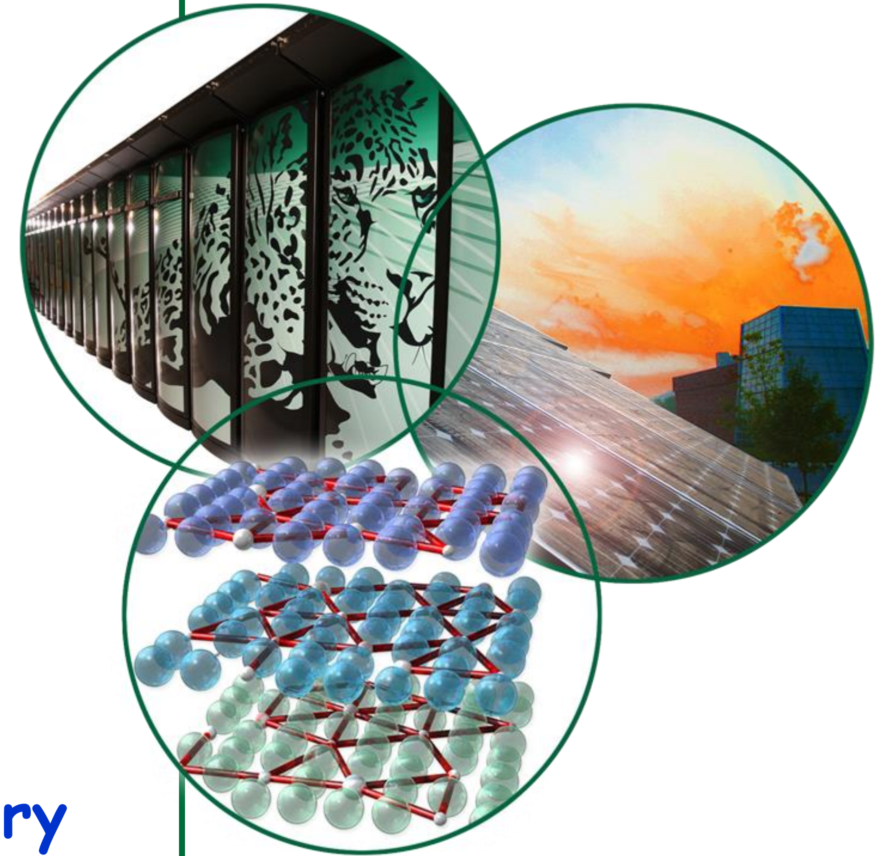
Powder Diffraction Application



Ashfia Huq

Spallation Neutron Source

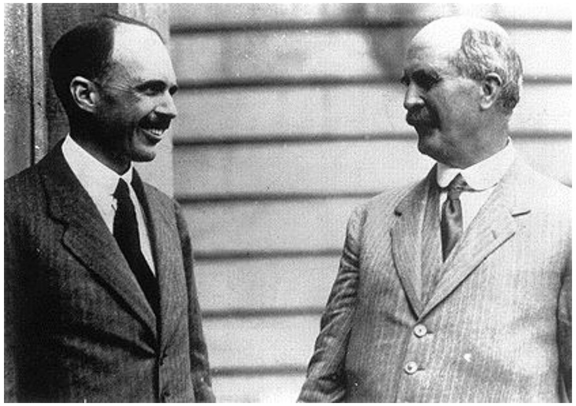
Oak Ridge National Laboratory

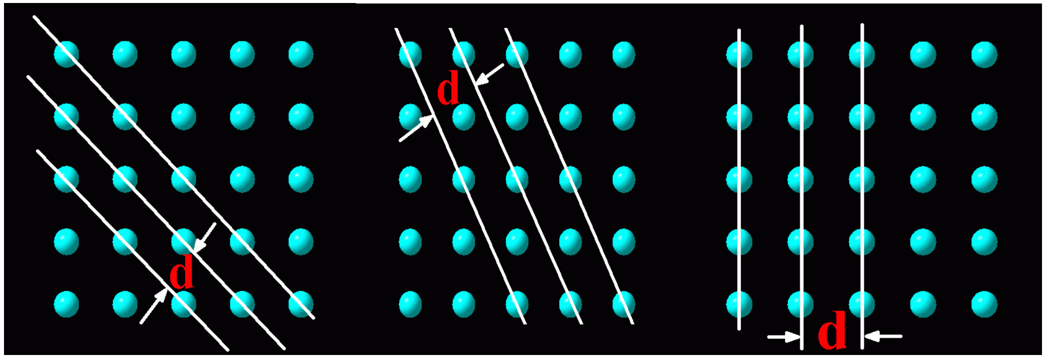
U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

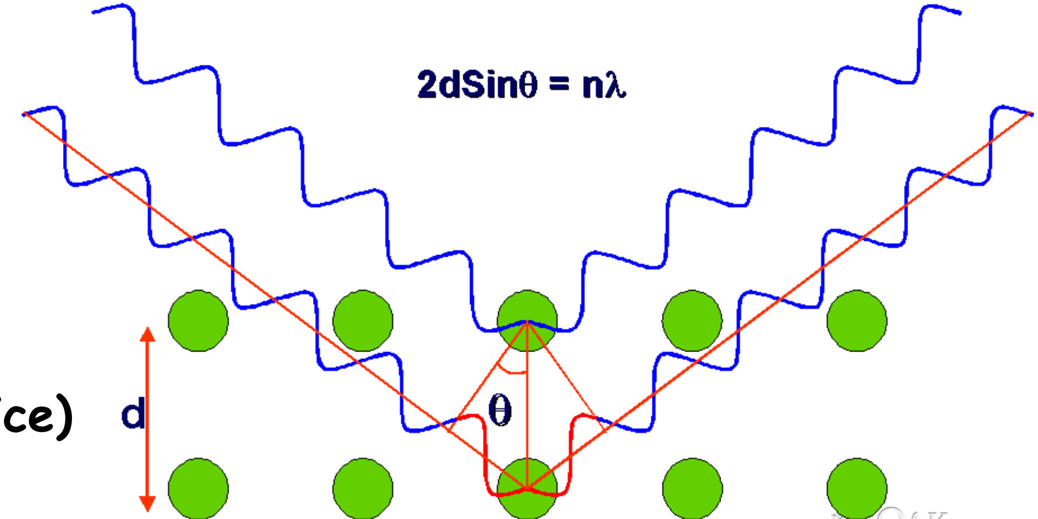
Bragg's law

W.H. Bragg (1862-1942)
W.L. Bragg (1890-1971)





Shared 1915 Nobel Prize

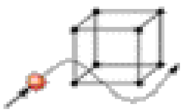


- Zinc Blend (fcc not sc)
- NaCl (not molecular)
- Diamond (two overlapping fcc lattice)

OAK RIDGE National Laboratory

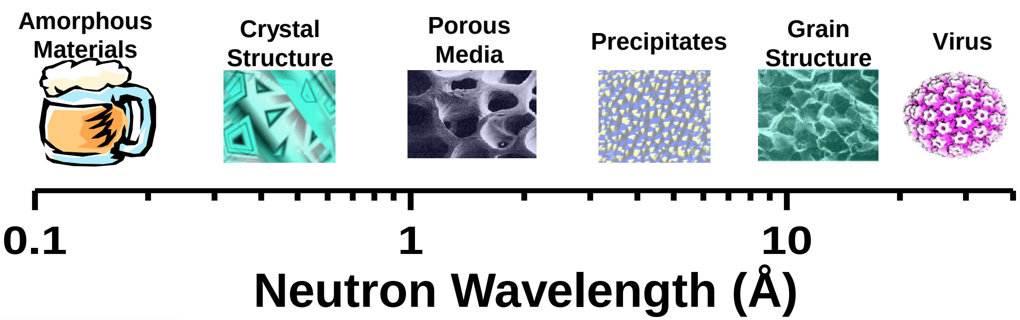
Where are the atoms?

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]

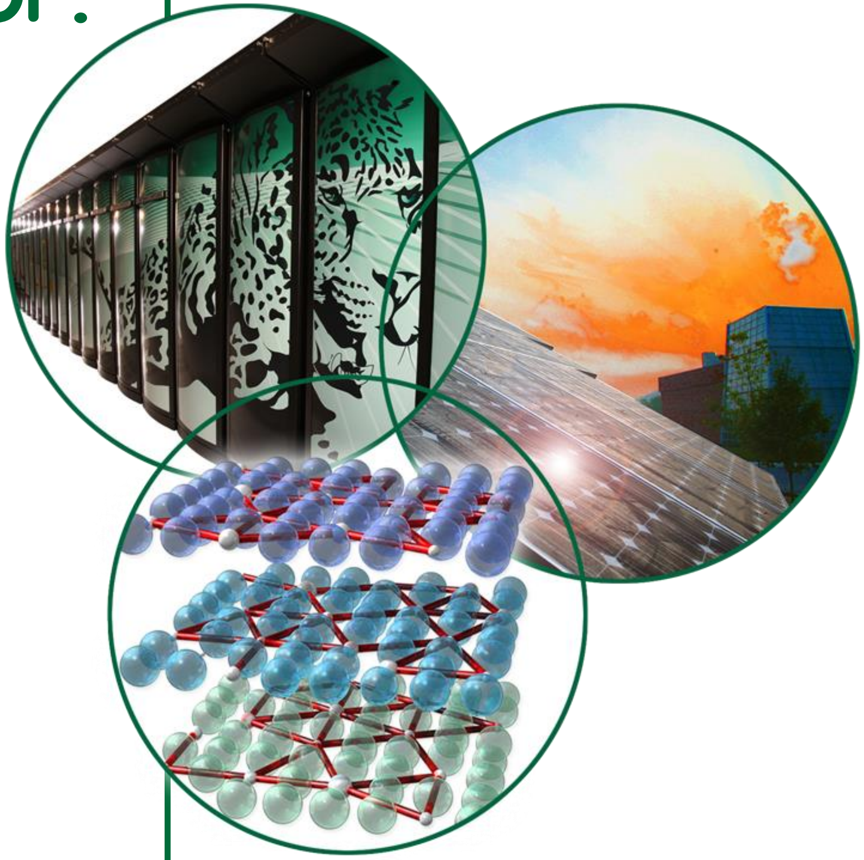
Source:

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

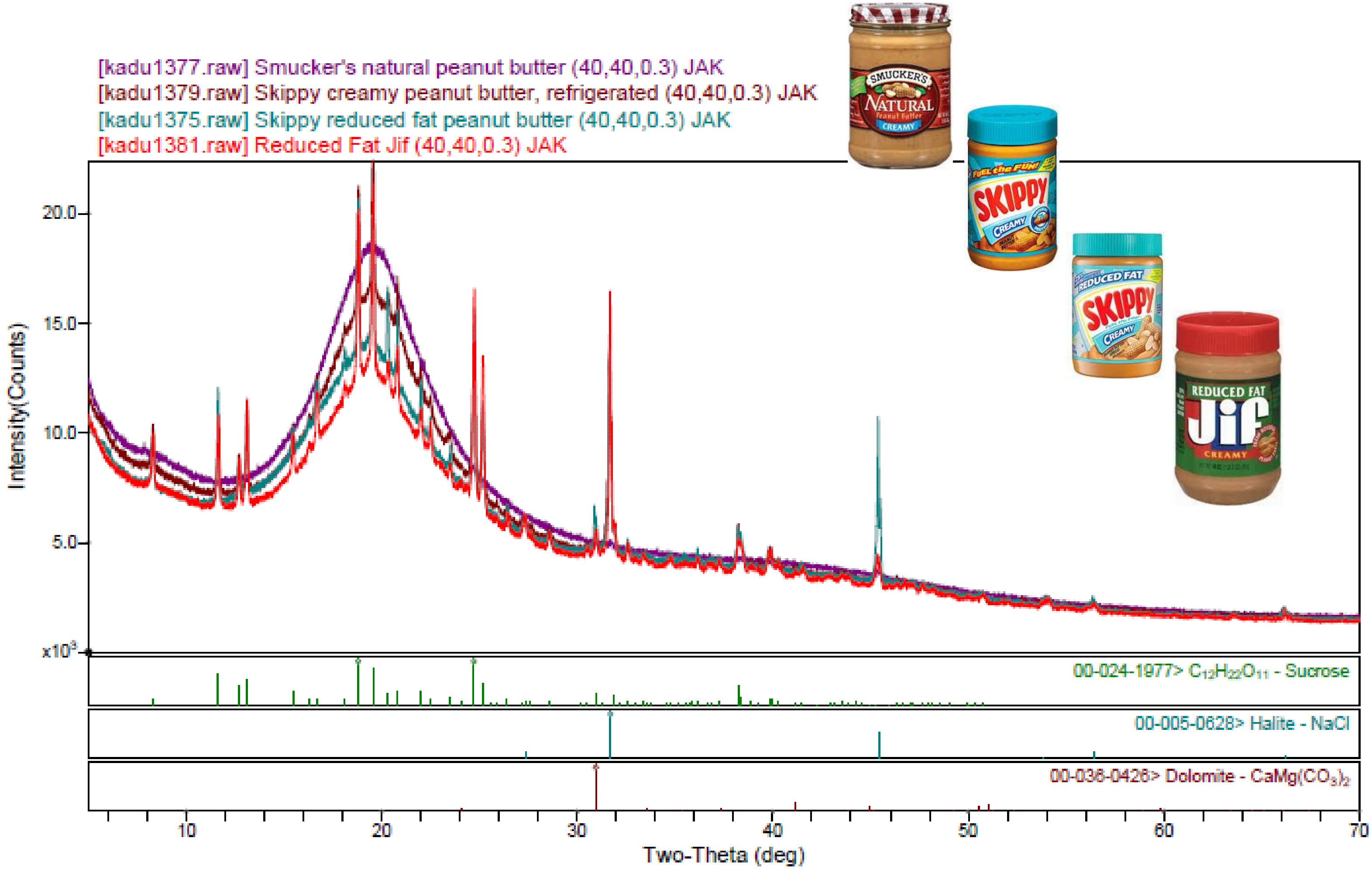
Outline

- Phase ID and Quantitative analysis
- Structure and transport
- Neutron Powder Diffraction
- Combine X-rays and Neutrons
- Time resolved in-situ studies
- Ab-initio structure solution
- Proteins and Powder Diffraction

Finger Printing and Quantitative Phase Analysis (First two Slides from Dr. Jim Kaduk)



Peanut Butter



Managed by UT-Battelle
for the U.S. Department of Energy

OAK RIDGE National Laboratory

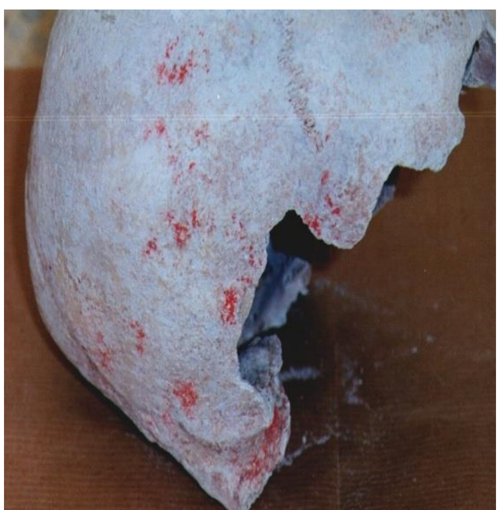
Sample	Skippy creamy	Skippy reduced fat	Jif reduced fat	Smucker's Natural
Ingredients	peanuts sugar salt hydr. veg. oils	peanuts corn syrup sol. sugar soy protein salt hydr. veg. oils mono/diglyc. minerals vitamins	peanuts corn syrup sol. sugar soy protein salt hydr. veg. oils molasses minerals vitamins	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	-

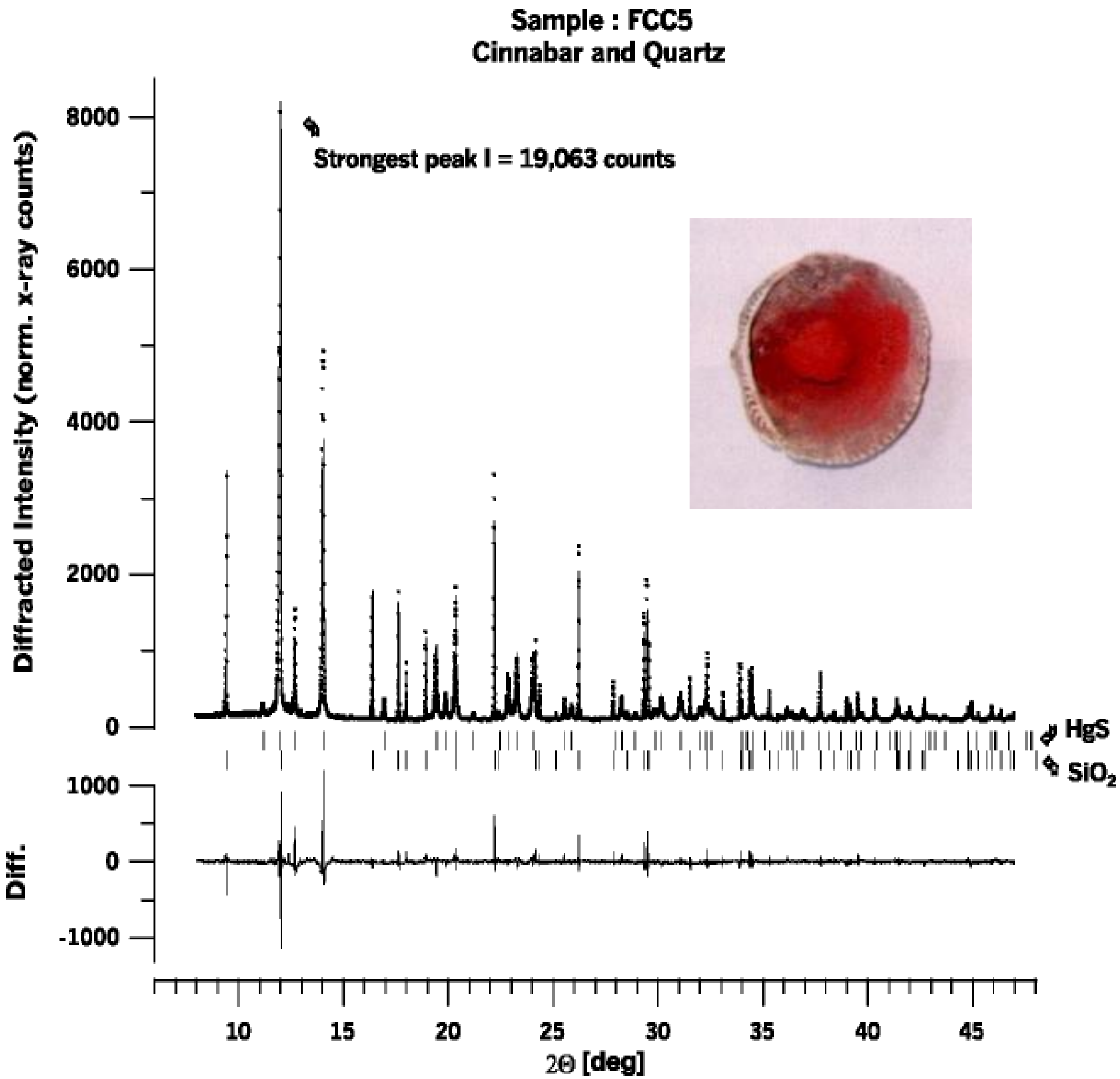
Powder Diffraction in Archeology

Huq et.al. Appl. Phys. A 83, 253 (2006)

Natural antique colorants include red pigments such as cinnabar and ochre and pink pigments such as madder. These archaeological pigments have been used as ritual and cosmetic make-up and they are a material proof of handcraft activities and trade in the Mediterranean.

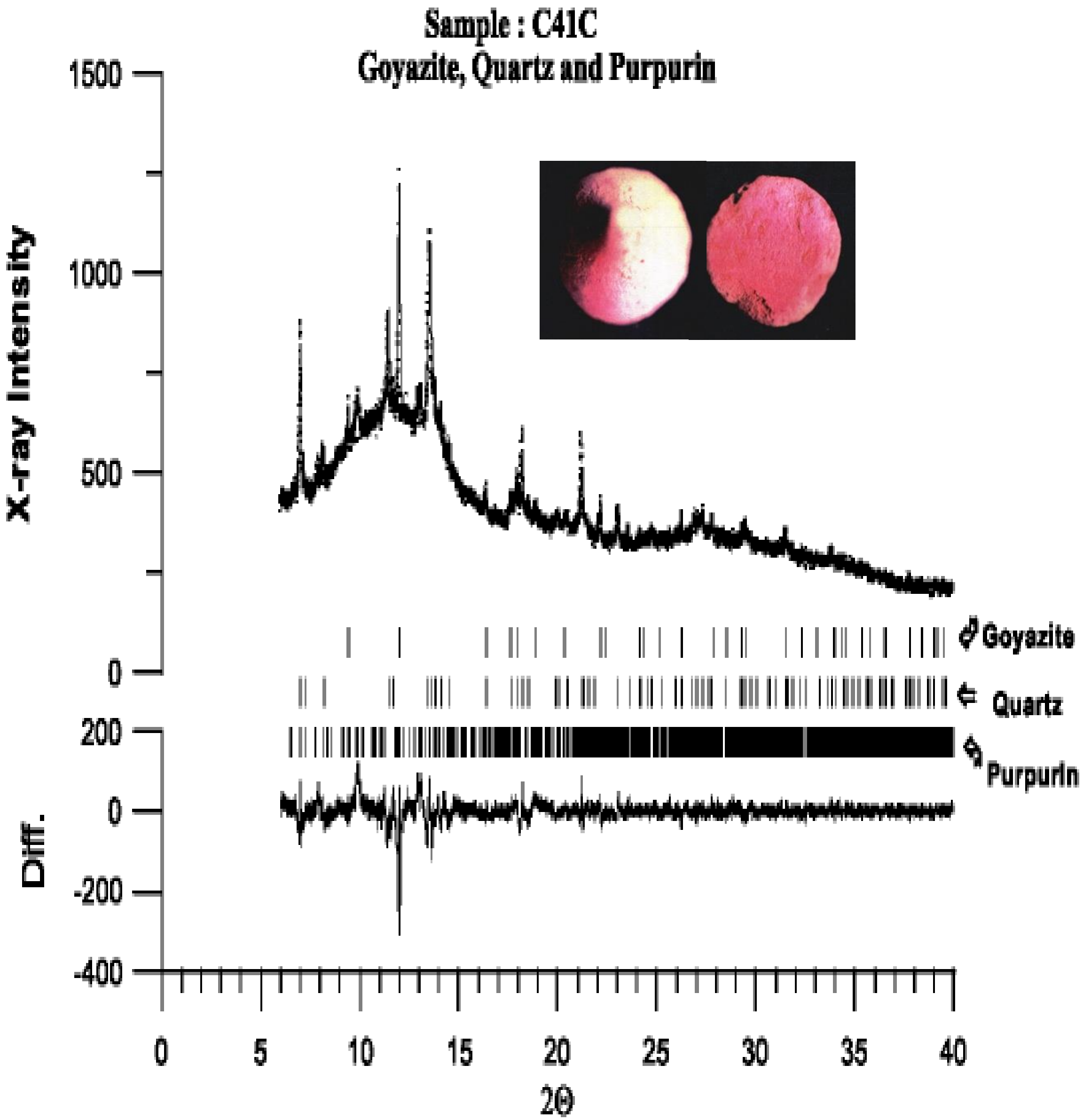
The pigments were discovered during different excavations in archaeological sites of Tunisia (Carthage, Kerkouane, Bekalta, Bouaarada and elsewhere).





