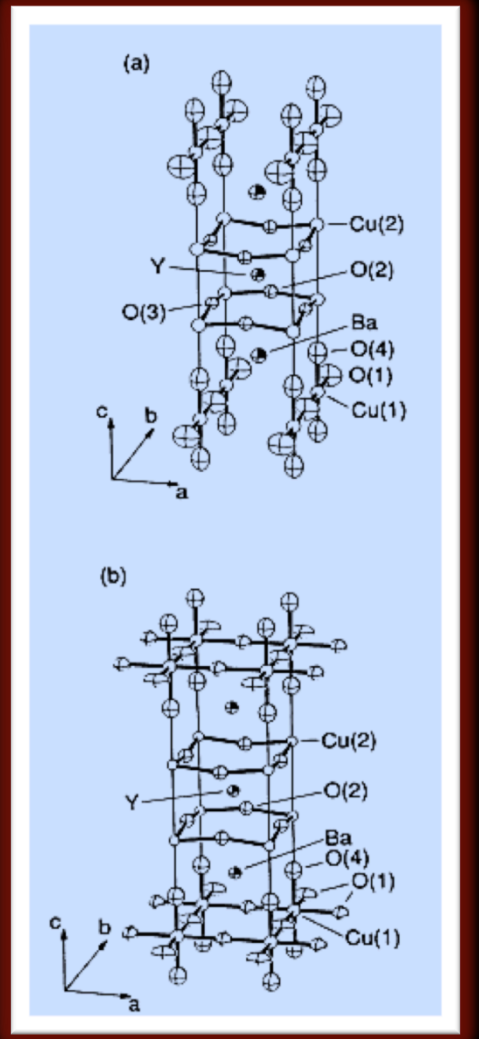
Universal ground state for the parent compound: 3D antiferromagnet

www.paperscape.org



Structure of High T_c Superconductors



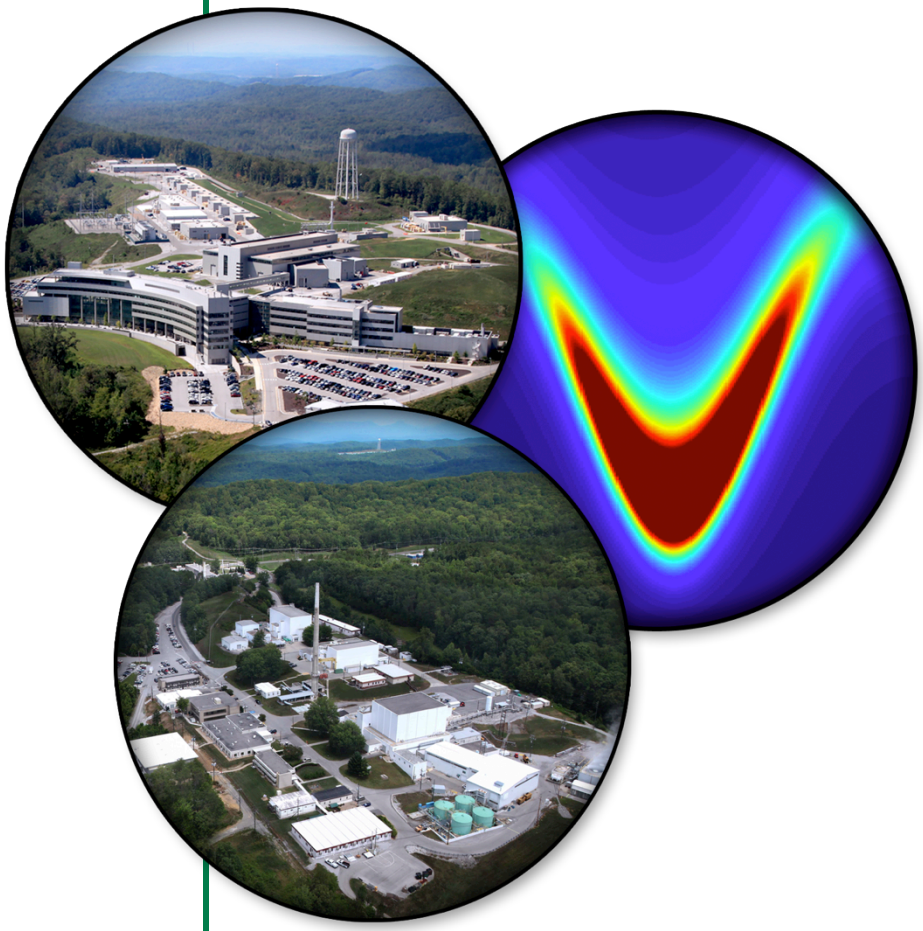


J. D. Jorgensen et al PRB , Received June 1987
>1000 citations

Powder diffraction is an extremely powerful technique to study the physics, chemistry and material science problems in a very wide variety of materials

Fundamental answers to "where are the atoms?" and "what's the magnetic ground state?" derived from powder diffraction measurements can take you a long way