- ❖fit peak: search database for matches.
- ❖Look up structure.
- ❖Rietveld refinement.
- ❖For mixture quantitative phase analysis.

Oak Ridge National Laboratory



Conclusions

Ten punic make-up samples were studied with SR-XRD using a 2D CCD detector and high angular resolution powder diffraction. Four samples (B1, B2, B3 and FCC5) contain quartz and cinnabar while four other samples (B10, FCC4, FCC6 and OCRB) contain quartz and hematite. The presence of quartz is probably due to sand/clay from the excavation area.

These results are similar to what would be obtained from raw materials indicating that these eight samples were not subject to any preparation by the Carthaginians. These eight samples were used as ritual make-up. However, the last two samples (FCC2 and C41C) showed an amorphous background, their preparation required sophisticated techniques corresponding to cosmetic make-up; they contain purpurin as major pigment which is formulated in a similar fashion as a lacquer.

Resources (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).

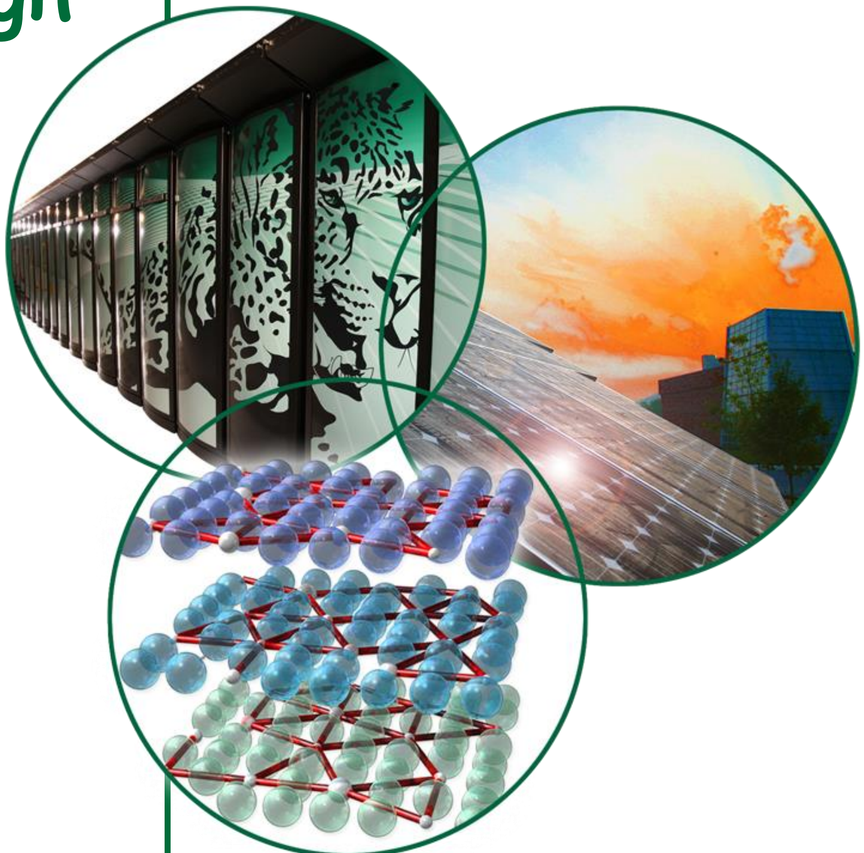
† PDF-4/Organics is the sole product that contains data sourced from the Cambridge Structural Database (CSD) published by Cambridge Crystallographic Data Centre (02-CSD).

‡ 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

OAK RIDGE National Laboratory

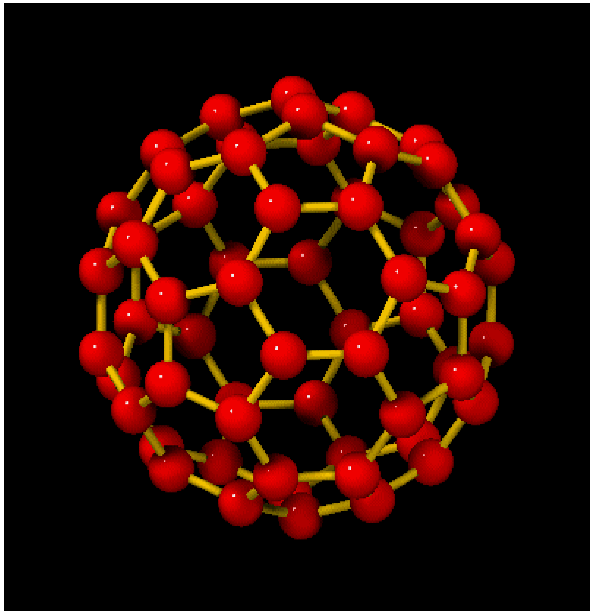
Superconductivity in Fullerenes and Scientific Ethics! (Publishing in high profile journal)



U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Buckminsterfullerene

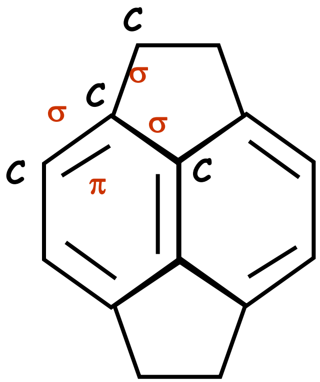


1985 : R.F Curt, H.W. Croto & R.E. Smalley discover C_{60}. They are awarded the Nobel prize in Chemistry in 1996.

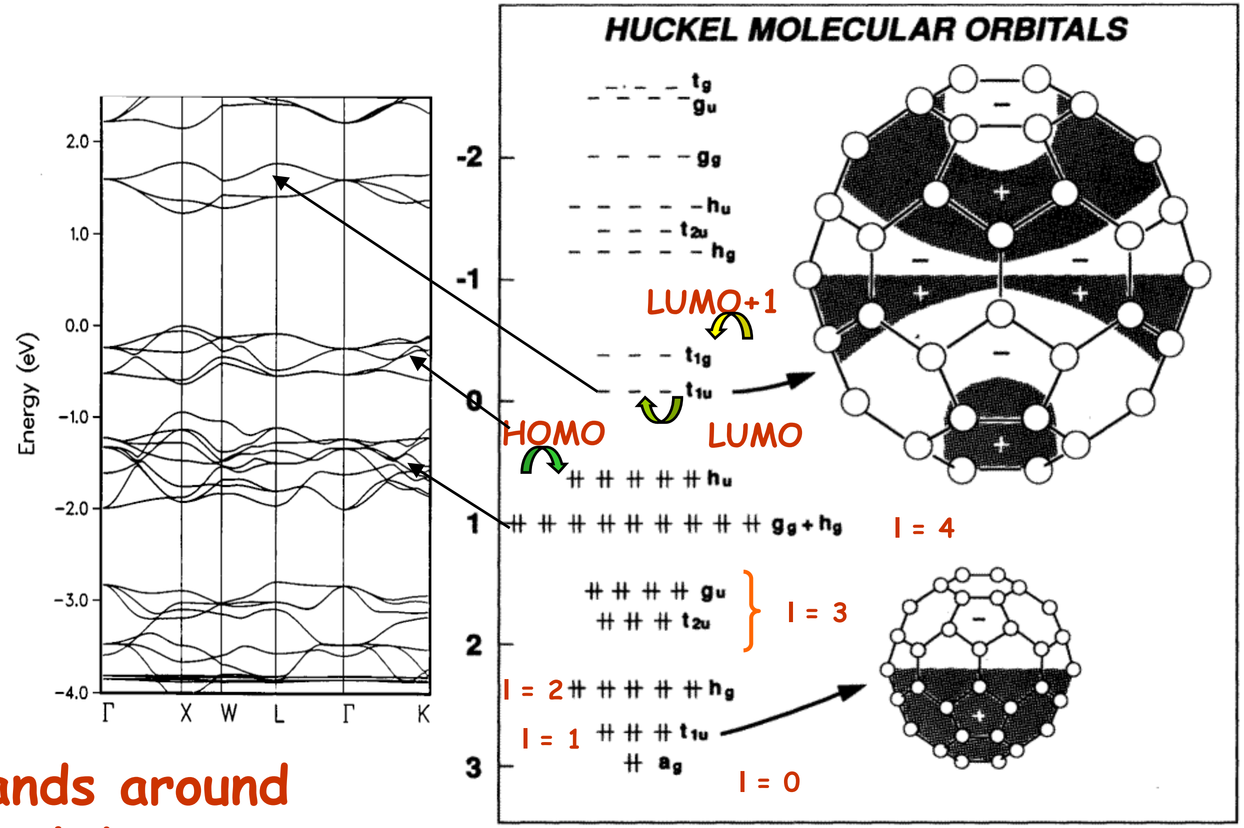
1990 : W. Kratchmer and D.R. Huffman produces isolable quantities of C_{60}.

1991 : A group at AT&T Bell labs, finds superconductivity in alkali doped C_{60} with Tc=18K for K_3C_{60}. Later Tc=28K is observed for Rb_3C_{60}

Diameter of molecule 10Å. The atoms are positioned at the 60 vertices of a truncated icosahedron. 90 edges, 12 pentagons, 20 hexagons.



60 electrons that take part in conduction



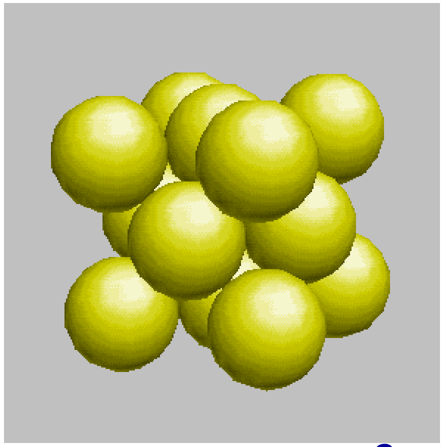
sub bands around E_F of solid C_{60}.
(Erwin 1993)

n=2(2l+1)
works
up to l=4

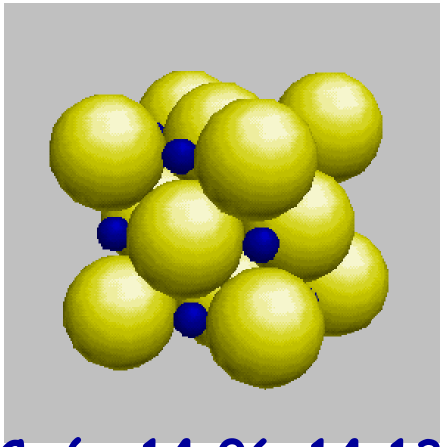
Single bond ~1.45Å
Double bond ~1.39Å

HOMO - LUMO
~2ev

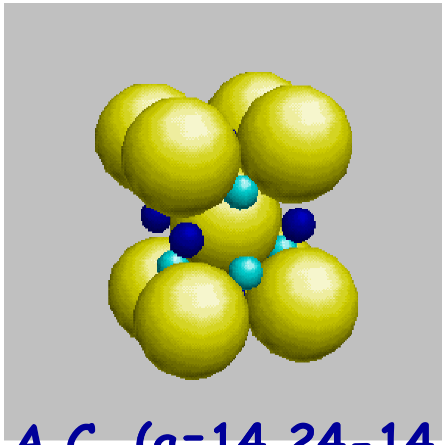
Alkali(K,Rb,Cs) doped C_{60}



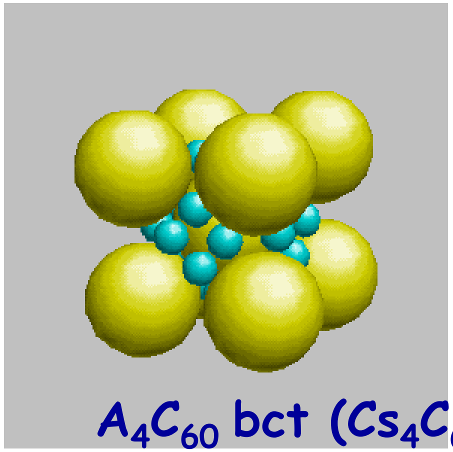
fcc C_{60}(a=14.17Å)



AC_{60}(a=14.06-14.13Å)
A in octahedral site

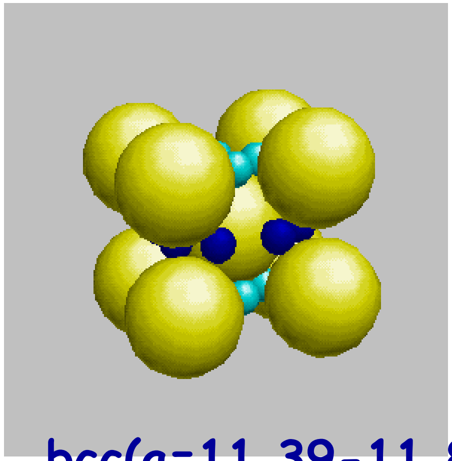


A_3C_{60}(a=14.24-14.44)
A in both tetrahedral
And octahedral site



A_4C_{60} bct (Cs_4C_{60}
orthorhombic &
orientationally ordered.)

2/3 filling
but a band
insulator !



A_6C_{60} bcc(a=11.39-11.84Å)

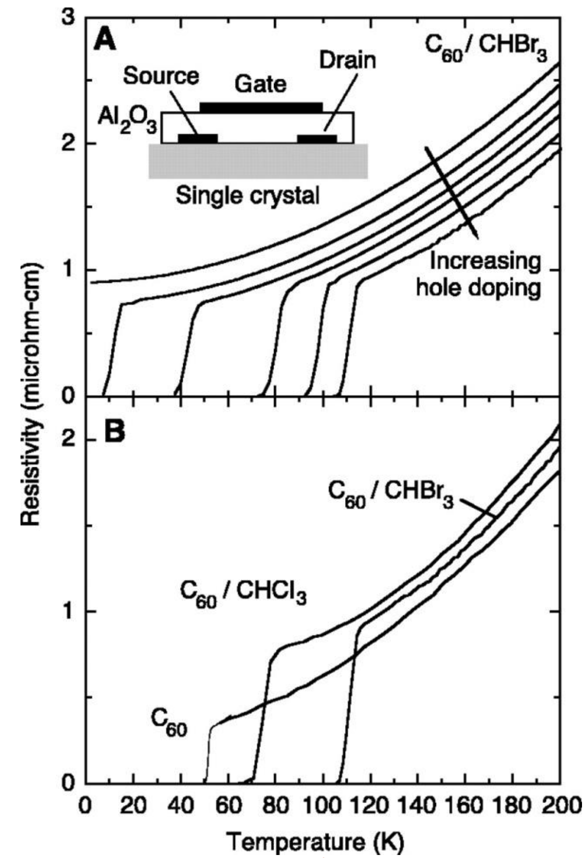
C_{60} base Superconductors:

Changing the lattice parameter in Alkali doped fullerides, (either decreasing it with pressure or increasing it by substitution of a larger cation) increases the DOS $N(E_F)$.

According to BCS theory

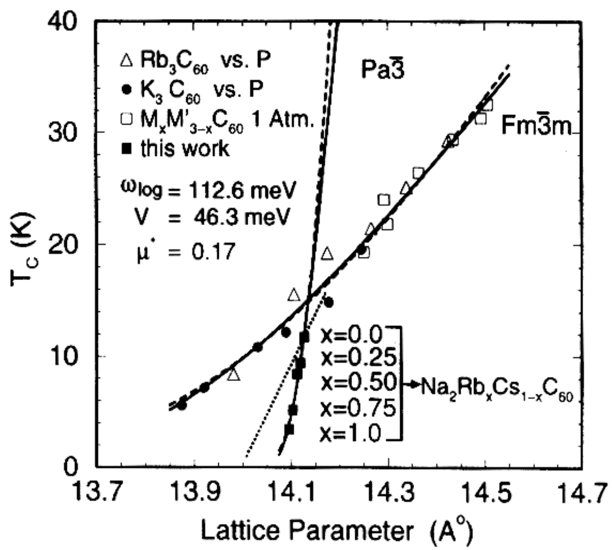
$$T_c = 1.13\frac{\hbar\omega_{log}}{k_B}\exp\left(\frac{-1}{N(E_F)V}\right)$$

Increase in $N(E_F)$ => Increase in T_c



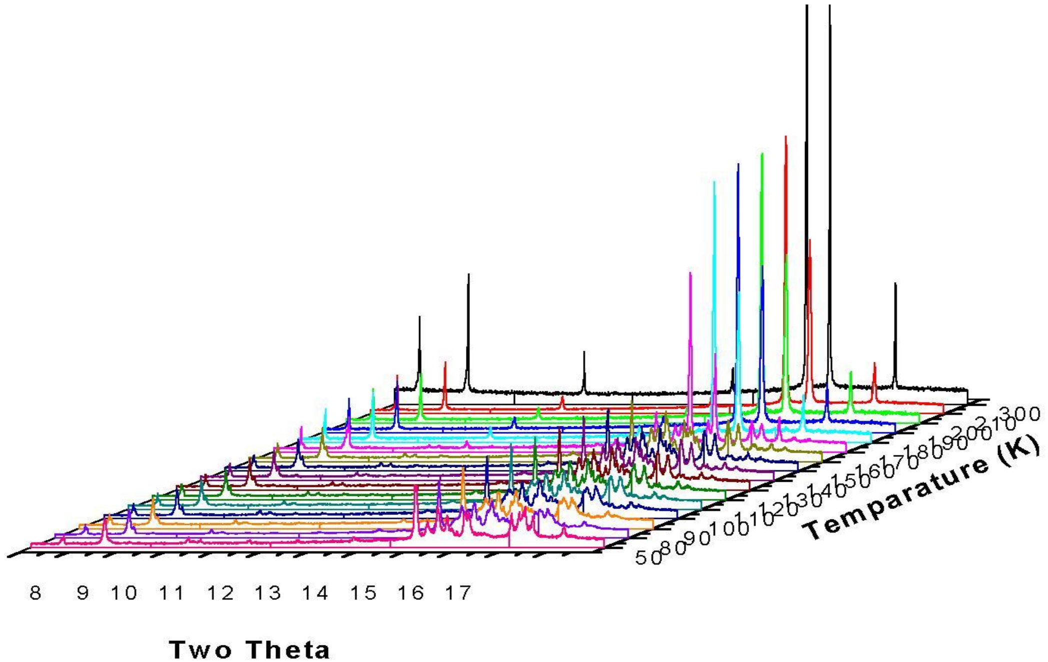
Interesting new superconductors, FET of organic materials (anthracine, pentacene, tetracene C_{60}. Record T_c=117K for C_{60} / $CHBr_3$. (Tc=80K for C60 / CHCl3)

J.H. Schön, Ch. Kloc, B. Battlogg, *Science* 293, 2432-4 (2001).



*Yildrim T et. al., 1995, Solid State Commun. 93 269-74

What happens to the crystal structure as we decrease T ?



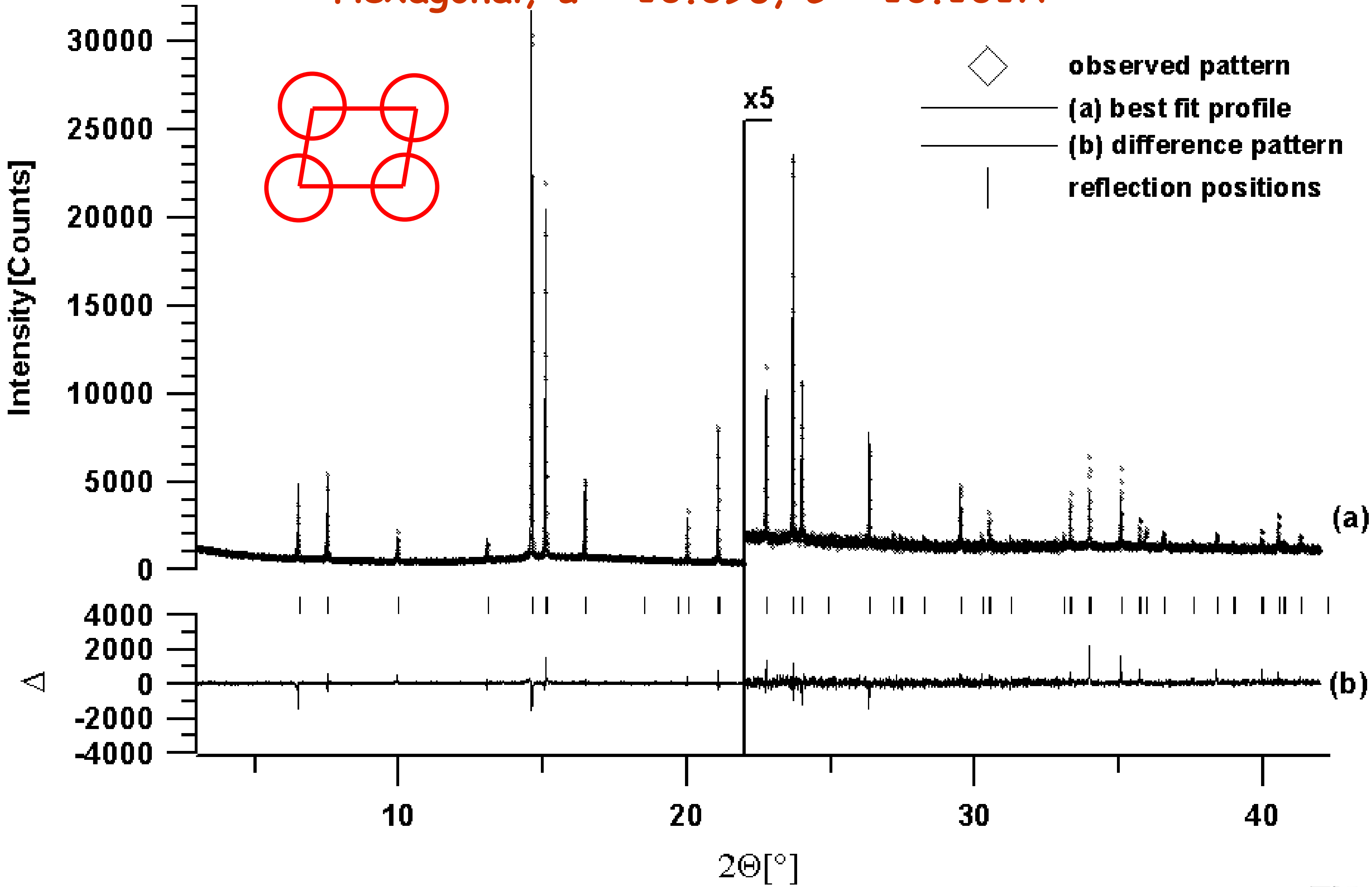
Hexagonal → Monoclinic → Triclinic

Heating-cooling cycles showed pronounced hysteresis and co-existence of the different phases over a large temperature range.