AB-INITIO STRUCTURE SOLUTION FROM POWDER DIFFRACTION



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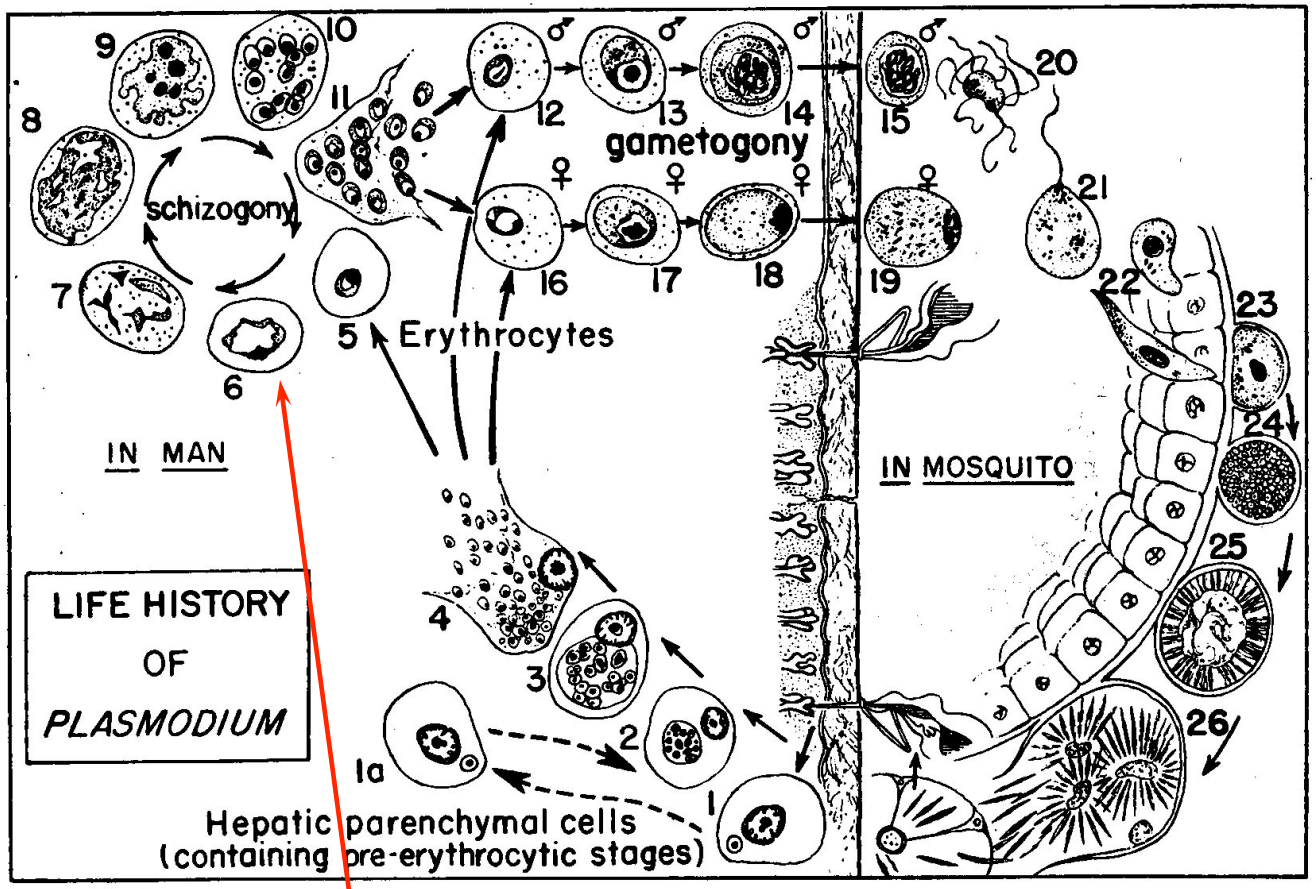
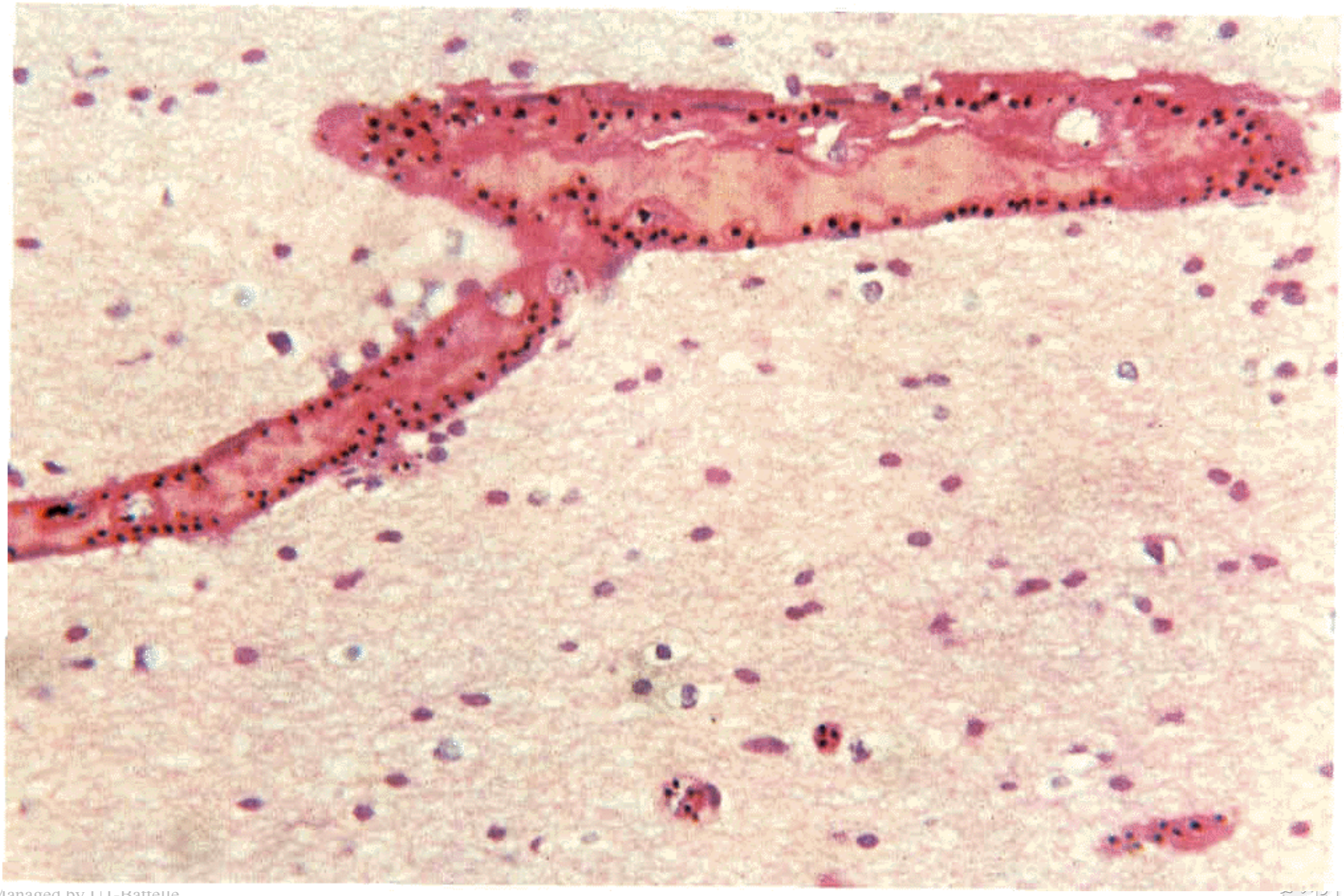
Malaria



Trophozoites infect red blood cells, digest hemoglobin, squester Fe-porphyrin (would be toxic if it remained in solution).

Infected erythrocytes, with lumps of hemozoin, in a capillary in the brain



SCIENTIFIC CORRESPONDENCE

Haem polymerization in malaria

SIR — Haem that is derived from the breakdown of host cell haemoglobin by malarial parasites. Acetonitrile extracts of authentic haemoglobin-derived haem may be critical to the survival and successful maturation of the malarial parasite.

FEBS 18681

FEBS Letters 409 (1997) 297–299

Non-iron porphyrins inhibit β-haematin (malaria pigment) polymerisation

Diego Monti[b], Piero Olliaro[c], Donatella Taramelli[a,*]

[a] ... 36, 20133 Milan, Italy
... Milan, Italy

THE JOURNAL OF BIOLOGICAL CHEMISTRY

Vol. 273, No. 47, Issue of November 20, pp. 31103–31107, 1998
Printed in U.S.A.

A Common Mechanism for Blockade of Heme Polymerization by Antimalarial Quinolines*

LETTERS TO NATURE

Inhibition by chloroquine of a novel haem polymerase enzyme activity in malaria trophozoites

A. F. G. Slater & A. Cerami

The Picower Institute for Medical Research, 350 Community Drive, Manhasset, New York 11030, USA

Malarial haemozoin/β-haematin supports haem polymerization in the absence of protein

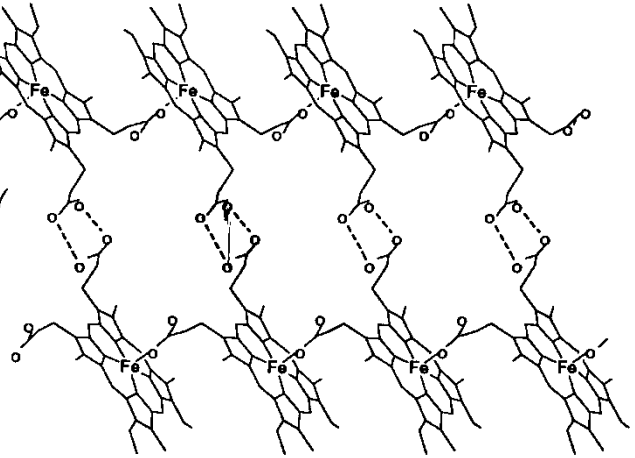
Chapter 37

Structural and Spectroscopic Studies of β-Hematin (the Heme Coordination Polymer in Malaria Pigment)

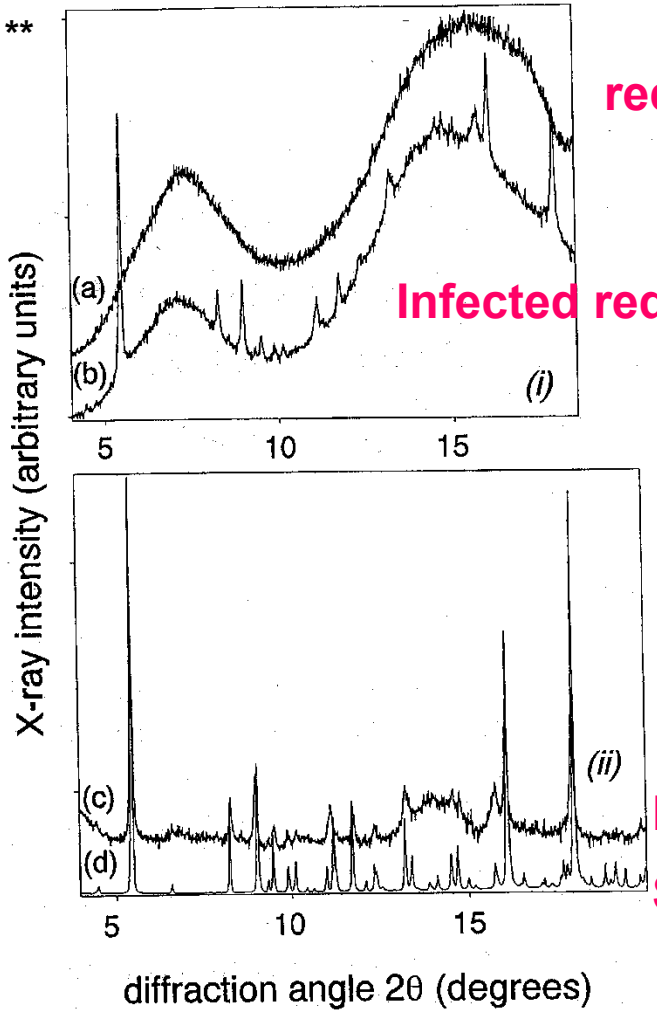
D. Scott Bohle[1], Brenda J. Conklin[2], David Cox[3], Sara K. Madsen[1], Scott Paulson[1], Peter W. Stephens[4], and Gordon T. Yee[2]

[1]Department of Chemistry, University of Wyoming, Laramie, WY 82071–3838
[2]Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309–0215
[3]Department of Physics, Brookhaven National Laboratories, Upton, New York 11973
[4]Department of Physics, State University of New York at Stony Brook, NY

Heme Polymer?



β-hematin and malaria pigment



red cell

Infected red cell

Difference = Malaria pigment

Synthetic β-hematin

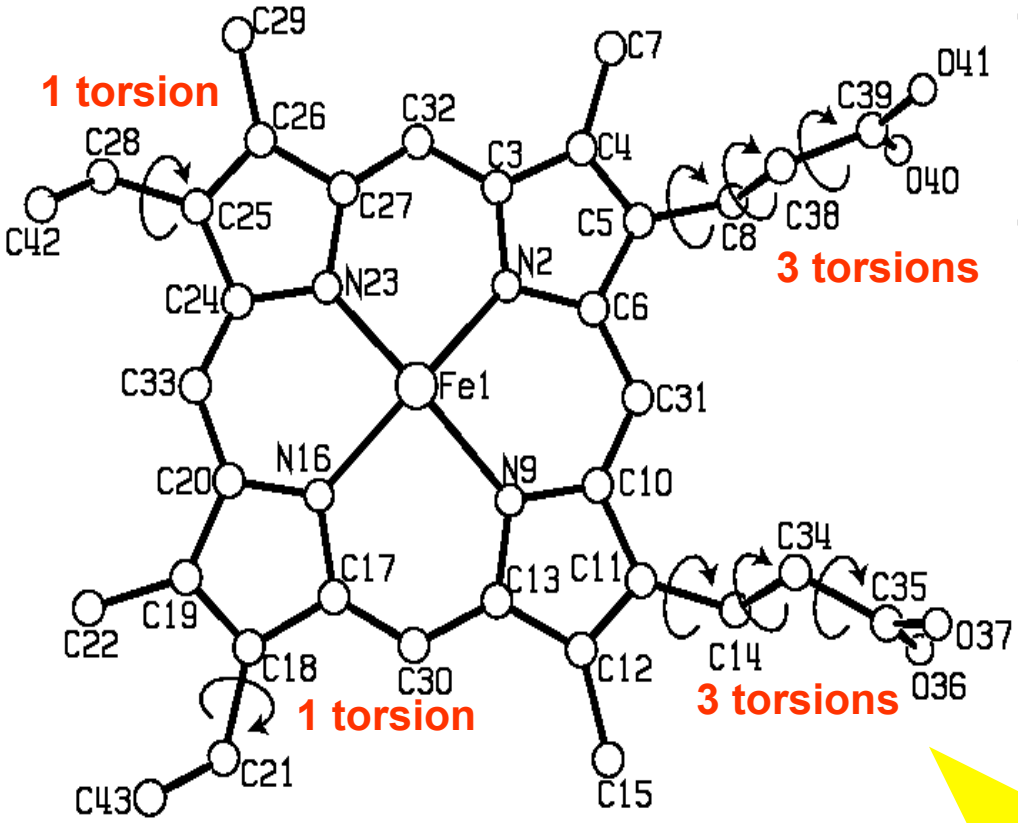
- β-hematin is chemically and crystallograpically identical to the malaria pigment isolated from infected red cells.
- it was prepared in the laboratory as a powder, by dehydrohalogenation of hemin*.