Oak Ridge National Laboratory

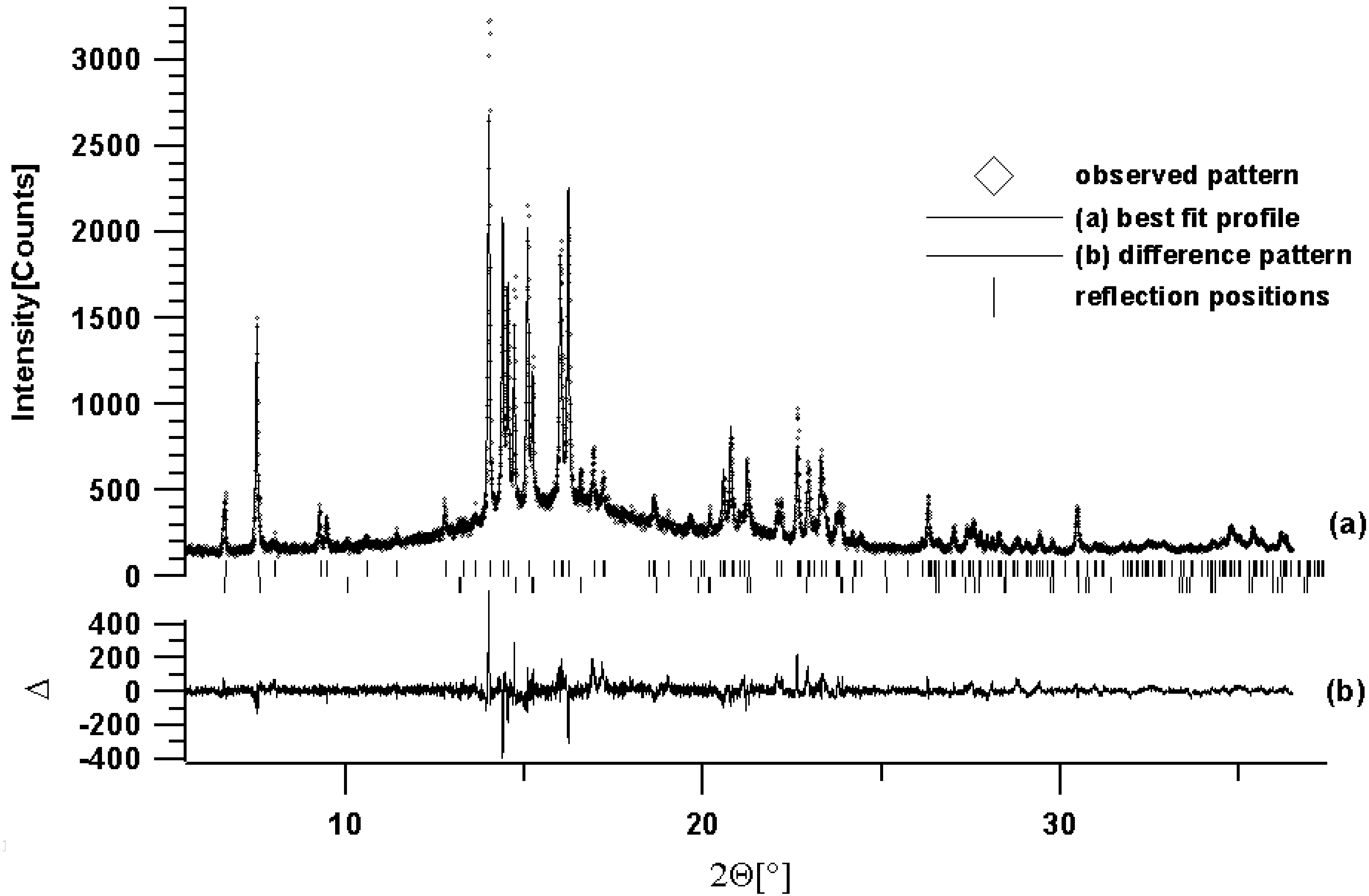
$C_{60} \cdot 2CHCl_3$ at room temp.

Hexagonal, *a* = 10.096, *c* = 10.101Å



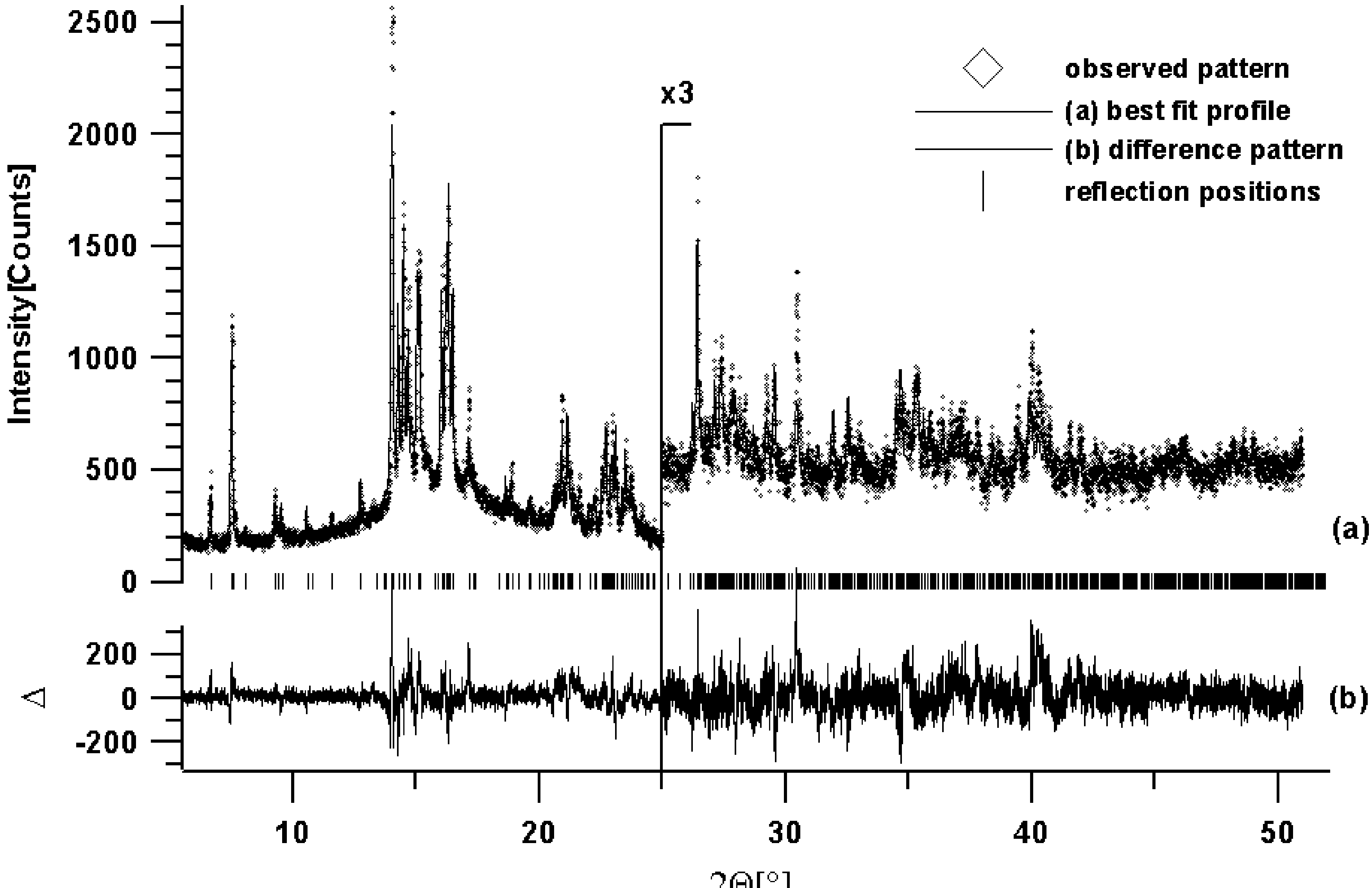
$C_{60} \cdot 2CHCl_3$ at 170K

monoclinic(16.821Å, 10.330Å, 10.159Å, 102.051°)



$C_{60} \cdot 2CHCl_3$ at 50K

(9.836Å, 10.091Å, 9.818Å, 101.36°, 116.46°, 79.78°)



Managed by UT-Battelle
for the U.S. Department of Energy

The crystal structure of C_{60} intercalated with $CHCl_3/CHBr_3$ is not fcc but hcp. More over when it is cooled it undergoes a phase transition and at ~150K they are converted into a fully order triclinic phase.

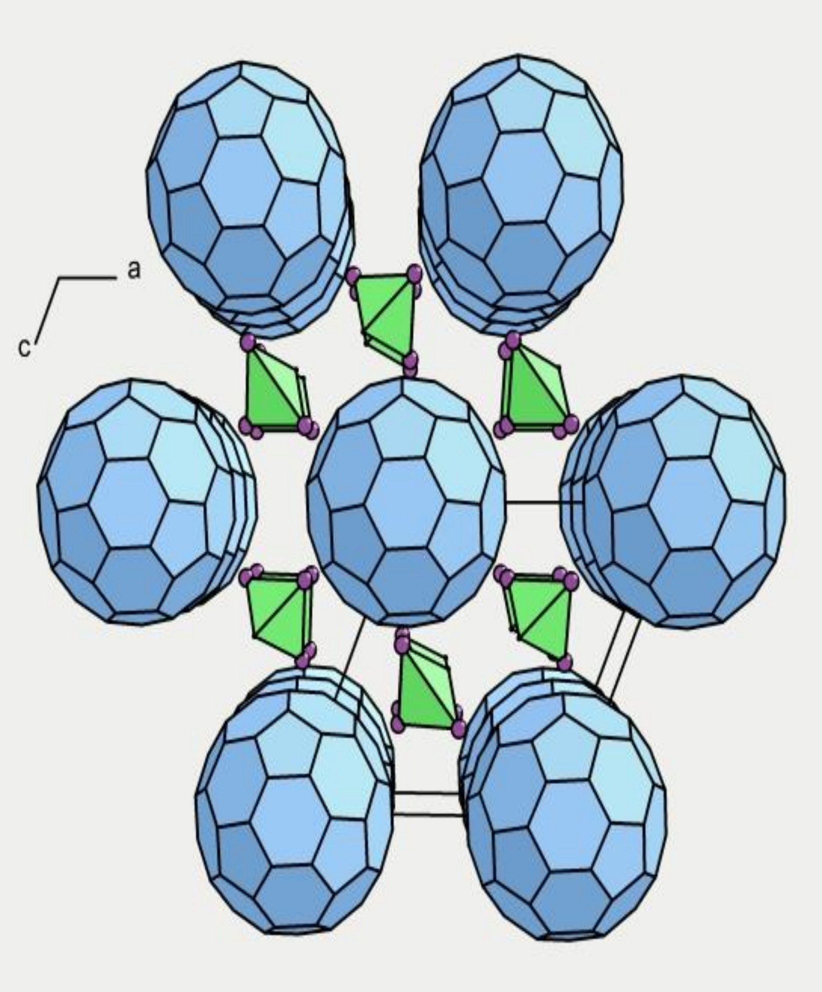
	Sp Group	Lattice	T_c	d_{nn}
K_3C_{60}	Fm3m	14.24	18 (e-)	10.069
Rb_3C_{60}	Fm3m	14.44	28 (e-)	10.211
C_{60}	Fm3m, (Pa-3)	14.16, (14.04)	52	10.013
$C_{60}.2CHCl_3$	P 6/mmm	10.09, 10.095	80	10.09
$C_{60}.2CHBr_3$	P 6/mmm	10.211, 10.216	117	10.211

along	d_{nn} (Å)
001	9.8179
100	9.8361
010	10.091
101	10.348
011	12.6165
-110	12.781

C60.2CHCl3 (P –1)

 Managed by UT-Battelle
for the U.S. Department of Energy

OAK RIDGE National Laboratory



Interfullerene distances

$C_{60} \cdot 2CHCl_3$
In plane:
9.82, 9.84, 10.35
Between plane: 10.09

$C_{60} \cdot 2CHBr_3$
In plane:
9.90, 9.90, 10.50
Between plane: 10.34

cf. C_{60}: 9.93 (5K)
K_3C_{60}: 10.07

Conclude: Strong increase of T_c from intercalations is not just an effect of simple lattice expansion.

Evidence against lattice expansion as the sole explanation for T_c increase in chloroform- and bromoform- doped C_{60}

R. E. Dinnebier[1], O. Gunnarssson[1], H. Brumm[1], E. Koch[1], A. Huq[2], P. W. Stephens[2], M. Jansen[1,*]

Structure of Haloform Intercalated C_{60} and Its Influence on Superconductive Properties

Robert E. Dinnebier,[1] Olle Gunnarsson,[1] Holger Brumm,[1] Erik Koch,[1] Peter W. Stephens,[2] Ashfia Huq,[2] Martin Jansen[1*]

www.sciencemag.org SCIENCE VOL 296 5 APRIL 2002

The New York Times — Technology

Similar Graphs Raised Suspicions on Bell Labs Research

By KENNETH CHANG

What had been hailed a few months ago as a ... molecule-size electronics is now in doubt, a ... Bell Laboratories is under suspicion of improperly m... in research papers published in prestigious scientifi...

The accusations, by scientists not connected with t... came to light this week, when Bell Labs appointed ... panel to look into them. Yesterday, the scientists sa... concerns focused on graphs that were nearly identi... they appeared in different scientific papers and rep... from different devices. In some graphs, even the t... should arise from purely random fluctuations match...

This is the first time in its 77-year history that Bell ... distinguished research division of Lucent Technolog... convened such a panel to look at possible miscond... researchers. Lucent has forwarded five papers — ... Science, one in Nature and one in Applied Physics ... panel for investigation. The lead author of all five is ... Schön, 31, a Bell Labs physicist in Murray Hill, N.J. ...

Science now — 20 May 2002

Pioneering Physics Studies Under Suspicion

Officials at Bell Laboratories, the research arm of Lucent Technologies in Murray Hill, New Jersey, are forming a committee of outside researchers to investigate questions about a recent series of acclaimed scientific studies. Outside researchers presented evidence to Bell Labs management last week of possible manipulation of data involving five separate papers published in *Science*, *Nature*, ...

The papers describe a series of different device experiments, but physicists are voicing suspicions about the figures, portions of which seem almost identical even though the labels are different. Particularly puzzling is the fact that one pair of graphs show the same pattern of "noise," which should be random.

The groundbreaking papers include Bell Labs physicist Jan Hendrik Schön as lead author and his colleagues at Murray Hill and elsewhere as co-authors. Schön is the only researcher who co-authored all five papers in question. Everyone involved agrees that the questions need further ... be devastating for Bell Labs ... that he stands behind his ... with similar devices

The New York Times — Science

A Sudden Host of Questions on Bell Labs Breakthroughs

By KENNETH CHANG

On a ski slope in Utah in March, Paul Grant and Rick Greene made a bet — about superconductors.

Dr. Grant and Dr. Greene, who had been longtime colleagues at the I.B.M. Almaden Research Center in San Jose, Calif., had debated all day a sensational scientific report that molecules of carbon shaped like soccer balls had been turned into superconductors — materials that carry electricity with virtually no resistance — at surprisingly warm temperatures.

Dr. Grant doubts the findings. Dr. Greene said he thought that they they would be verified.

Last week, Dr. Grant sent an e-mail message reminding Dr. Greene of the wager, because the lead researcher of the experiment was Dr. J. Hendrik Schön, the Bell Labs scientist who is now the center of a scientific misconduct investigation. Nearly identical graphs appear in several of Dr. Schön's scientific papers, even though the graphs represent different data from different experiments. Bell Labs, part of Lucent Technologies, has convened an independent panel to investigate.

But even before the two main papers cited in the investigation were published, a debate had arisen over the superconductor claims.

"There's been a lot of buzz for well over a year," said Dr. Grant, now a science fellow at the Electric Power Research Institute in Palo Alto, Calif.

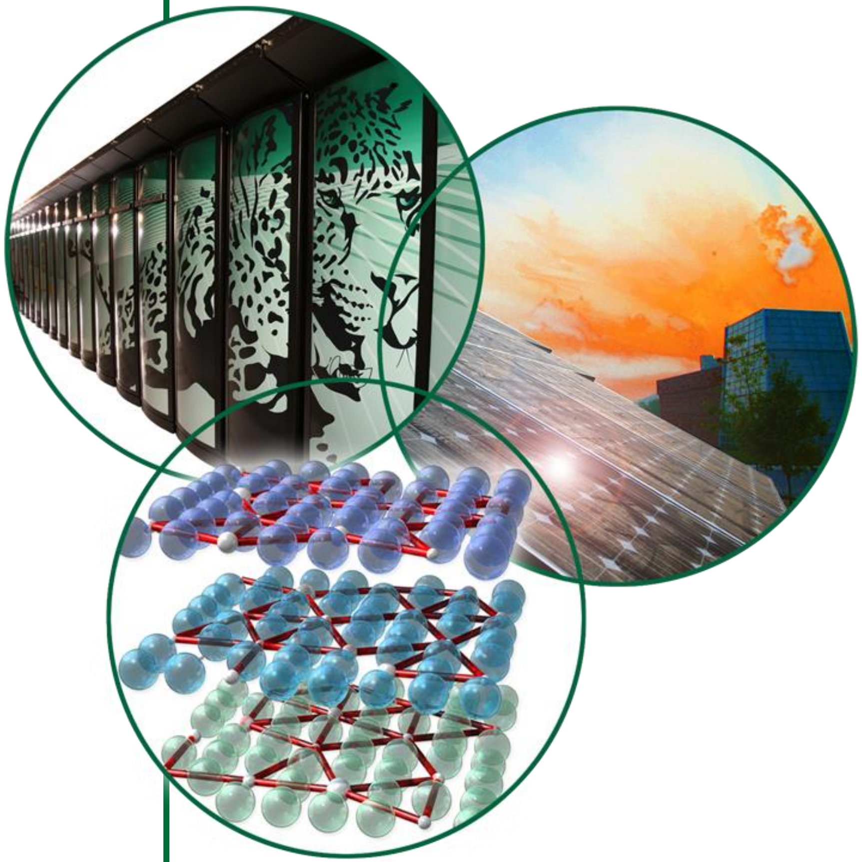
Dr. Schön and his collaborators have developed a revolutionary technique that allows them to explore systematically the electronic properties of various materials. Dr. Grant had called the team's "buckyball" work paper "a tour de force of physics" when it was announced. Other scientists said it might be worthy of a Nobel Prize.

In 2001 he was listed as an author on an average of one research paper every eight days!

On October 31, 2002, *Science* withdrew eight papers written by Schön. On December 20, 2002, the *Physical Review journals* withdrew six papers written by Schön. On March 5, 2003, *Nature* withdrew seven papers written by Schön.

OAK RIDGE National Laboratory

Neutron Powder Diffraction



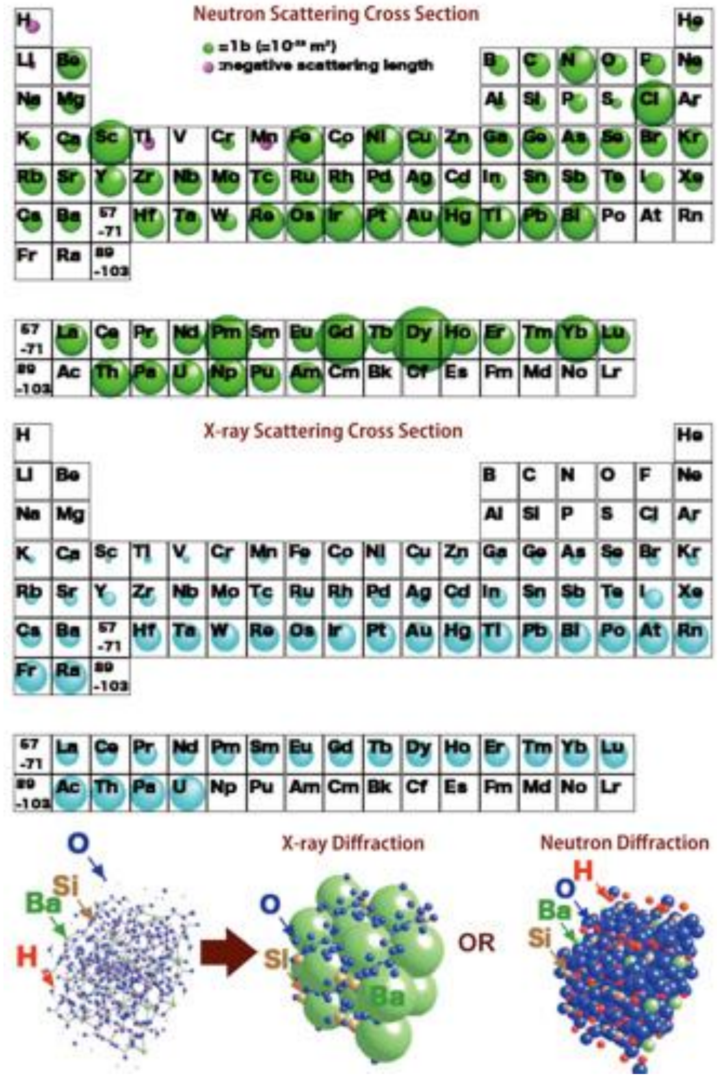
U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Why Neutrons ?

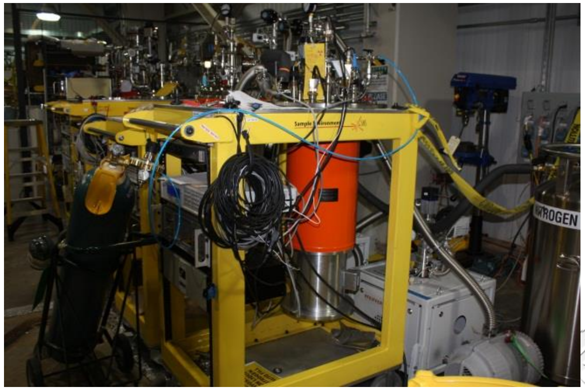
- Detects light atoms even in the presence of heavy atoms (organic crystallography) – H is special!
- Distinguishes atoms adjacent in Periodic table and even isotopes of the same element (changing scattering picture without changing chemistry)
- Magnetic moment (magnetic structure)
- Electrically neutral; penetrates centimeters of bulk material (allows non-destructive bulk analysis). Ease of *in-situ* experiments, e.g. variable temperature, pressure, magnetic field, chemical reaction etc.



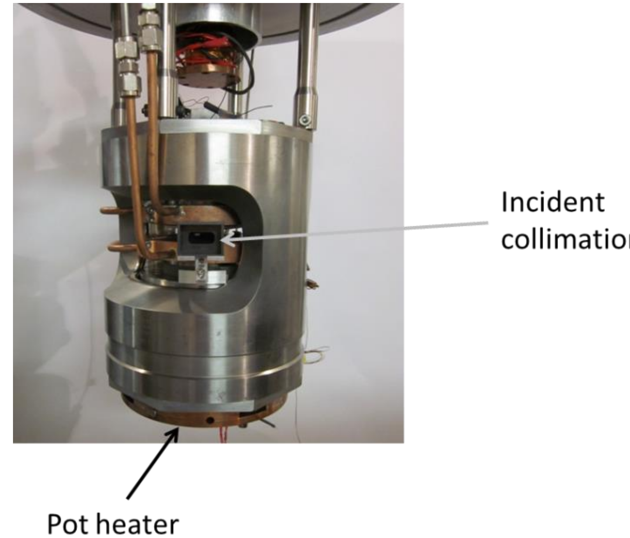
Oak Ridge National Laboratory

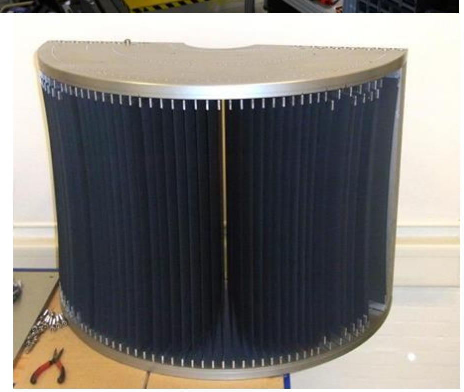
Sample Environment

- **Sample Containers**
  - Usually V can
  - Capillaries for small sample
- **Low Temperature**
  - CCR (4K-300K)
  - CCR with sample changer
  - Orange Cryostat (2K-300K)
  - OC with Dilution insert(mK-300K)
  - Cryofurnace (4K-650K)
- **Magnets**
  - 14T on WISH
  - 11T on NPDF
  - 5T on Powgen (commission)

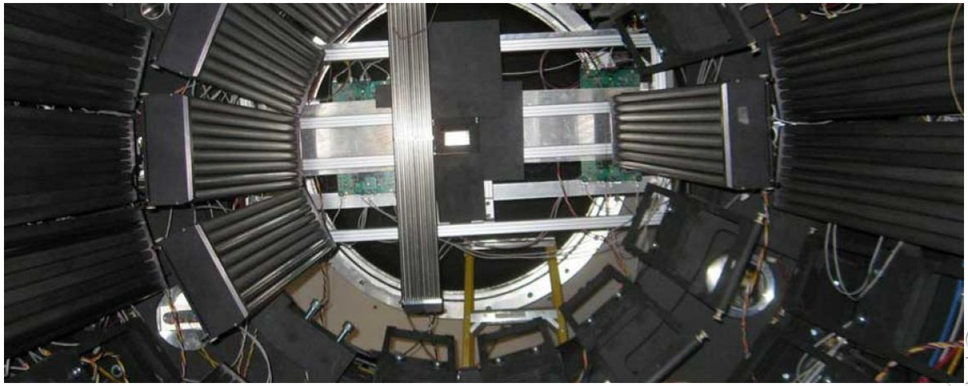


- **High Temperature**
  - **V (ILL) Vacuum furnace (RT-1100C)**
  - **Nb (ILL) Vacuum furnace (RT-1600C)**
- **Gas Handling**
  - **AGES (combined with pO_2 sensor and RGA)**
  - **Sievert Absorption Setup**
- **Engineering (dedicated instruments)**
  - **Load Frames**
  - **Euler crates**
- **Pressure**
  - **Gas Pressure Cells**
  - **Paris Edinburgh (25GPa)**
  - **Anvil Cell (50GPa)**

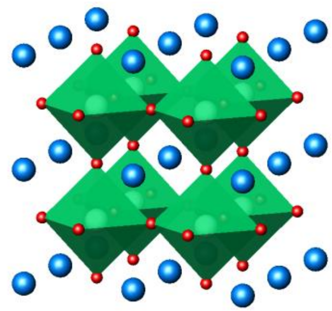




Detectors

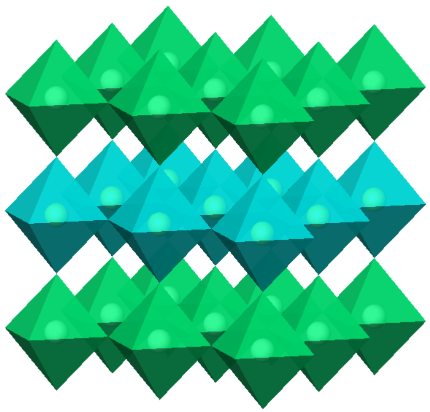


Ba_2CuWO_6: An Ordered Tetragonal Perovskite

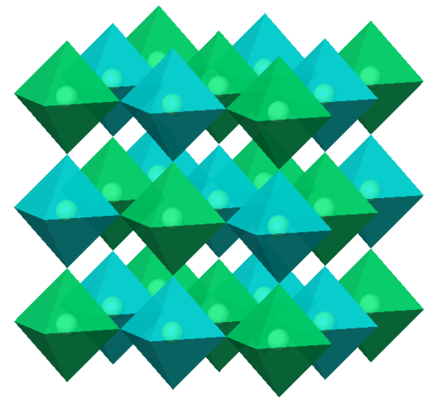


Simple cubic AMX_3 perovskite: a = 3.8045.

Double Perovskites $A_2MM'O_6$: Out of 3 possible ordering only 2 observed



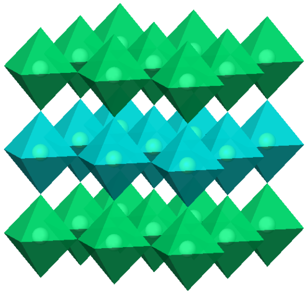
Model #1: Ordered alternation of MO_6 and $M'O_6$ octahedra in one direction, leading to formation of layered perovskite.



Model #2: Ordered alternation in the three directions of space, resulting in rock-salt ordered superstructure.

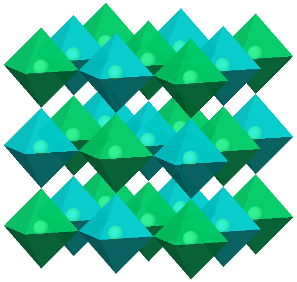
Model #1 – Layered Ordering:

Space Group	P 4/m m m			
unit cell	a 3.9350Å c 8.6350Å			
Atom	x	y	z	frac
Ba	0.5	0.5	0.25	1
Cu	0	0	0	1
W	0	0	0.5	1
O	0	0	0.25	1
O	0.5	0	0	1
O	0.5	0	0.5	1

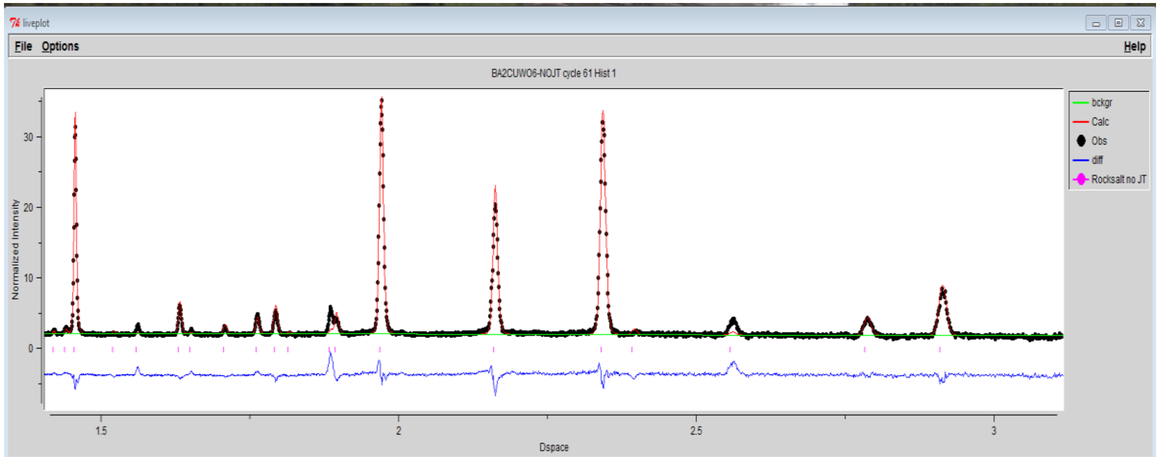


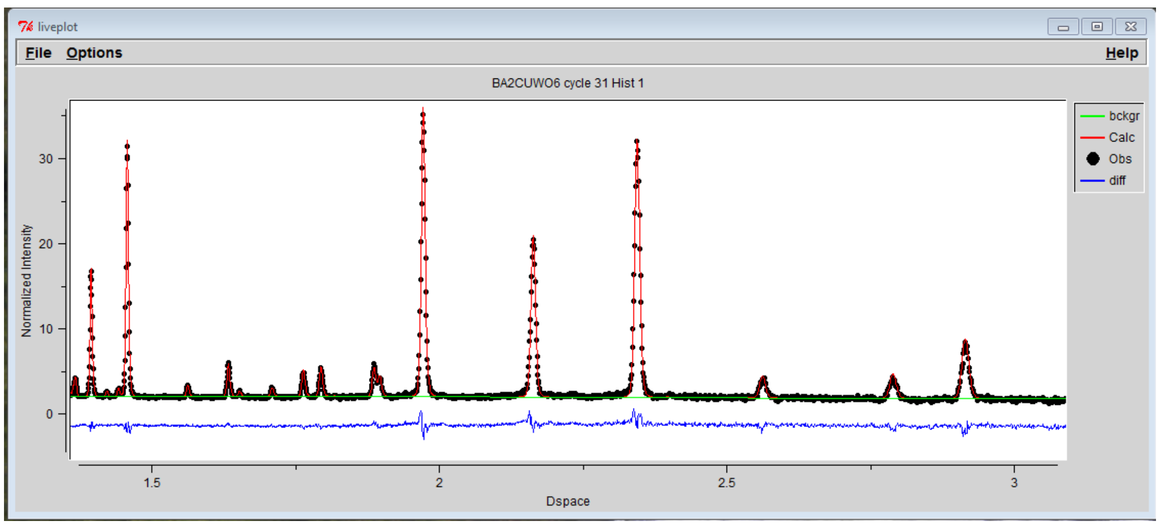
Model #2 – Rock Salt Type Ordering:

Space Group	I 4/m			
unit cell	a 5.5648Å c 8.6352Å			
Atom	x	y	z	frac
Ba	0	0.5	0.25	1
Cu	0	0	0	1
W	0	0	0.5	1
O	0	0	0.2500	1
O	0.2500	0.2500	0	1



Oak Ridge National Laboratory





Recall Cu^{2+} electronic configuration $(t_{2g})^6(e_g)^3$: Jahn Teller Distortion?

So in fact CuO_6 octahedra are elongated along the c axis. The e_g orbital is split into

$(d_{x^2-y^2}$ and $d_{z^2})$

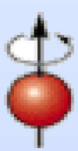
Iwanaga et. al. J. Solid State. Chem. 147, 291(1999)

Managed by UT-Battelle
for the U.S. Department of Energy
OAK RIDGE
National Laboratory

Magnetism using Powder Diffraction

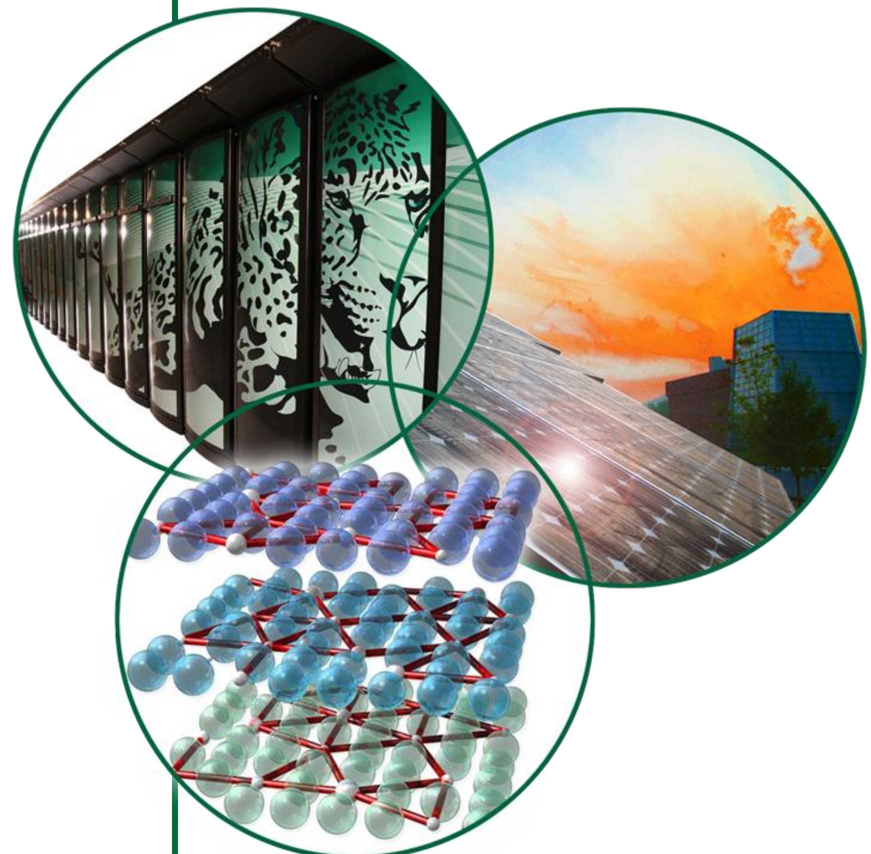
Neutrons have a **MAGNETIC** moment

- determine microscopic magnetic structure
- study magnetic fluctuations



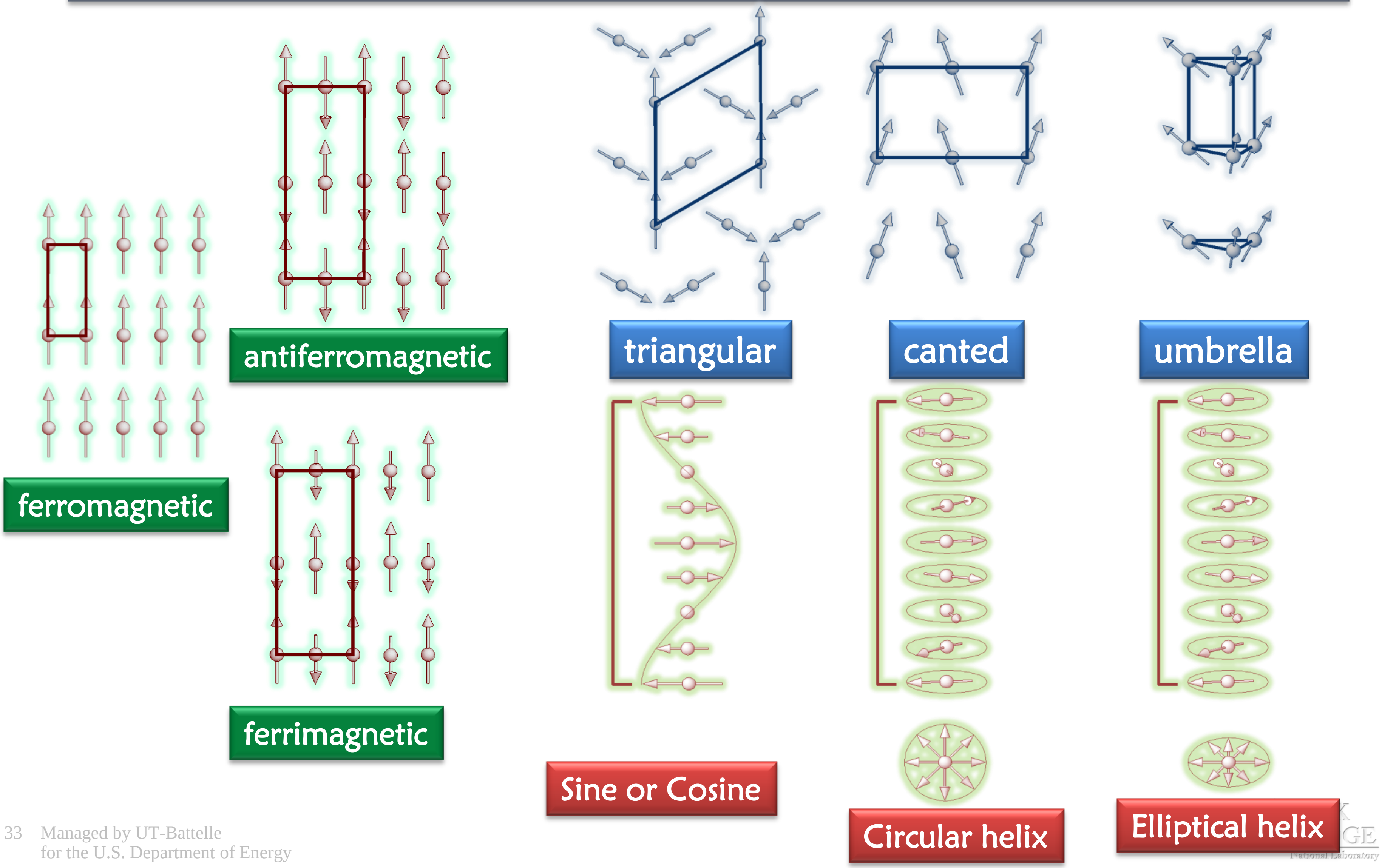
Neutrons have **SPIN**

- can be formed into polarized neutron beams



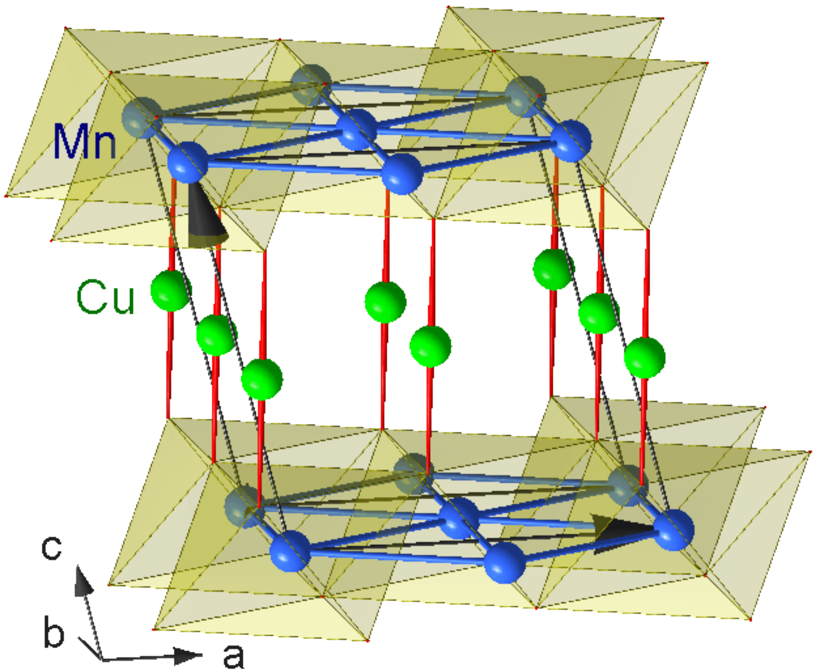
Magnetic structures

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



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 $Mn^{3+}O_6$ ($3d^4$)

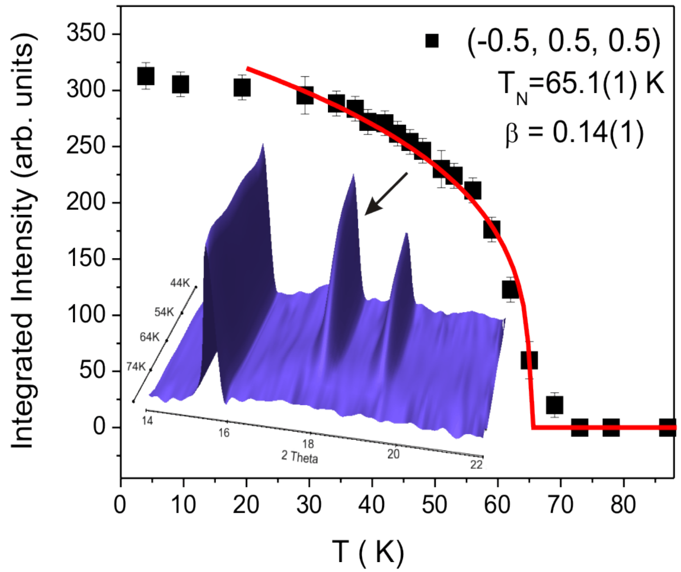
Ferro-orbital ordering $d_{3r^2-z^2}$

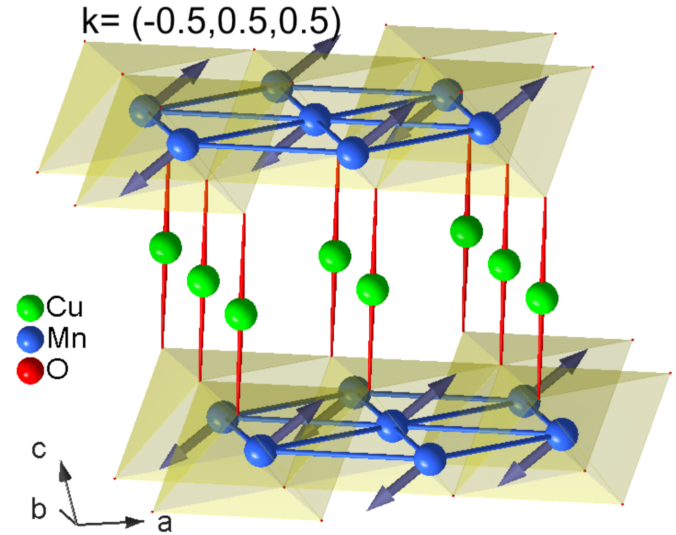
Ovi Garlea, QCMD, ORNL

Neutron Sciences
HFIR SNS
Managed by UT-Battelle for the U.S. Department of Energy
OAK RIDGE National Laboratory

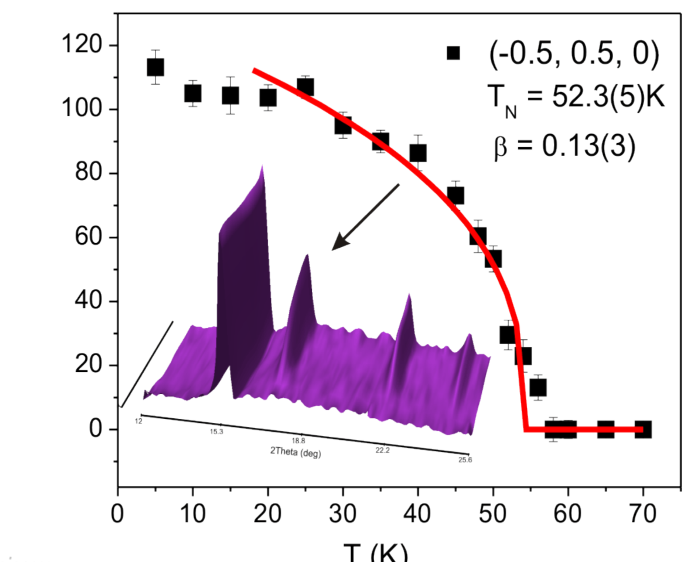
$Cu(Mn_{1-x}Cu_x)O_2$: Tuning of Magnetism by chemical substitution