Given atom positions, it is straightforward to compute the diffraction pattern

$$I_{hkl} = \left| \sum_{\text{atoms } j} f_j \exp(i\vec{Q}_{hkl} \cdot \vec{R}_j) \right|^2$$

Solve a new structure from powder data

1. Get data
2. Find the lattice
3. Space group (internal symmetries) systematic absences, density, guess, luck
4. Extract intensities of each individual (*hkl*) peak
5. Solve structure
   a. Momentum space - Direct methods
   b. Real space
6. Refine



Fe (protoporphyrin-IX)

Triclinic, Z=2.

a=12.204Å, b=14.722Å, c=8.042Å

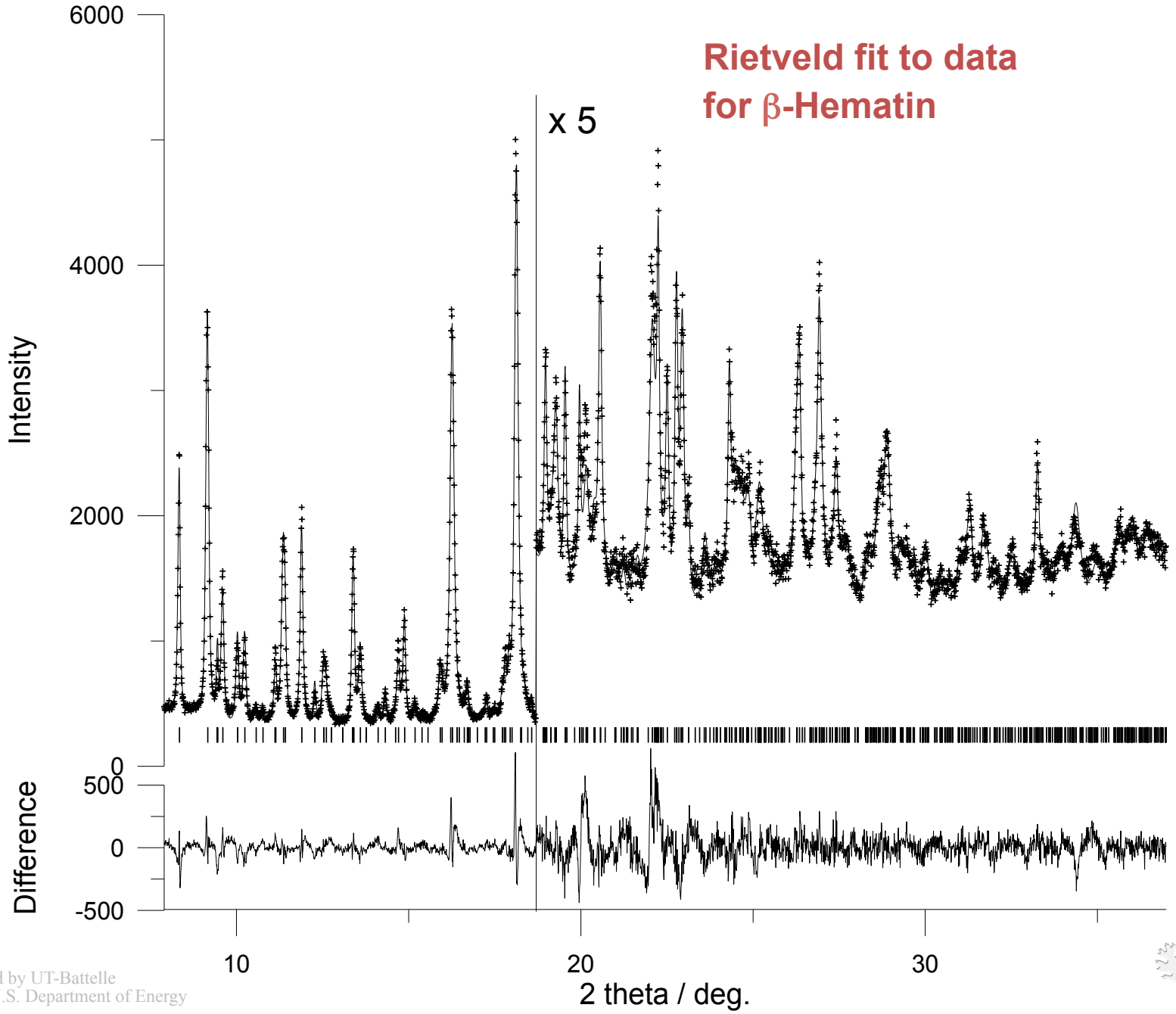
α=90.20°, β=96.85°, γ =96.996°

The solution in $\bar{P}1$ (two molecules related by inversion symmetry) consists of finding:

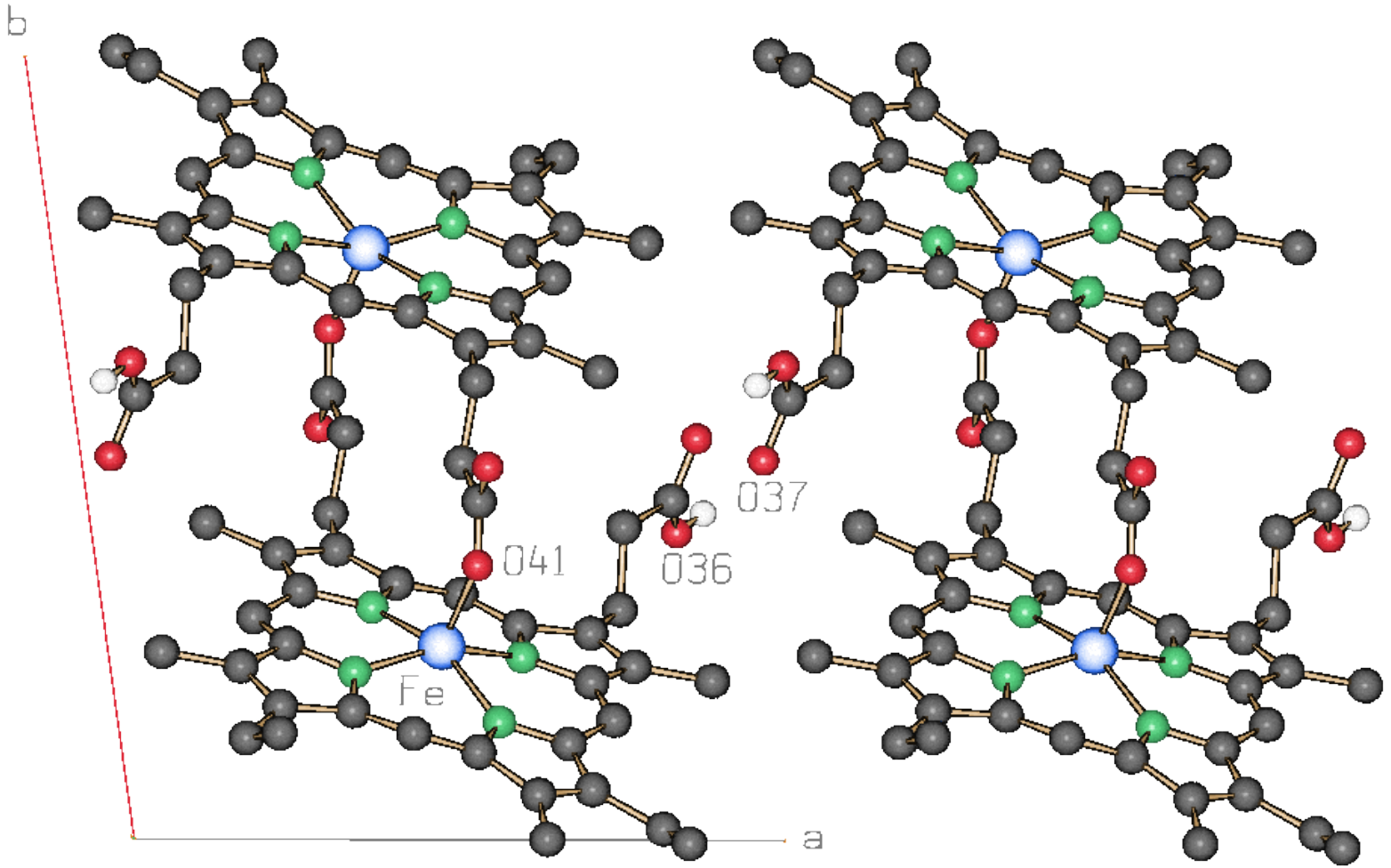
- ✓ **3 spatial coordinates,**
- ✓ **3 Eulerian angles,**
- ✓ **8 torsions.**