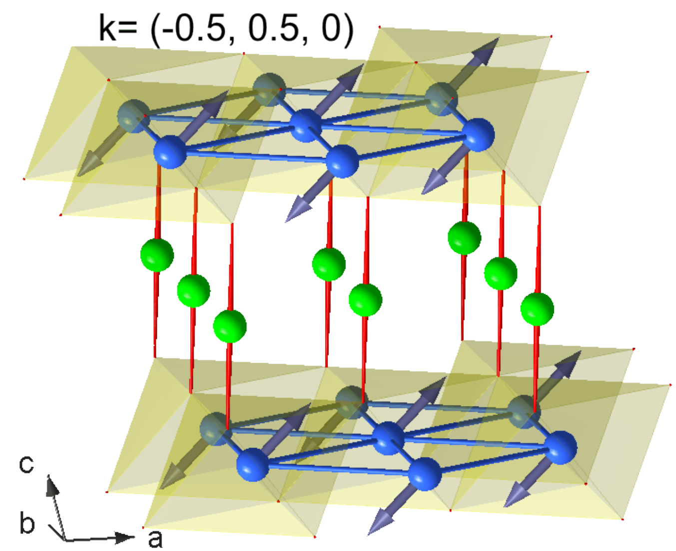
$CuMnO_2$



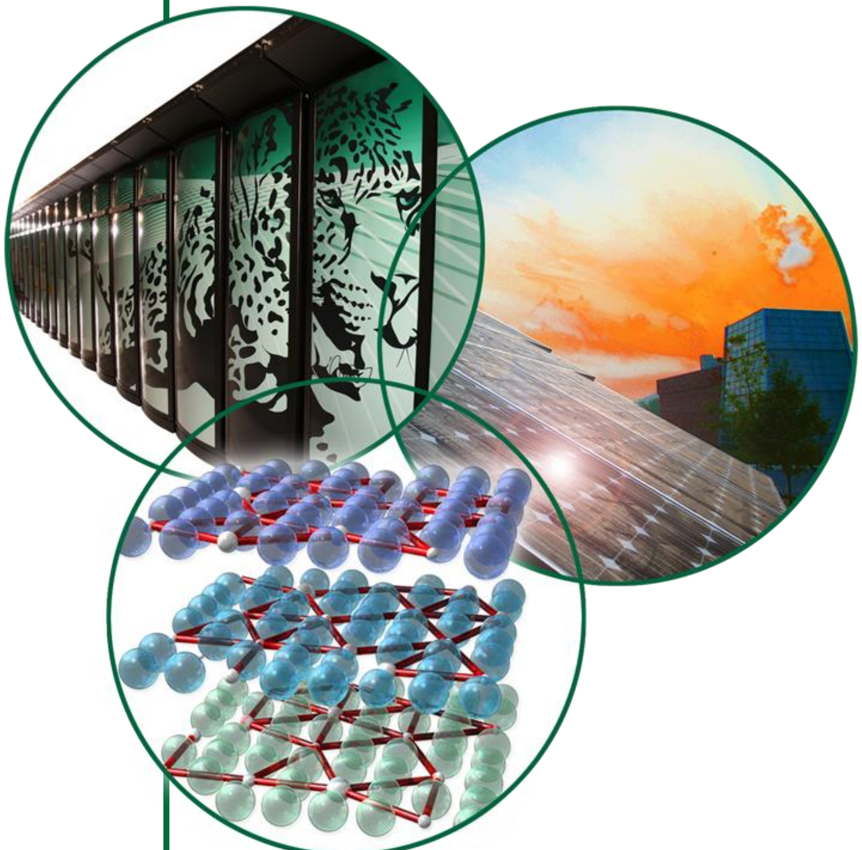


$Cu(Mn_{0.93}Cu_{0.07})O_2$





Very often life is not so simple and one has to use both X-rays and Neutrons to get to the right picture



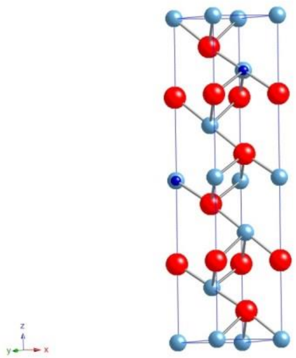
Neutrons & X-ray are complementary tools in battery research

Challenge

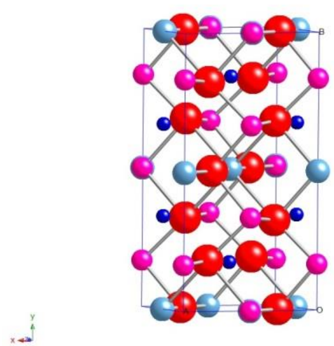
New materials are being developed in various user groups to improve performance of electrodes and electrolytes. Structural information is crucial to understand the electrochemical properties and motion of Li in the system.

We are doing detailed structural analysis using combined neutron and X-ray powder diffraction.

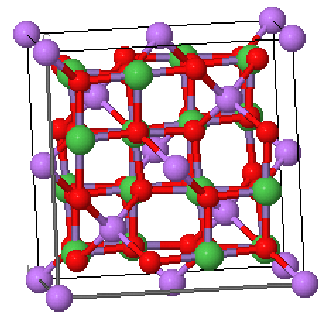
Elements	Neutron scattering length : b	Atomic Number : Z
Li (natural)	-1.9	3
Mn	-3.73	25
Co	2.49	27
Ni	10.3	28



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



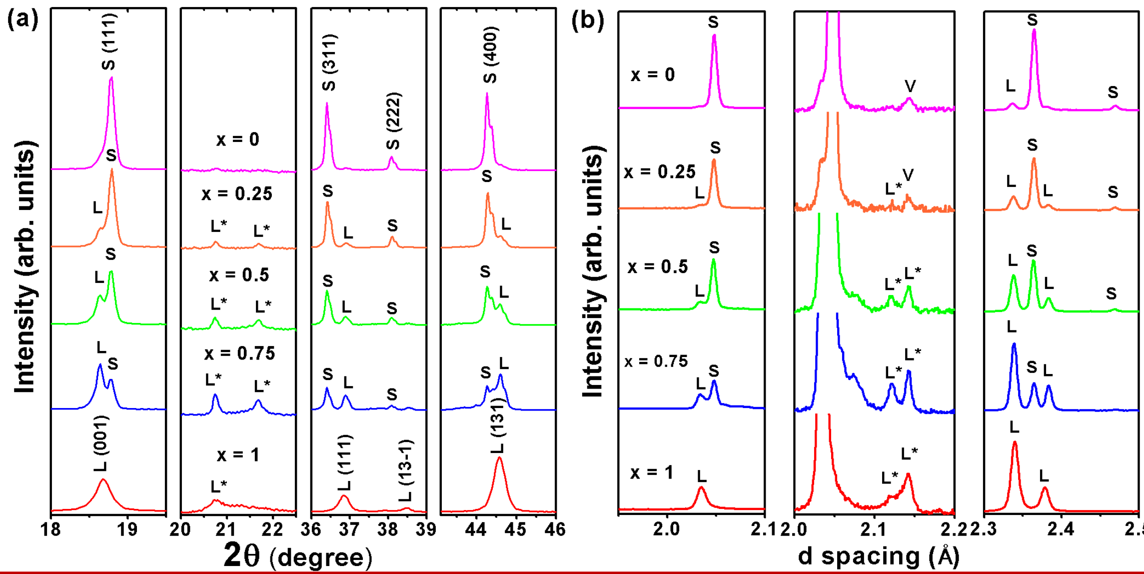
Space Group : C 2/m
a=4.94,b=8.55, c = 5.04, β =109.3
$Li(Li_{0.2}Ni_{0.17}Mn_{0.6}Co_{0.03})O_2$



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

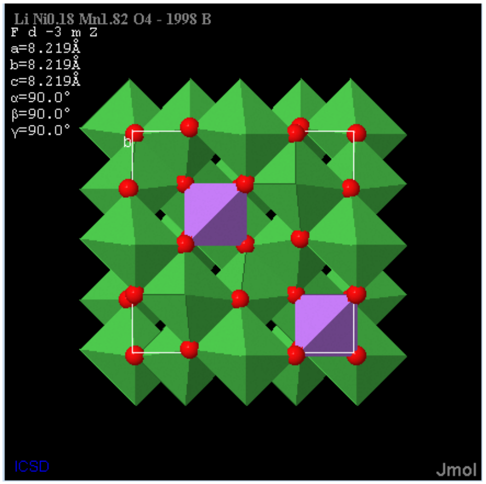


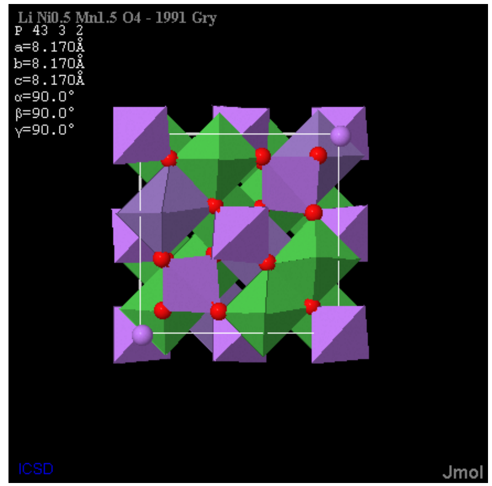
Neutron

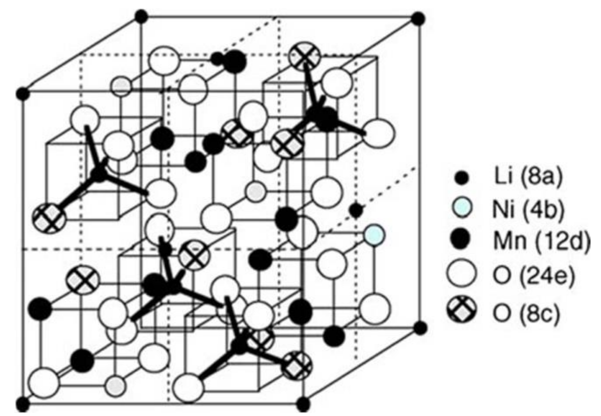
- No TM ordering in the spinel phase.
- Li and TM ordering converts the nominally layered (R3m) phase to form a monoclinic phase (C2/m) where superstructure reflections are observed.
- Impurity cubic phase is identified as Ni_6MnO_8, instead of the traditional cubic $Li_xNi_{1-x}O_y$.
- Ex-situ XRD reveals 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.

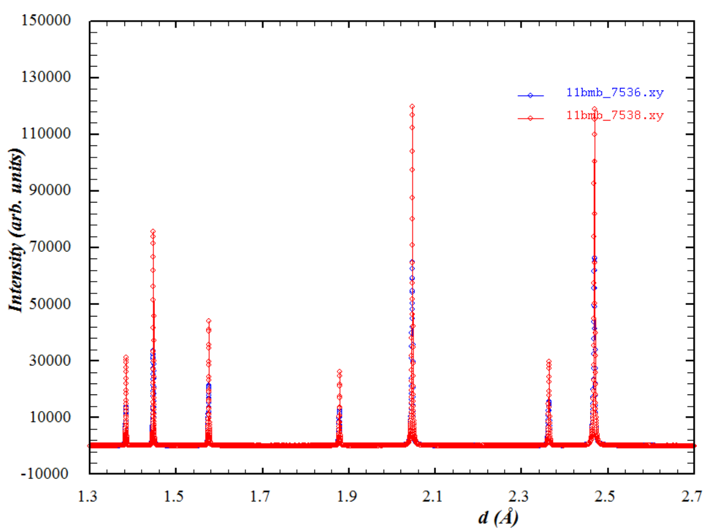
Cation ordering in Spinel
($LiMn_{1.5}Ni_{0.5-x}M_xO_4$; M=Cr, Fe, Ga)



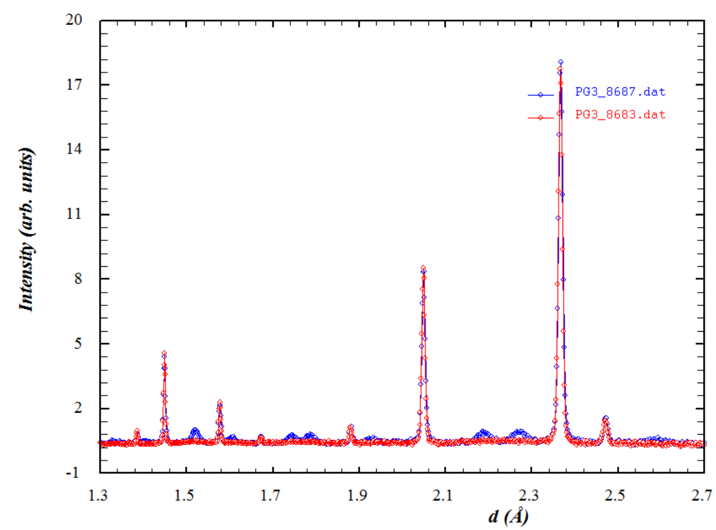




LiM1.5Ni0.42M0.08O4 Anneal vs Slow cool

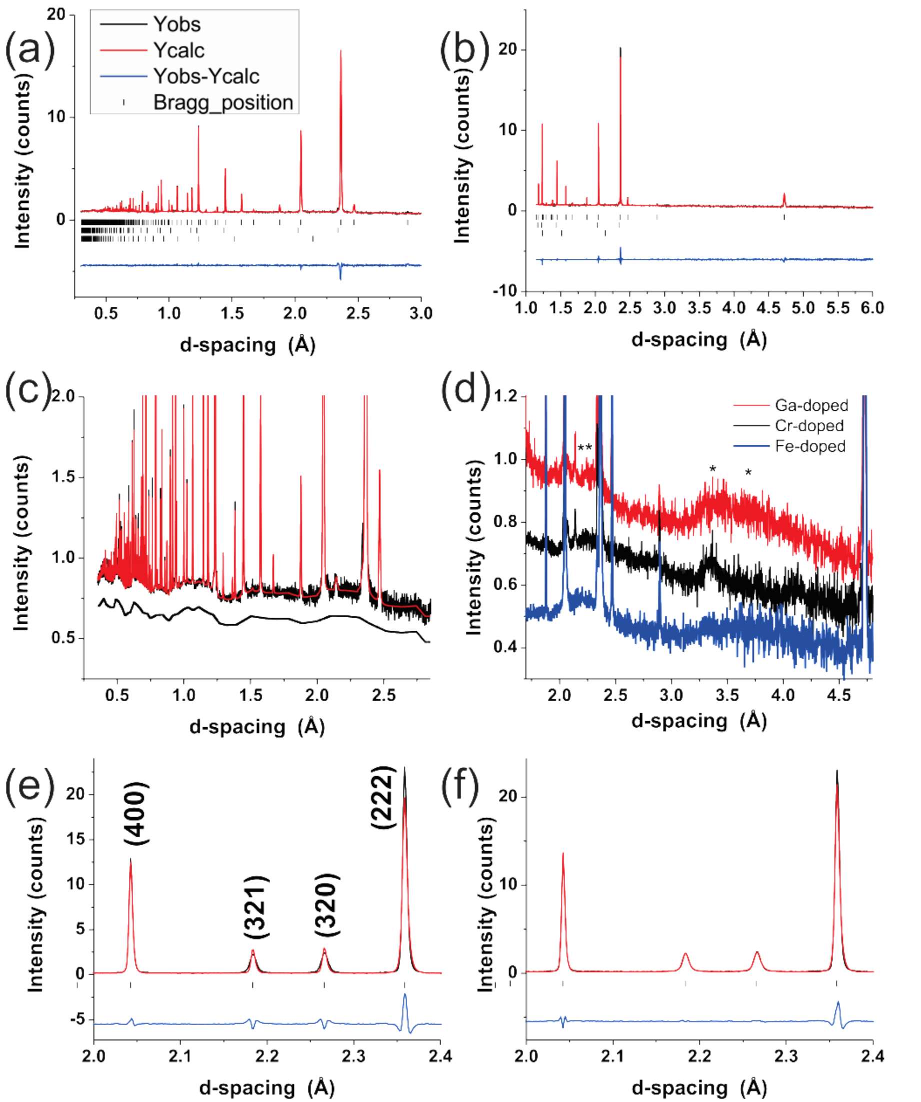


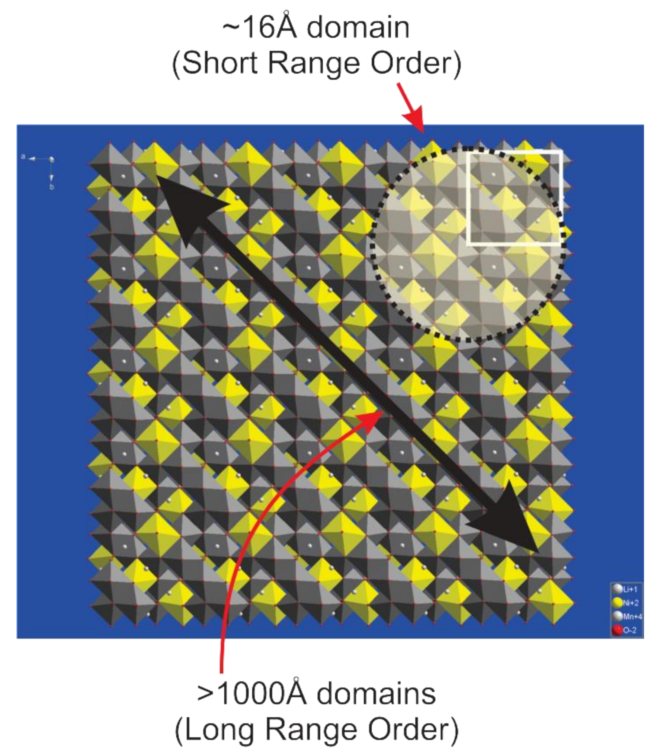
LiM1.5Ni0.42M0.08O4 Anneal vs Slow cool



for the U.S. Department of Energy

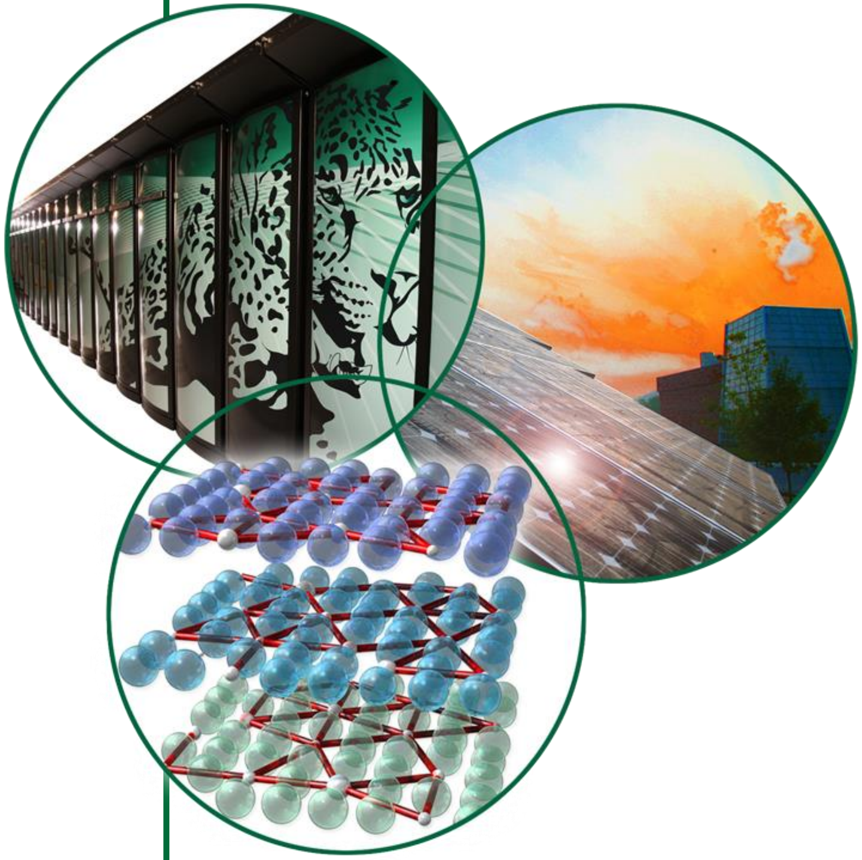
Controlling the level of cation ordering





D.W. Shin, C.A. Bridges, A. Huq, M. P. Paranthaman and A. Manthiram, "Role of Cation Ordering and Surface Segragation in High-Voltage Spinel $LiMn_{1.5}Ni_{0.5-x}M_xO_4$", *Chemistry of Materials* 24, 3720-3731 (2012).

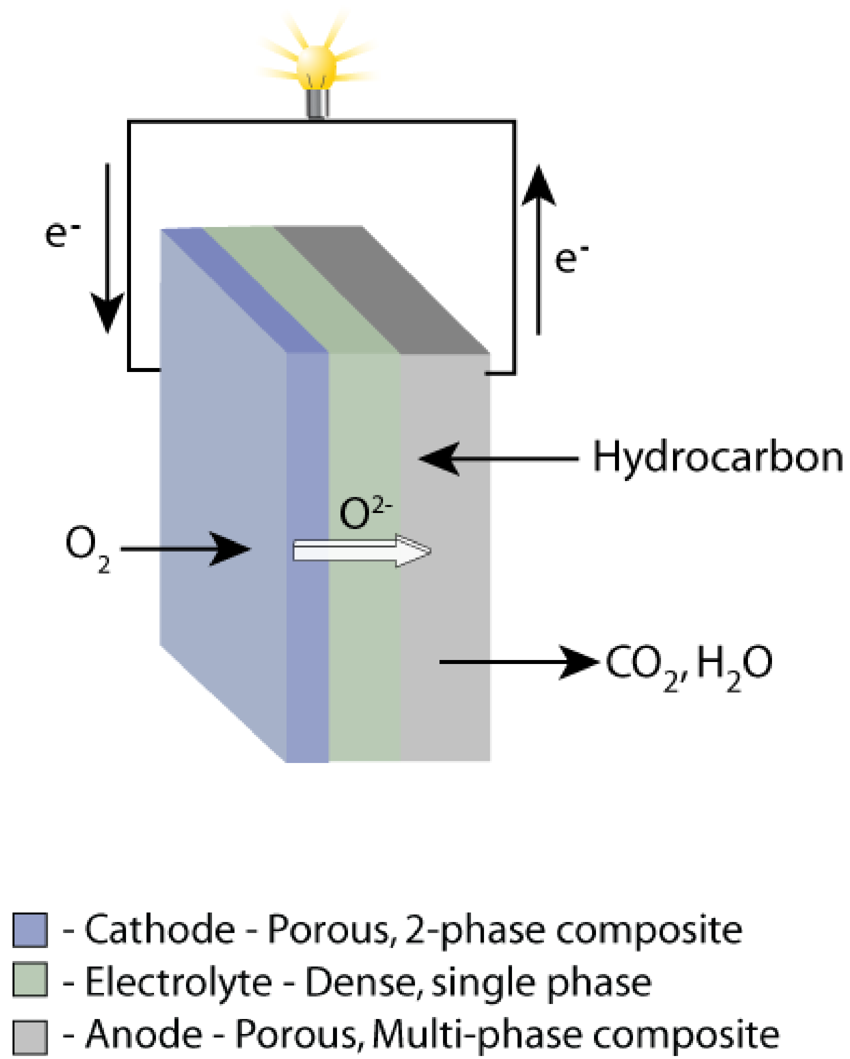
In situ studies of Solid Oxide Fuel Cell materials



U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Solid Oxide Fuel Cell (SOFC)



- **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.**

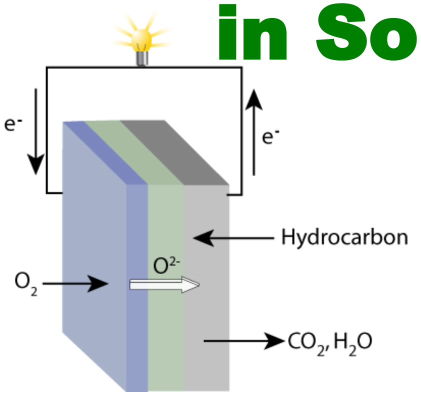
$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

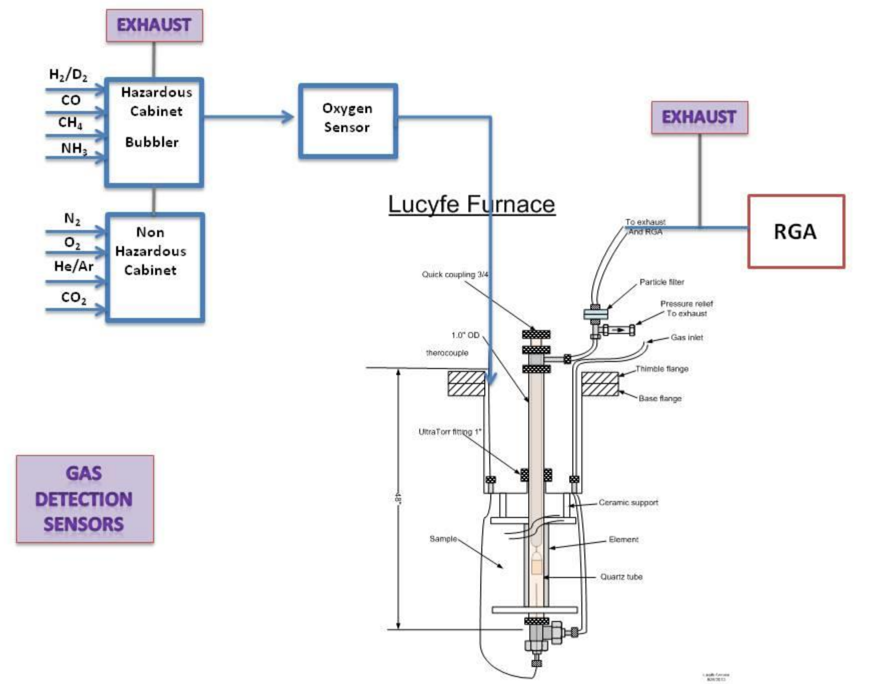
- **Ideally we can utilize hydrocarbons directly:**

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

Managed by UT-Battelle
for the U.S. Department of Energy
Oak Ridge National Laboratory

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.

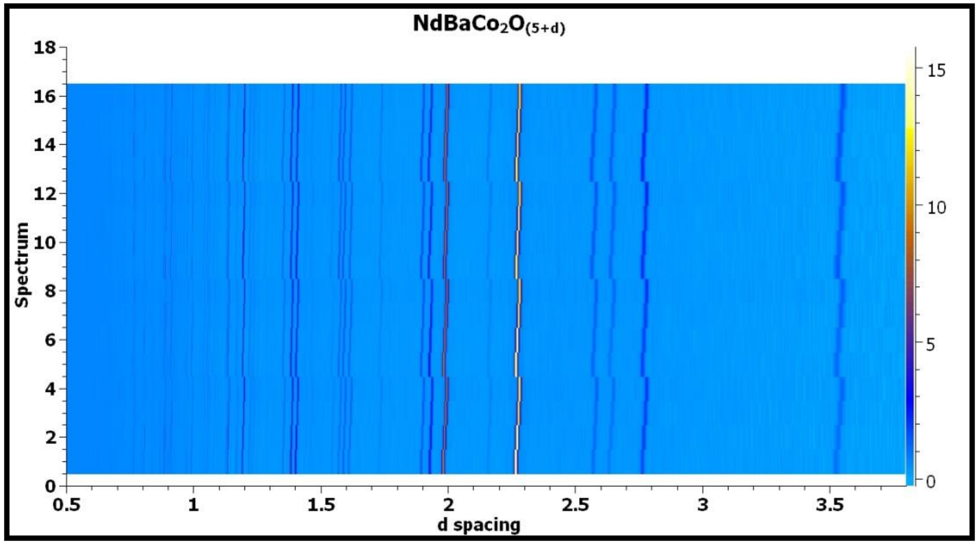
An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) make experiments possible under operational condition.

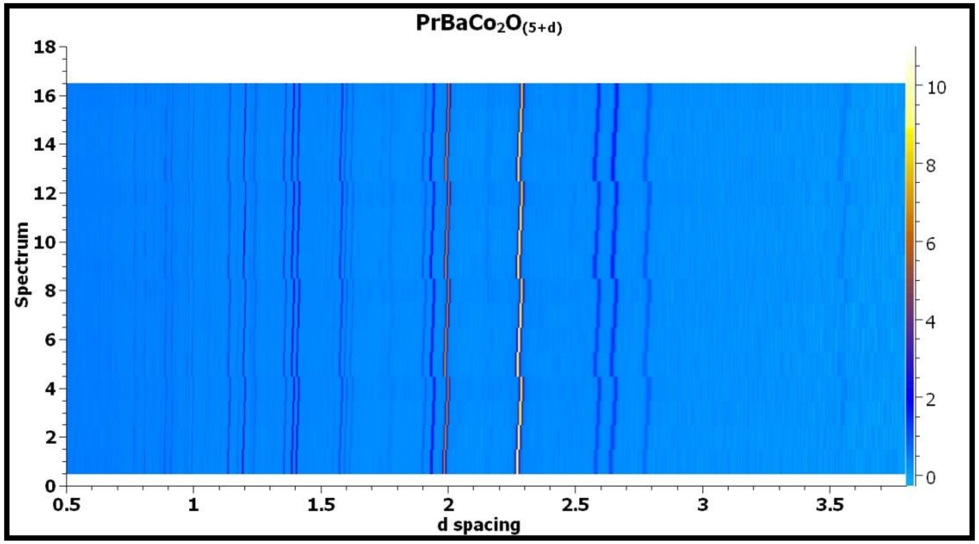
- Cathode - Porous, 2-phase composite
- Electrolyte - Dense, single phase
- Anode - Porous, Multi-phase composite

OAK RIDGE National Laboratory

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

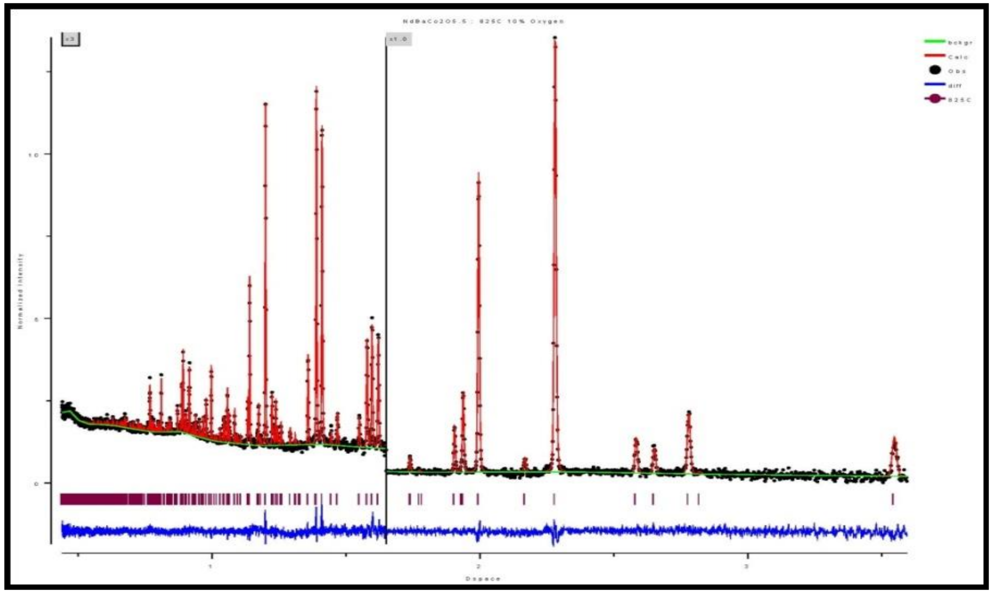
- Samples of (Nd and Pr)$BaCo_2O_{5\pm\delta}$ were measured @ four different pO_2 and four different temperature at each pO_2
- Equilibrium state was achieved by measuring the lattice parameter. Once the lattice parameter stopped changing, longer data was collected.
- Temperature of the sample was calibrated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

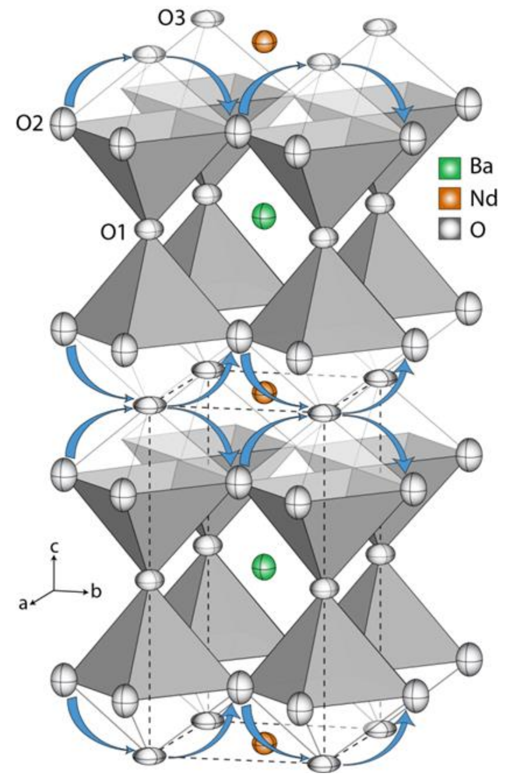




Neutrons show Oxygen migration pathway in $NdBaCo_2O_{5\pm\delta}$

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)

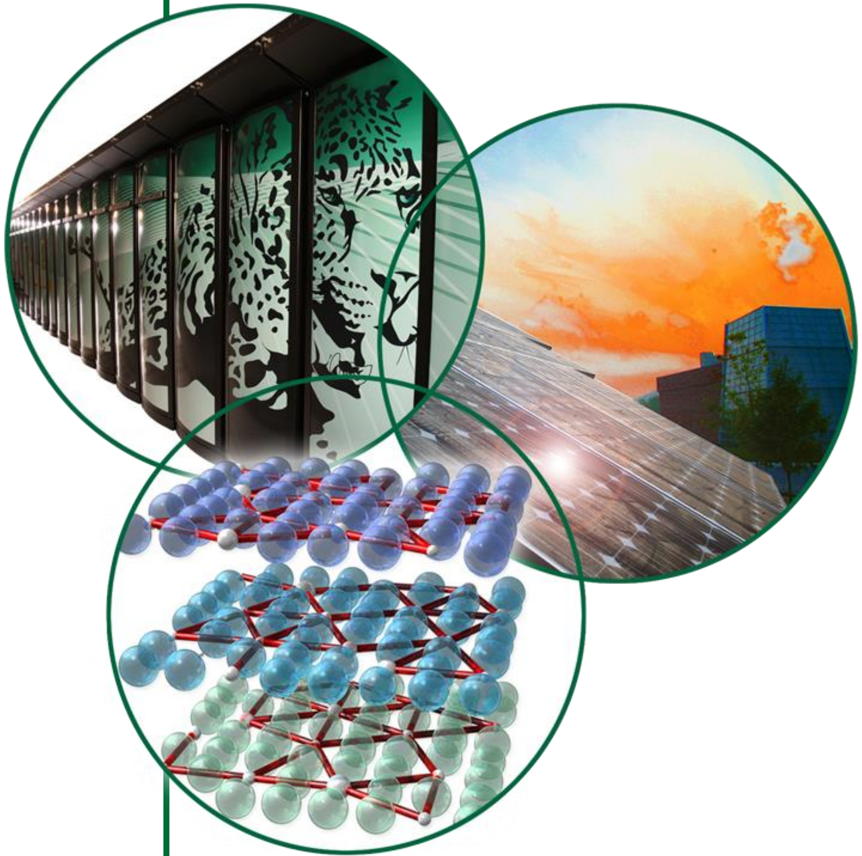




- **High Q data allows refinement of anisotropic thermal parameters and oxygen vacancy. Combined with near neighbor distances, it allows us to directly visualize the oxygen diffusion pathway.**
- **The structure is Tetragonal and not Orthorhombic as previously suggested in these pO_2 values.**
- **O3 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.**

Oak Ridge National Laboratory

Ab-initio Structure Solution from Powder Diffraction

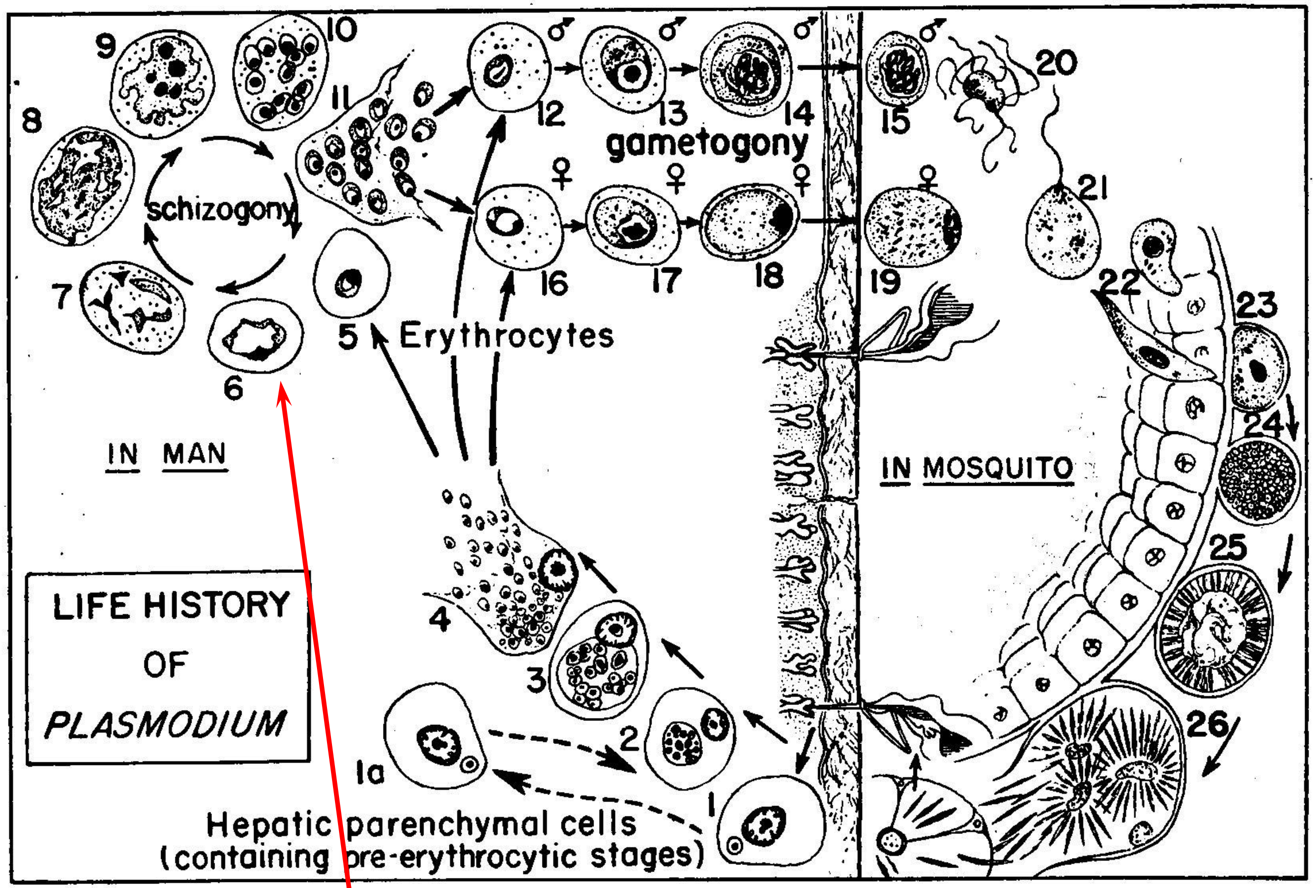


References:
Structure Determination from Powder Diffraction Data
W.I.F. David, Oxford University Press, 2002
http://www.cristal.org/iniref.html

U.S. DEPARTMENT OF ENERGY

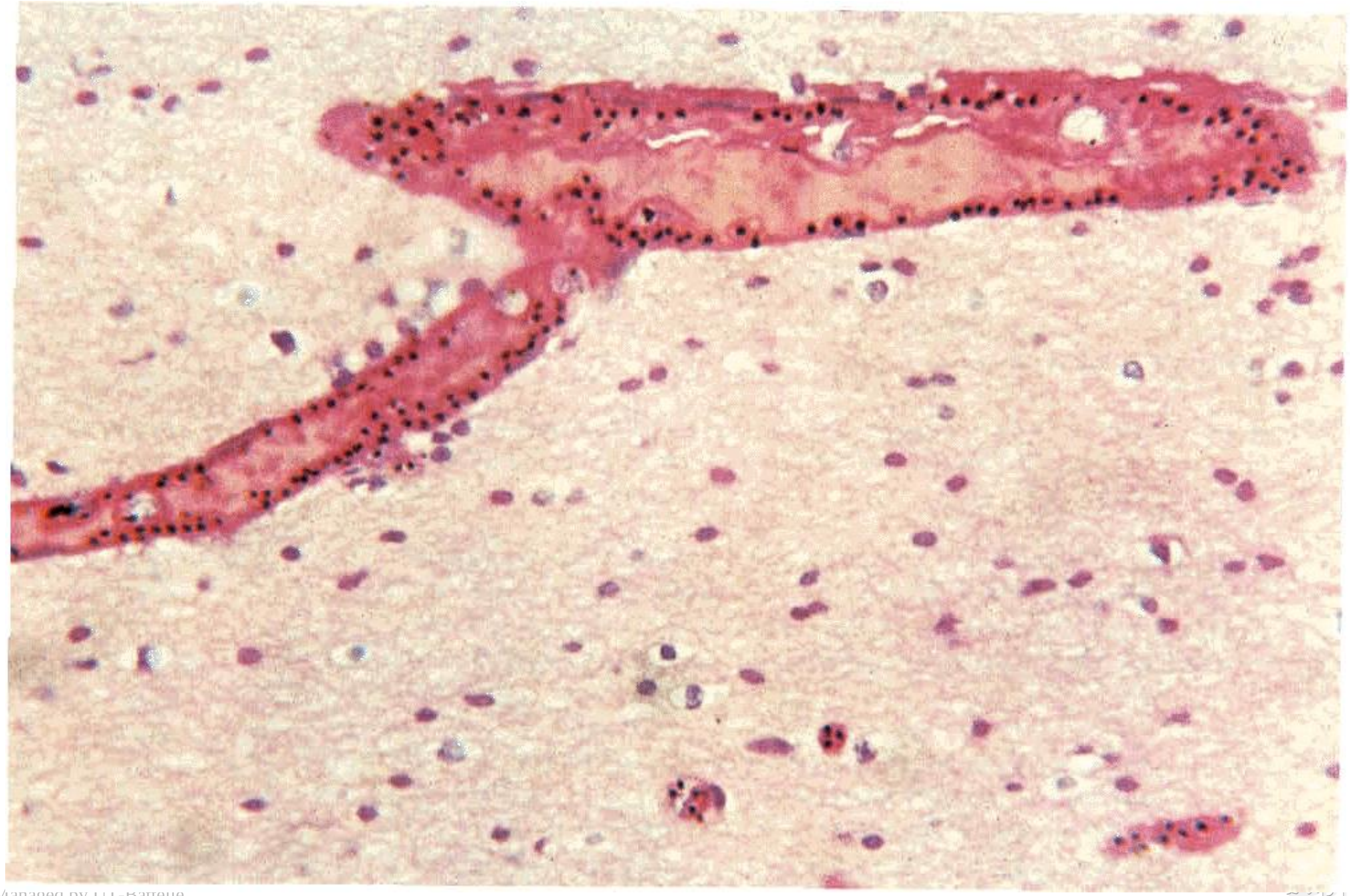
OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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



Oak Ridge National Laboratory

Heme Polymer?

SCIENTIFIC CORRESPONDENCE

18

Haem polymerization in malaria

SIR — Haem that is derived from the breakdown of host cell haemoglobin by malarial parasite

Acetonitrile extracts of

haemoglobin-derived haem may critical to the survival and succe maturation of the malarial

30

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,*]

20133 Milan, Italy

Milan, Italy

28

THE JOURNAL OF BIOLOGICAL CHEMISTRY
© 1998 by The American Society for Biochemistry and Molecular Biology, Inc.