(No solution in P1 was better)

The resulting 6 torsions in the propionic groups will show the molecular connectivity in β-hematin.

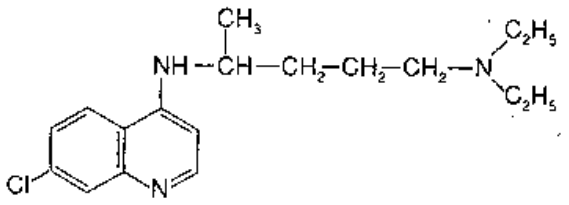


There is no polymer!
The structure consists of chains of hydrogen bonded dimers, in which each molecule is linked through iron-carboxylate bonds.



SCHAKAL

Current models of action of chloroquine and related drugs



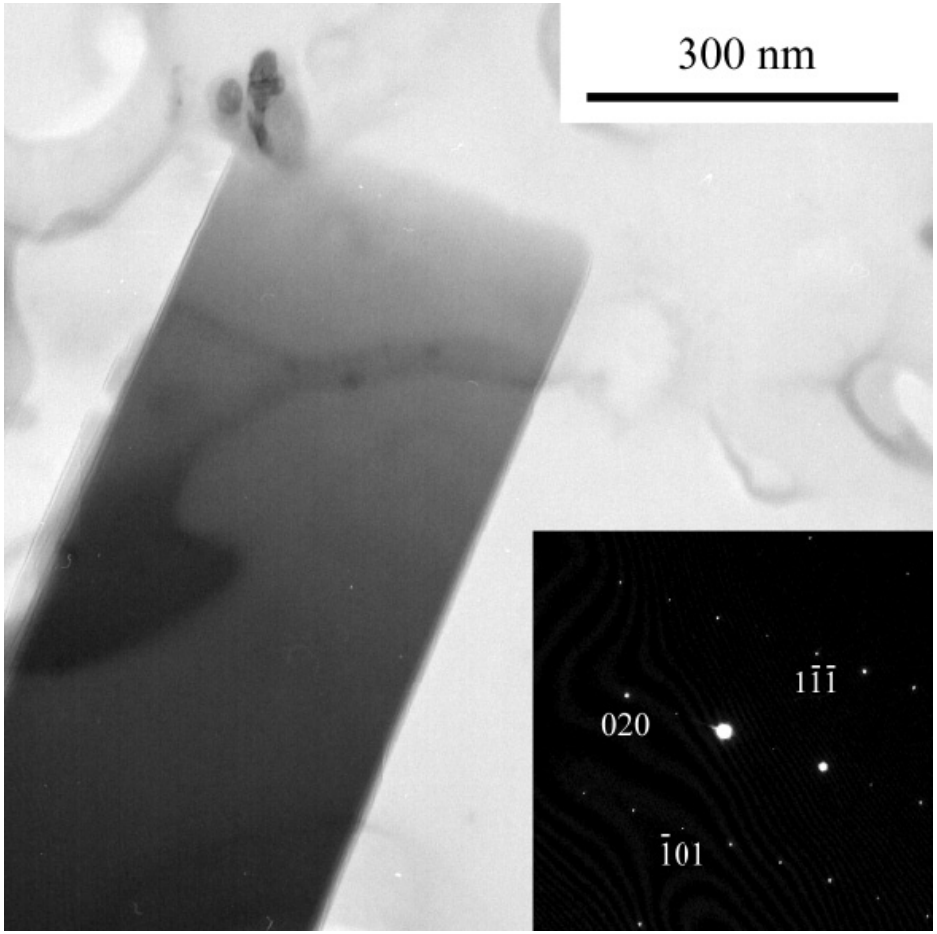
1. Caps the growth of the polymer

2. Inhibits a proposed polymerization enzyme

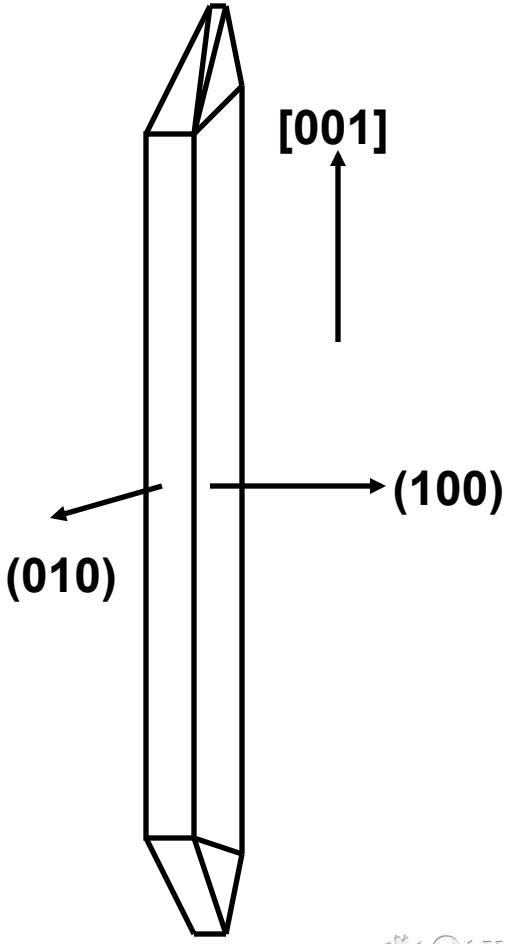
3 Otherwise interferes with the chemistry of heme oxidation and hemozoin crystal growth