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*

~~26~~ ~~9~~ 18

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

and haemozoin, the haem polymerase the pellet (data not shown). The trophozoites were extracted in 1% Triton X-100, although 1% SDS (data not of the pellet with

3

80

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

Dorn*, Ruedi

Matile*

parasite, we confin insoluble fraction of tive vacuoles (Fig. were then subfraction and haemozoin fraction support haem polymeriz enrichment of 'haem poly tion; activity in the memb accounted for by the presen fractions. Treatment of hae chloroform–methanol to re firmed by silver-stained SDS-P amide) gave material with acti haemozoin (Fig. 2c). Exposure of proteinases (proteinase K, pronase had no effect on haem polymerizatio These results suggested that haemoz 'haem polymerase' activity. We also haematin to promote haem polymerizati ture is similar to that of haemozoin; it a haem chloride solution to 70 °C at acid no protein. We found that it could support h at 37 °C like haemozoin and that its activity by chloroquine (Fig. 3a). The reported inhibition of haem occurred when polymerization (Fig. 3b), which suggests of protein denaturation structure of support

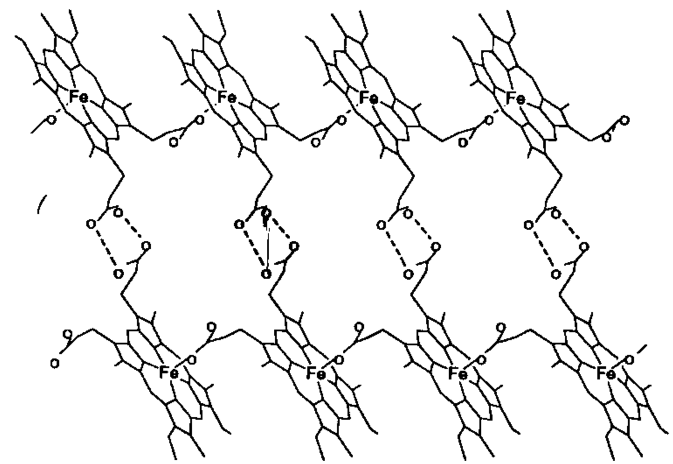
Stephens

Chapter 37

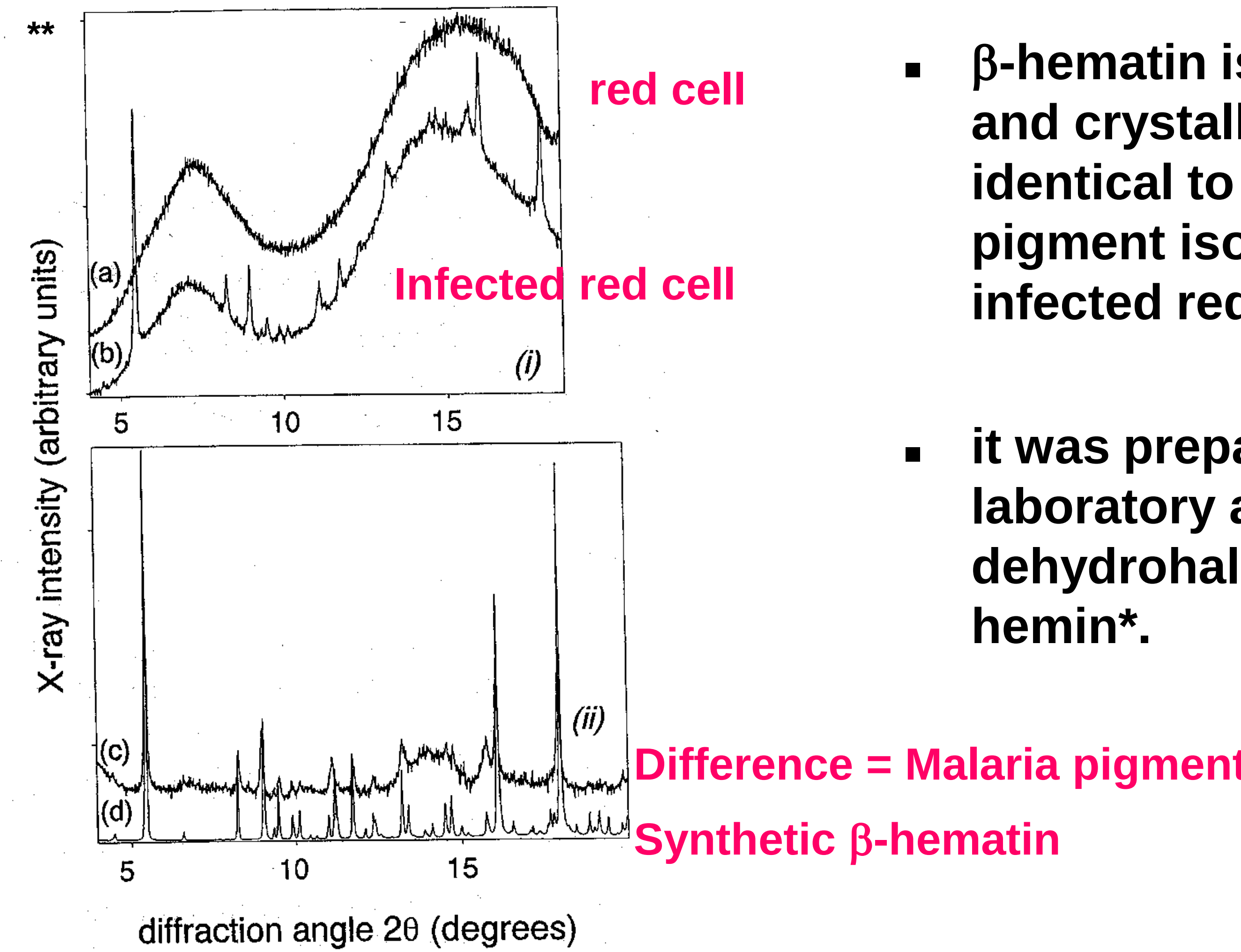
Structural and Spectroscopic Studies of β-Hematin (the Heme Coordination Polymer in Malaria Pigment)

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, Stony Brook, NY



β-hematin and malaria pigment



- **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*.**

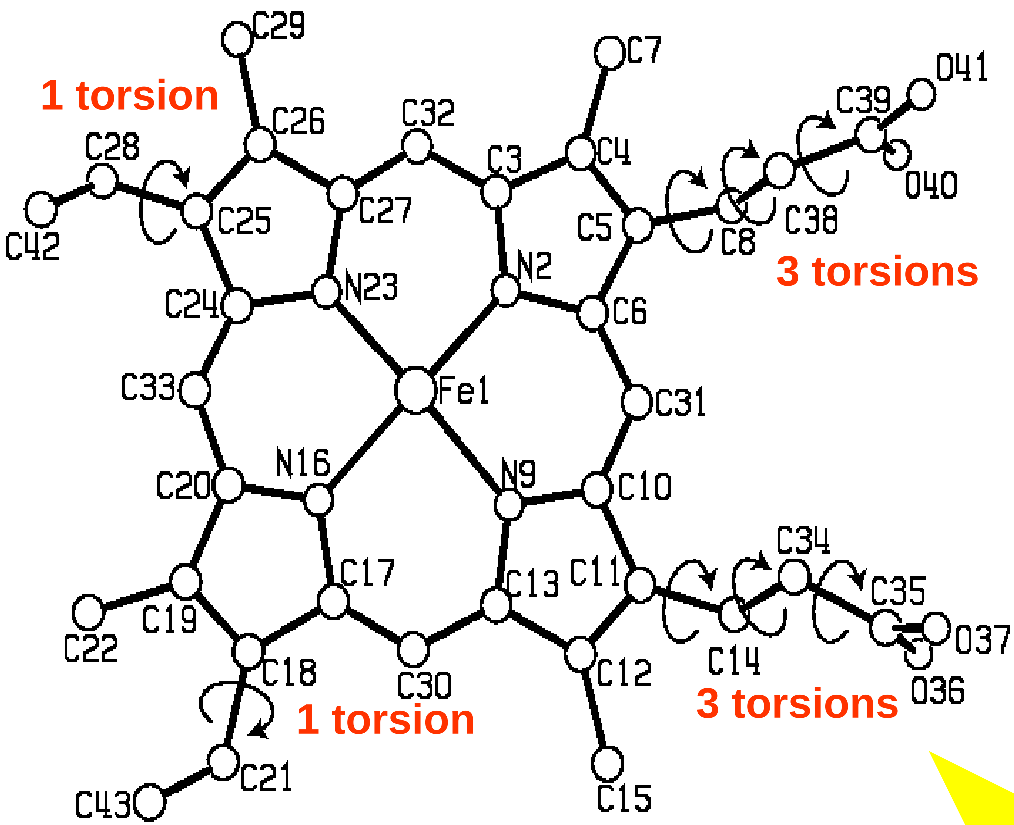
Given atom positions, it is straightforward to compute the diffraction pattern

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

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

OAK RIDGE National Laboratory



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

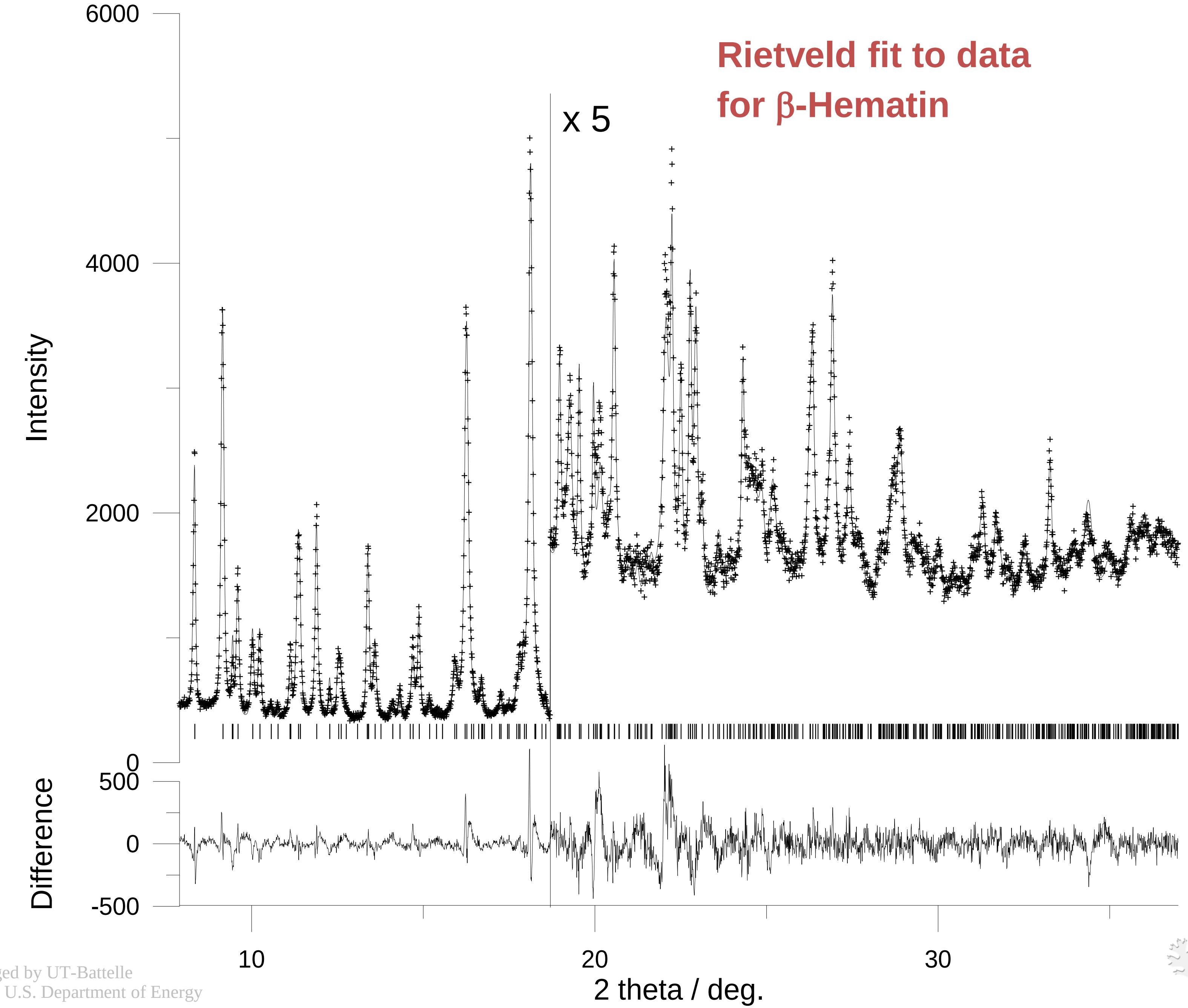
- **3 spatial coordinates,**
- **3 Eulerian angles,**
- **8 torsions.**

(No solution in P1 was better)

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

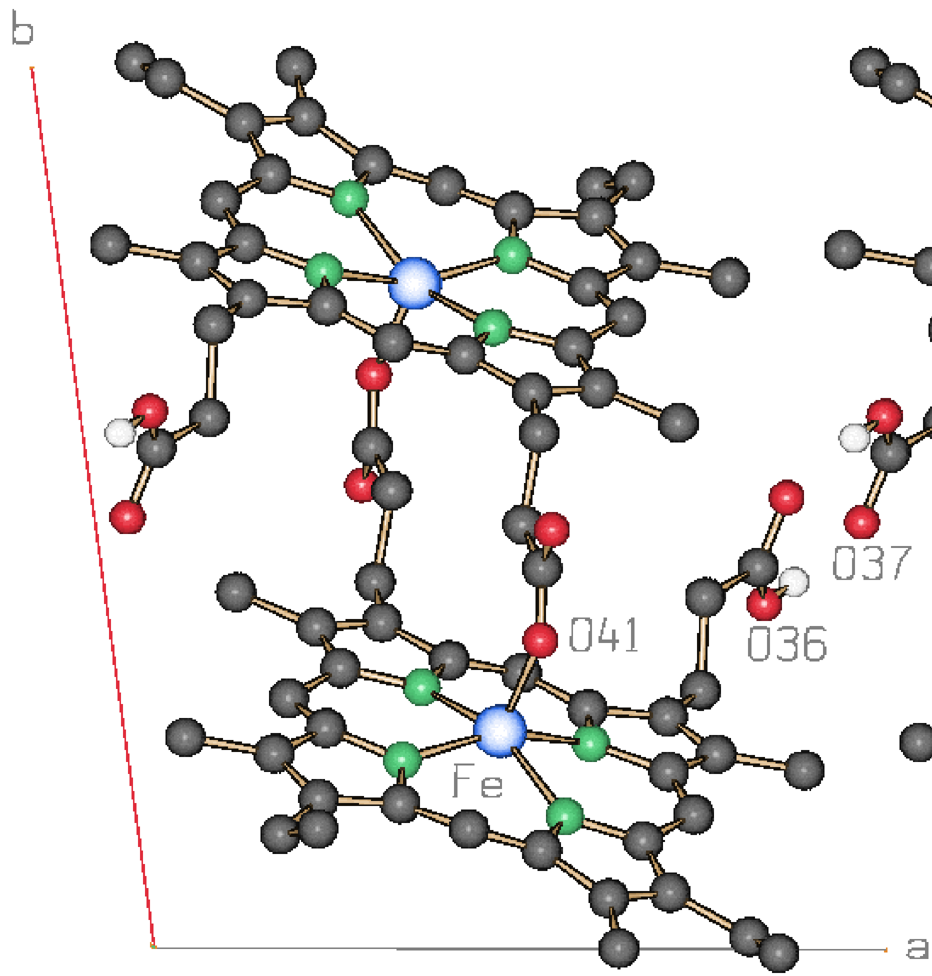
Oak Ridge National Laboratory

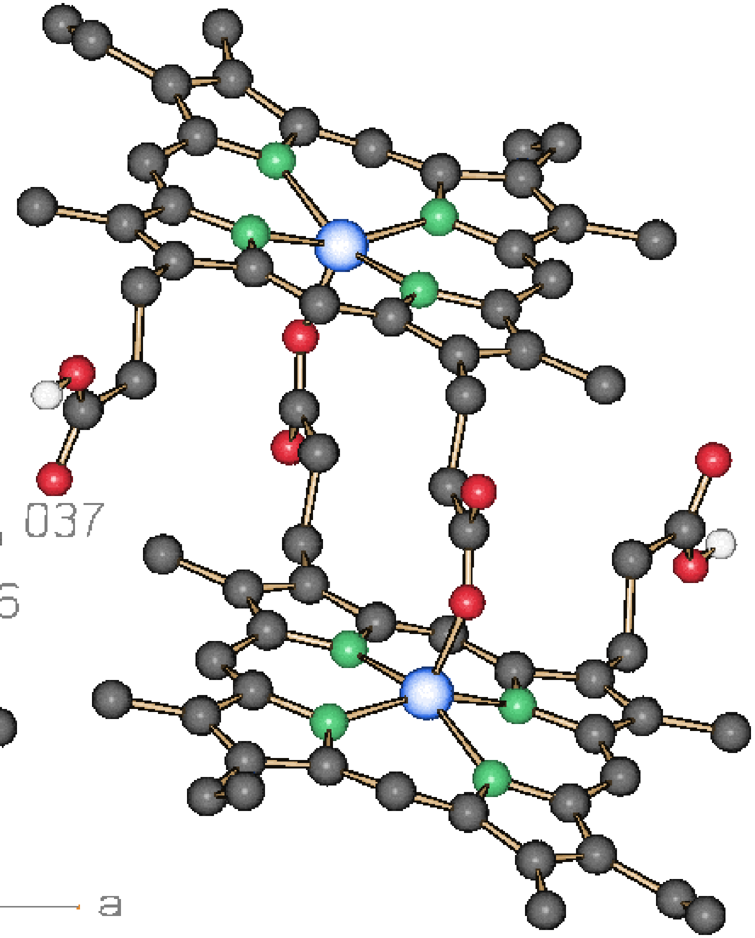
Rietveld fit to data for β-Hematin



Oak Ridge National Laboratory

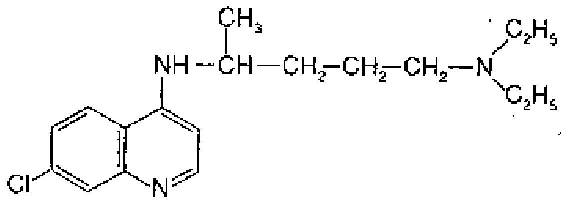
There is no polymer!
The structure consists of chains of hydrogen bonded dimers, in which each molecule is linked through iron-carboxylate bonds.





Managed by UT-Battelle
for the U.S. Department of Energy
SCHAKAL

Current models of action of chloroquine and related drugs



1. Caps the growth of the polymer

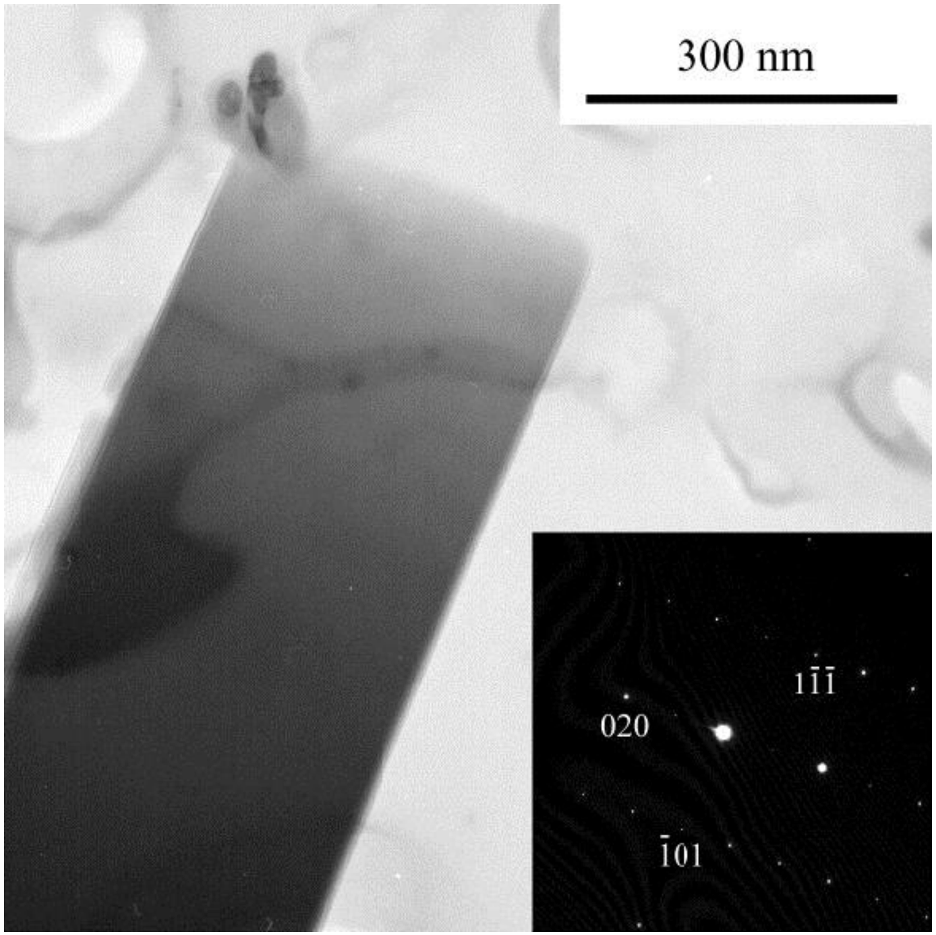
2. Inhibits a proposed polymerization enzyme

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

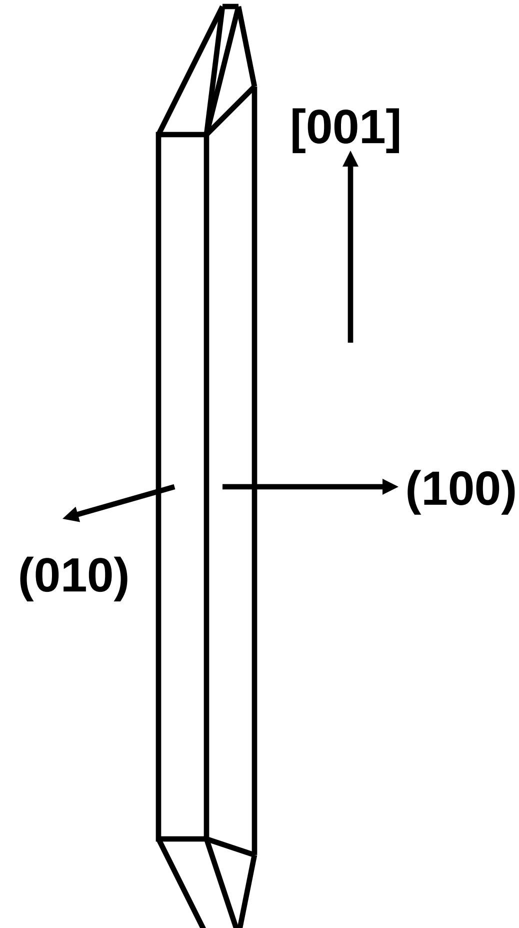
   3a. Adsorbs on growing surface and interferes with crystal growth
   Supporting evidence from autoradiography with labeled chloroquine

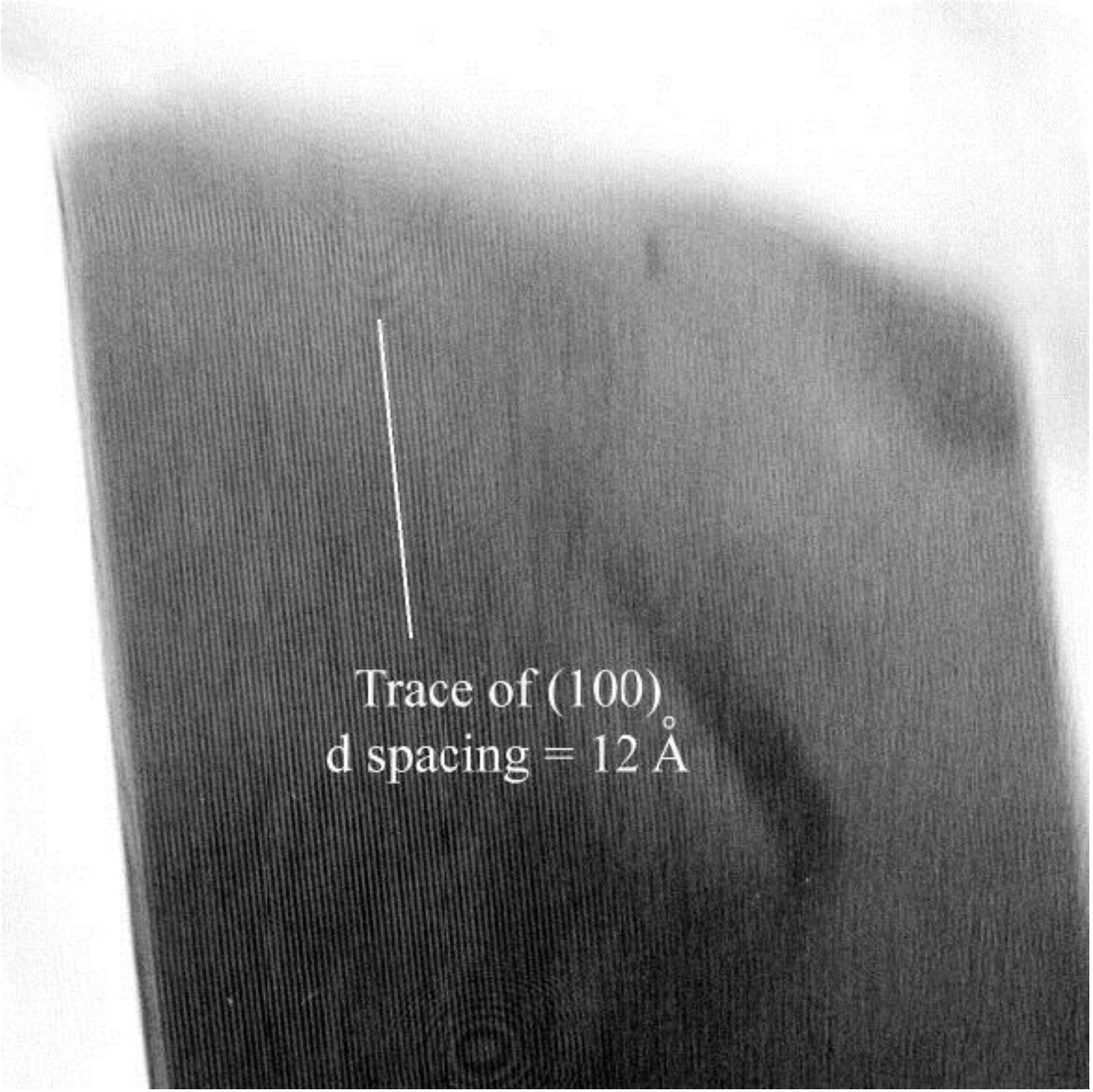
OAK RIDGE National Laboratory

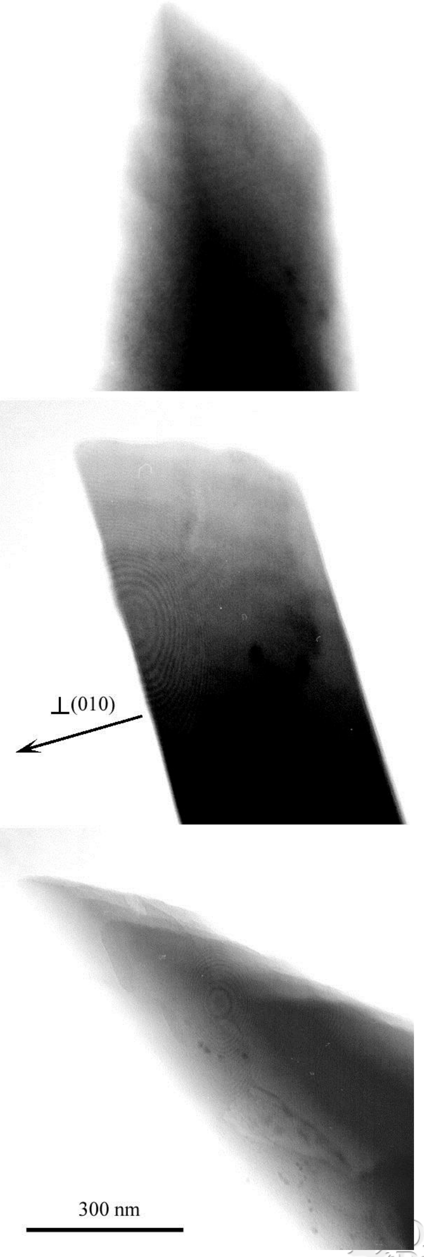
Strong motivation for understanding the morphology of hemozon/hematin crystals

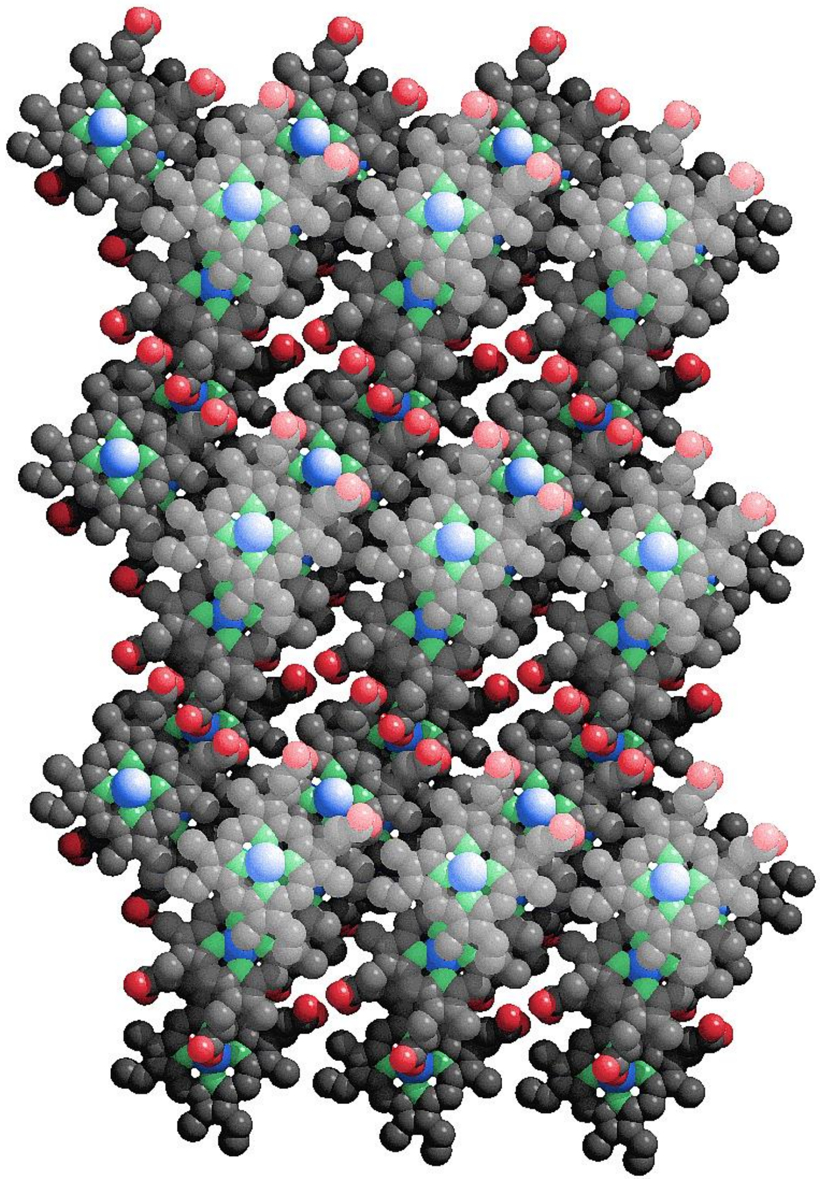


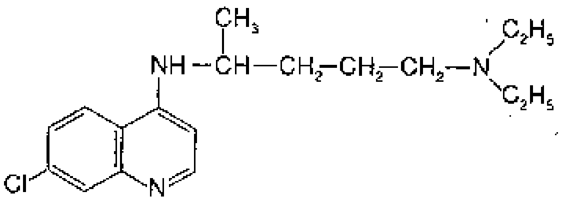
Growth along what faces?




Trace of (100)
d spacing = 12 Å


⊥(010)
300 nm



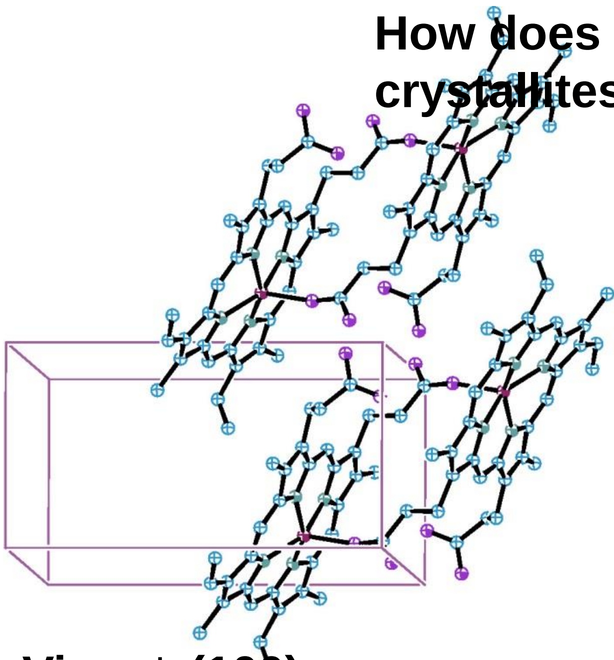


chloroquine

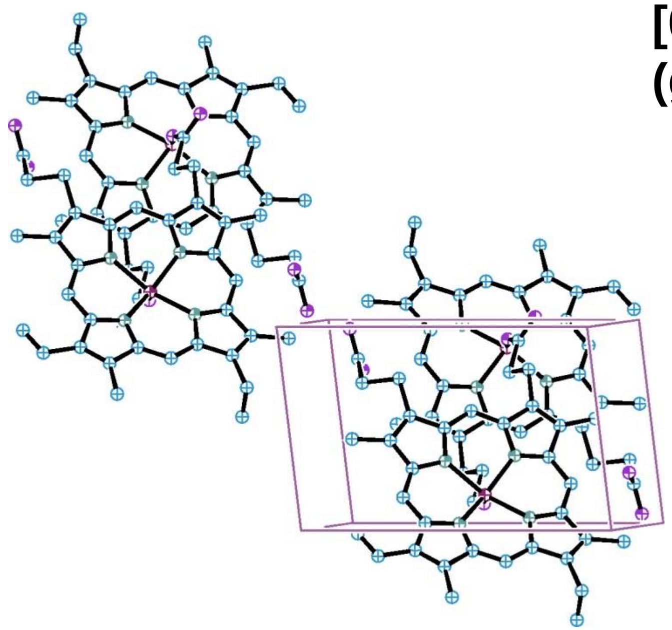
[131] surface of hemozoin

OAK RIDGE National Laboratory

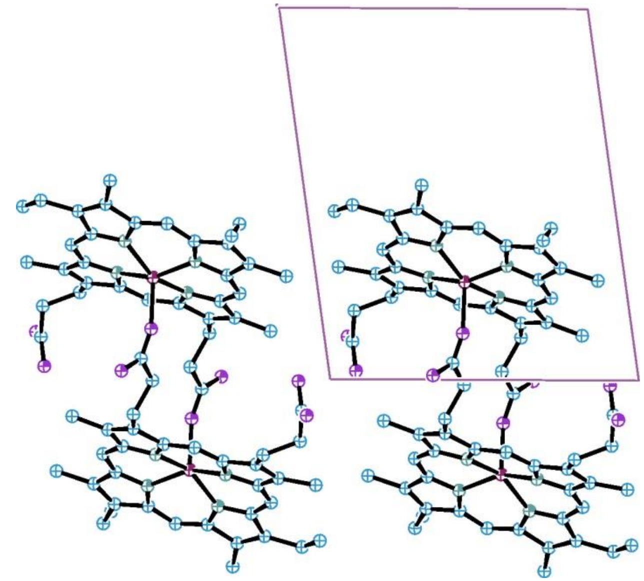
How does the structure fit into the crystallites?



View ⊥ (100) plane



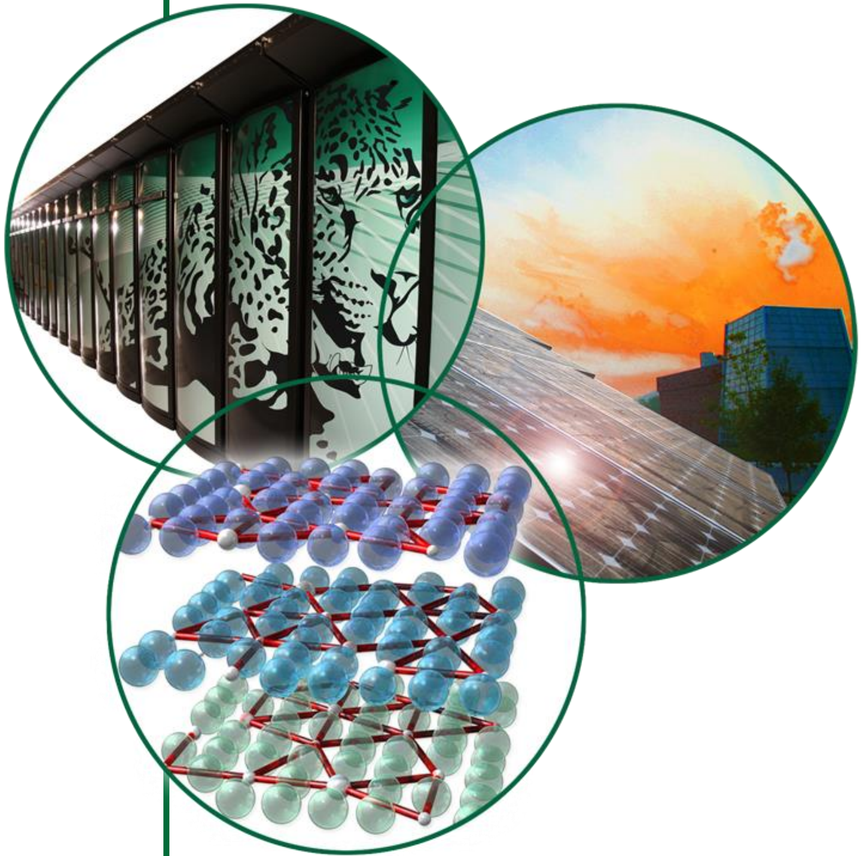
View ⊥ (010) plane



View along [001] axis (growth direction)

OAK RIDGE National Laboratory

Proteins and Powder Diffraction



U.S. DEPARTMENT OF ENERGY

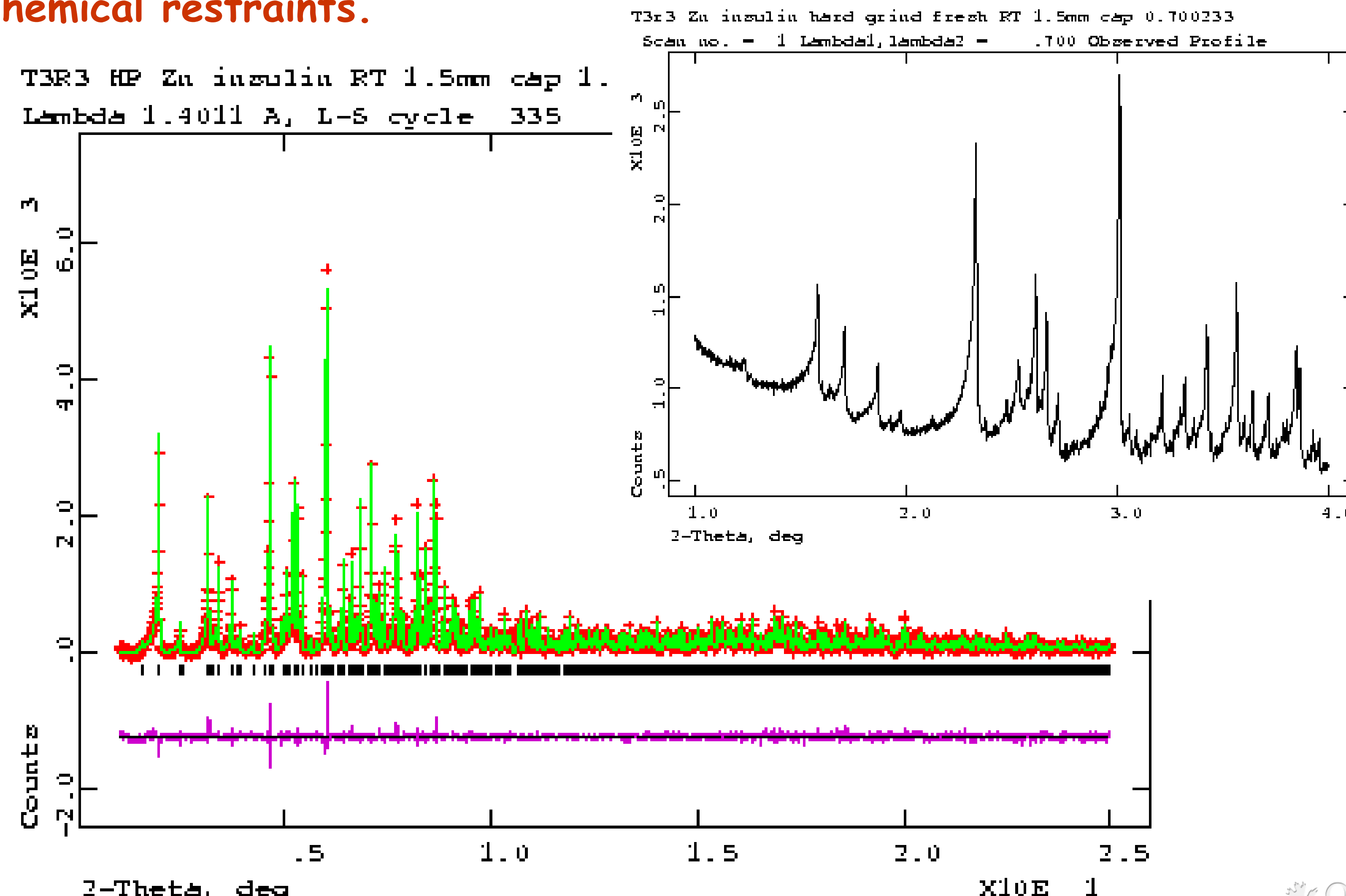
OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Extreme limit: Proteins

Work done by R. Von Dreele (Los Alamos) & P.W. Stephens

It is possible to get usable data, and to refine it with sufficient chemical restraints.



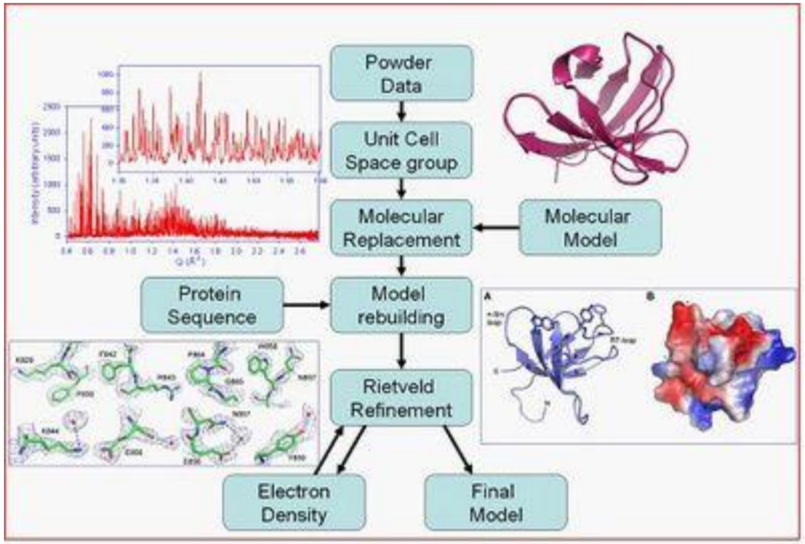
Oak Ridge National Laboratory

Structure solved from powder data & Rietveld refinement

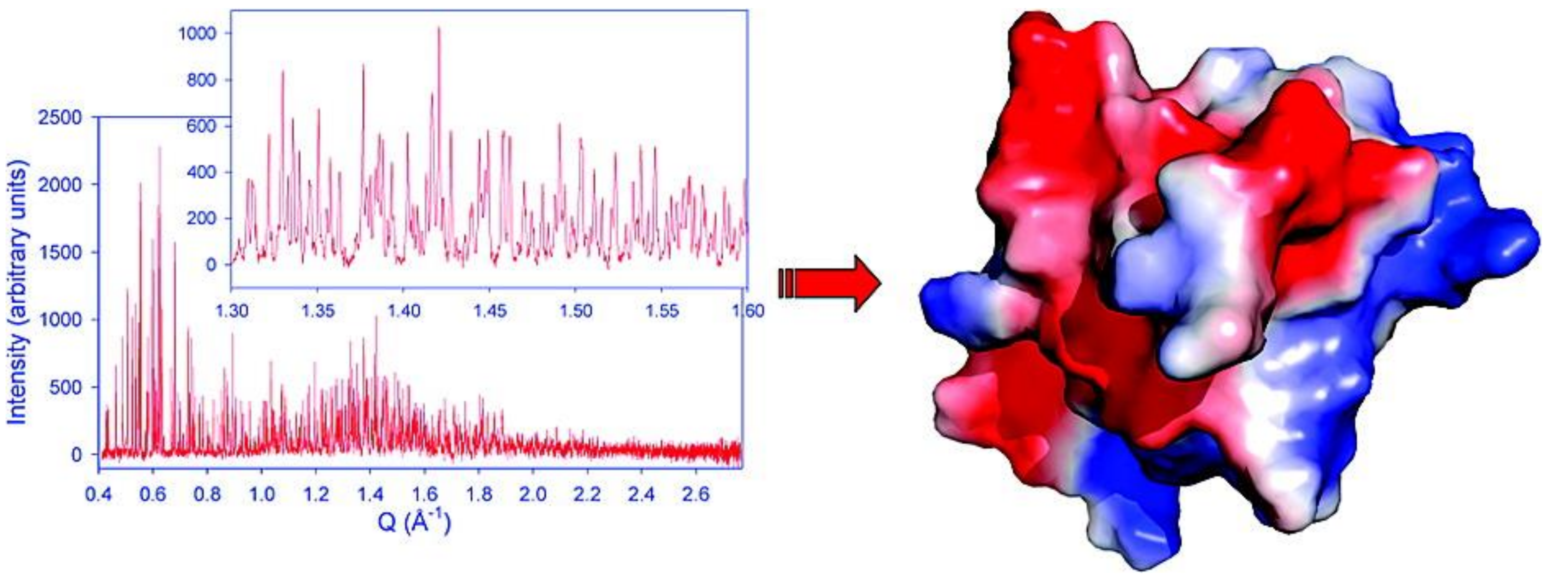
Human Insulin Zn complex

Native	Ground
a=80.96Å	81.28Å
c=37.59Å	73.04Å
Nrefined = 1754	2925
Nrestraints=3871	7934
Nreflections=9871	12734
Resolution 3.06Å	3.22Å
Rwp=3.34%	3.77%

R.B. Von Dreele, P.W. Stephens, G.D. Smith, and R.H. Blessing, "The First Protein Crystal Structure Determined from X-ray Powder Diffraction Data: a Variant of T_3R_3 Human Insulin Zinc Complex Produced by Grinding," ***Acta Crystallographica D*** **56, 1549-53 (2000).**



Powder diffraction data analysis procedure followed for structure solution via the molecular replacement method, model building and structure refinement. The data and model shown correspond to the second SH3 domain of ponsin and final omit maps are shown on the lower left



Margiolaki, Irene; Wright, Jonathan P.; Wilmanns, Matthias; et al.; JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 129, 38, 11865(2007)

Take home message

Powder diffraction is an extremely powerful technique to study structural properties of a very wide variety of materials. To understand physical and chemical properties of materials it is crucial that we know how the "atoms are put together" and if you cannot grow those big single crystals….you can still learn quite a lot about your system using powder diffraction.

OAK RIDGE National Laboratory

References:

- **Basics:**
  - Powder Diffraction: Theory and Practice: Edited by R.E. Dinnebier and S.J.L. Billinge
  - Fundamentals of Powder Diffraction and Structural Characterization of Materials (second edition): V.K. Pecharsky and P.Y. Zavalij
- **Software:**

  Rietveld Analysis: GSAS (GSAS-II), Fullprof, Topas

  Structure Solution: GSAS-II, Topas, Fullprof, DASH

OAK RIDGE National Laboratory