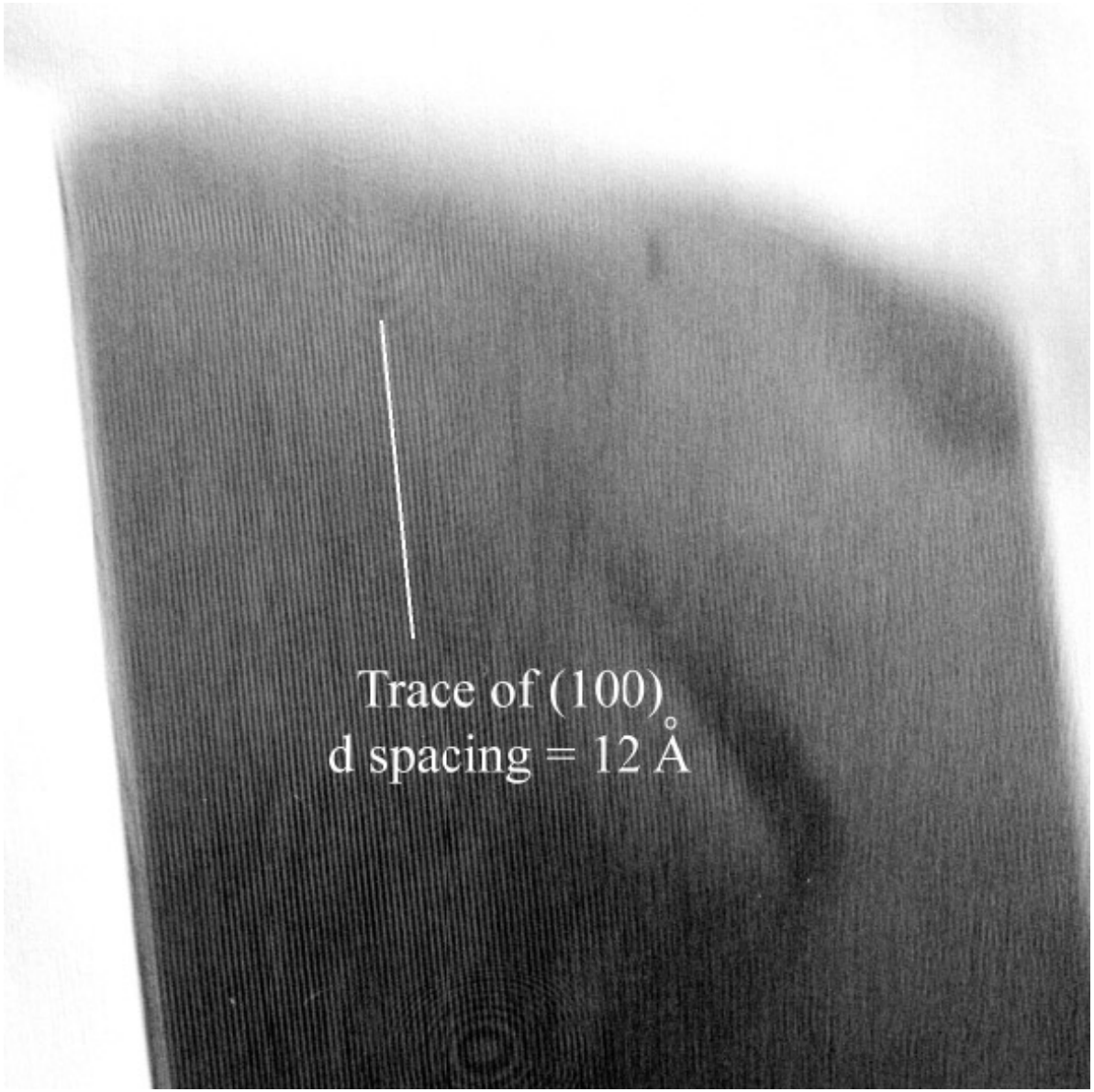
   3a. Adsorbs on growing surface and interferes with crystal growth
   Supporting evidence from autoradiography with labeled chloroquine

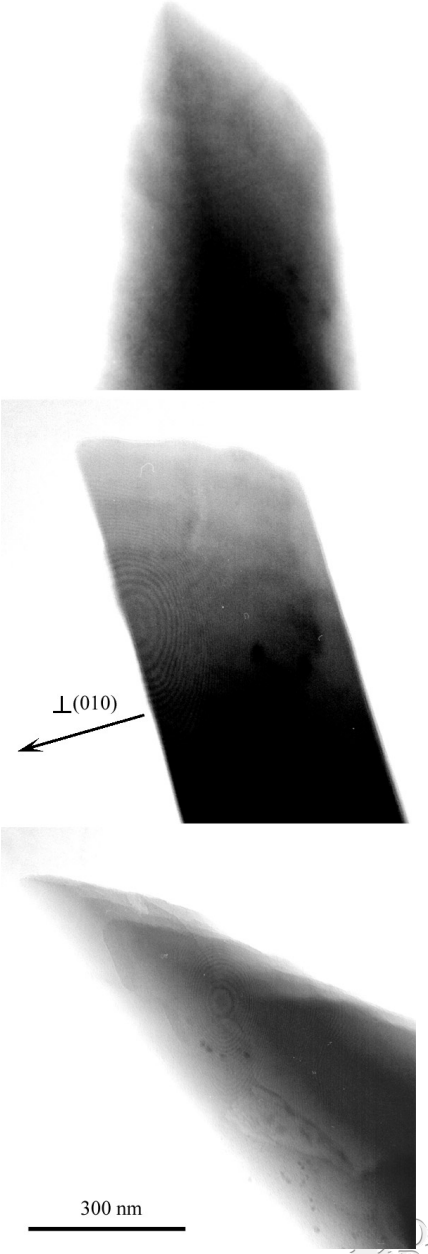
Strong motivation for understanding the morphology of hemozon/hematin crystals

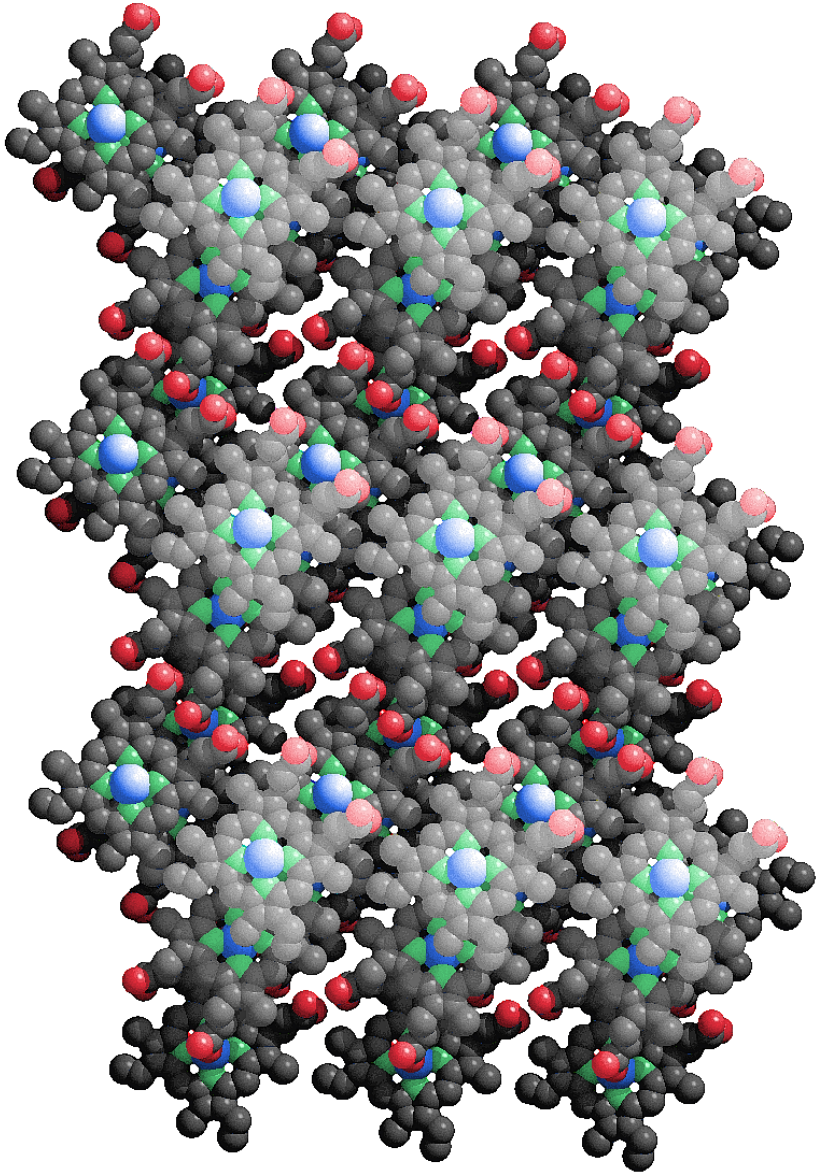


Growth along what faces?

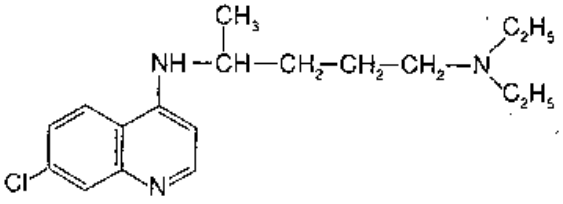






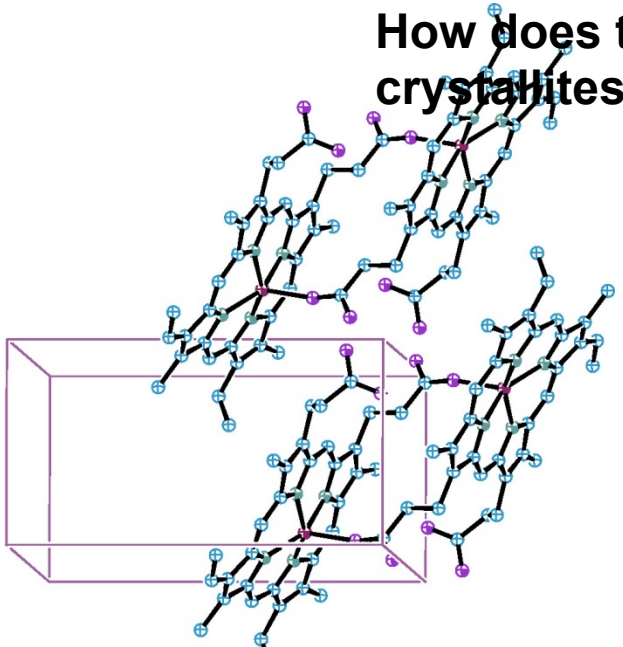


[131] surface of hemozoin



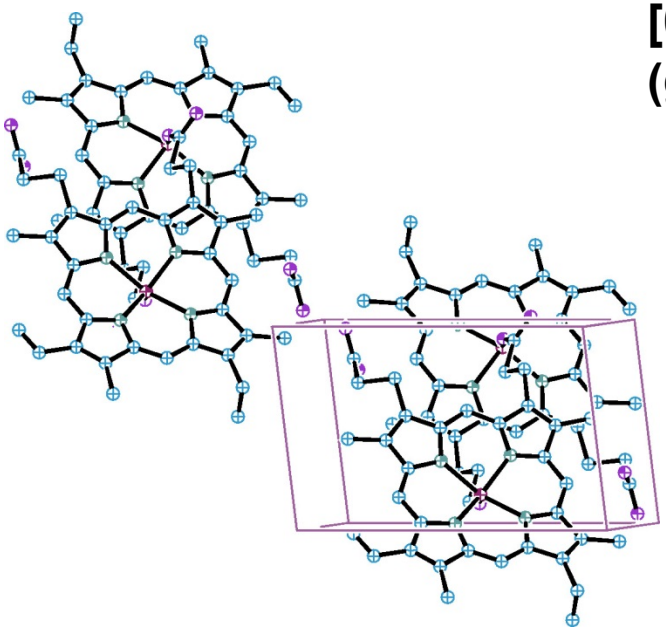
chloroquine

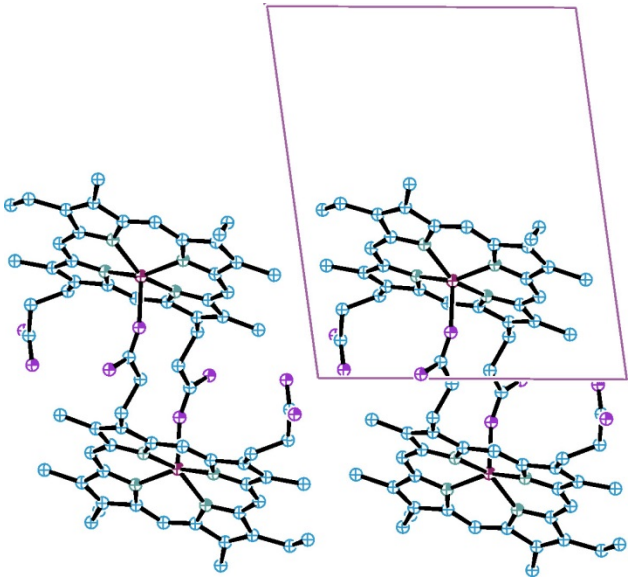
How does the structure fit into the crystallites?



View ⊥ (100) plane

View ⊥ (010) plane

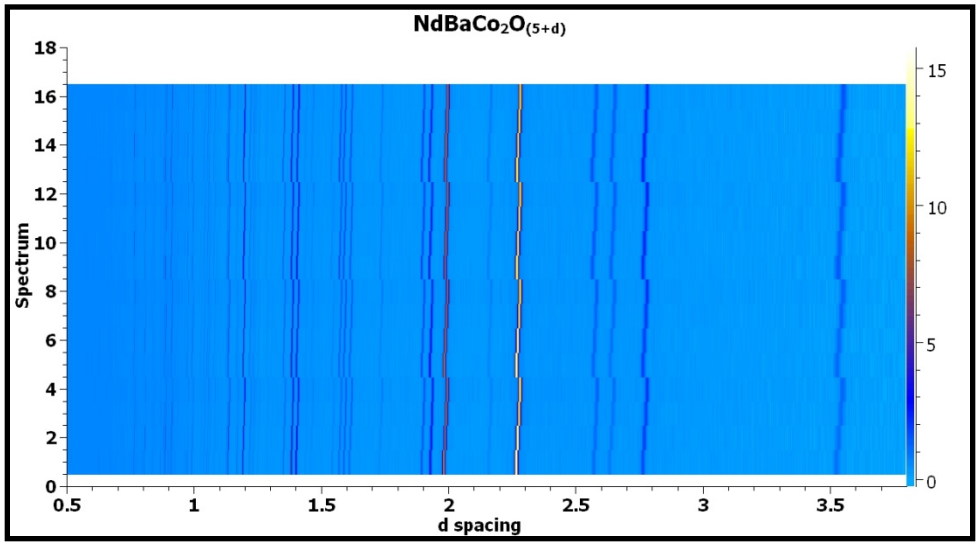


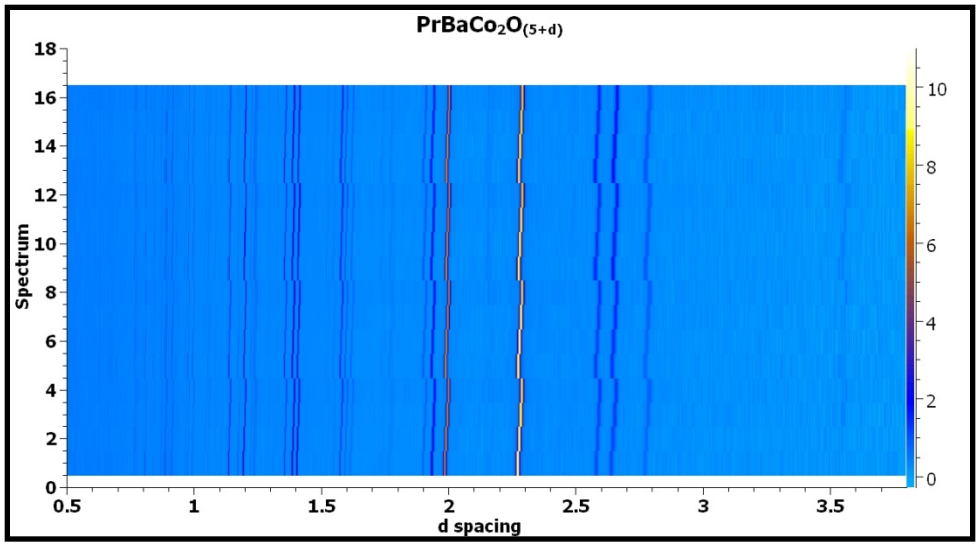


View along [001] axis (growth direction)

$REBaCo_2O_{5\pm\delta}$: cathode materials for SOFC

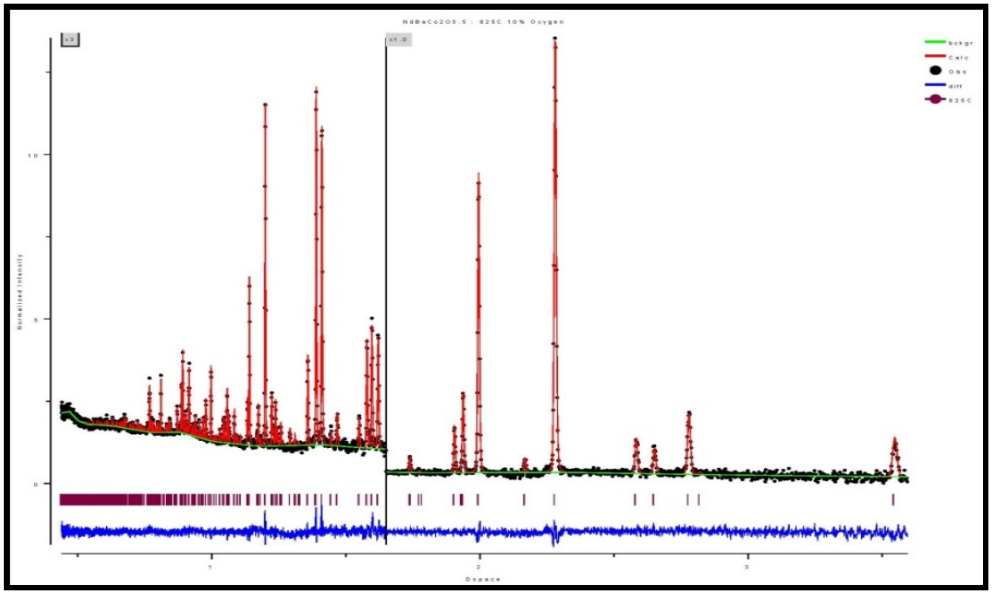
- Samples of (Nd and Pr)$BaCo_2O_{5\pm\delta}$ were measured @ four different pO_2 and four different temperature at each pO_2
- Equilibrium state was achieved by measuring the lattice parameter. Once the lattice parameter stopped changing, longer data was collected.
- Temperature of the sample was calibrated using a standard powder under identical condition.

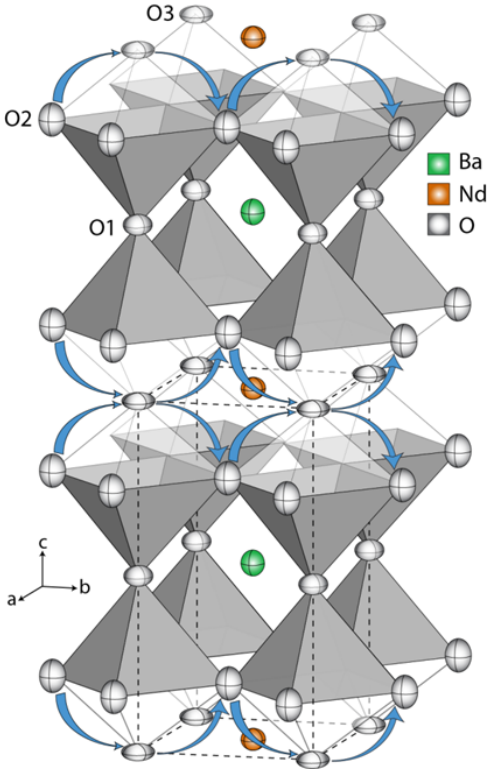




Neutrons show Oxygen migration pathway in $NdBaCo_2O_{5\pm\delta}$

R.A. Cox-Galhotra, A. Huq, J.P. Hodges, J.H. Kim, C. Yu, X. Wang, A. J. Jacobson, S. McIntosh, "Visualizing oxygen anion transport pathways in $NdBaCo_2O_{5+d}$ by in situ neutron diffraction", *J. of Mater. Chem. A 1*, 3091 (2013)





- High Q data allows refinement of anisotropic thermal parameters and oxygen vacancy. Combined with near neighbor distances, it allows us to directly visualize the oxygen diffusion pathway.
- The structure is Tetragonal and not Orthorhombic as previously suggested in these pO_2 values.
- O3 site exhibits the largest vacancy and anisotropic motion. Motion of O2 is also very anisotropic which can hop to the near neighbor in the vacancy rich NdO plane. Fully Occupied O1 site has very small displacement and hence limited motion.