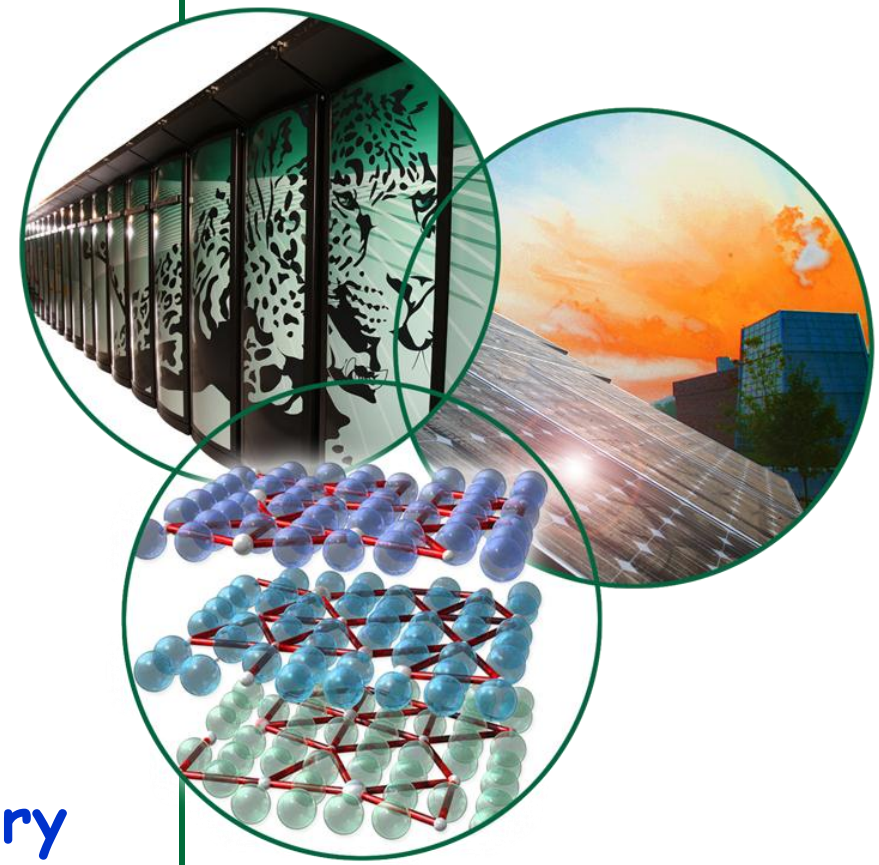
Powder Diffraction Application



Ashfia Huq

Spallation Neutron Source

Oak Ridge National Laboratory

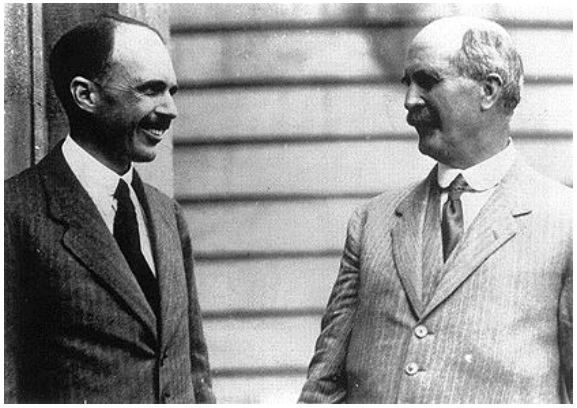
U.S. DEPARTMENT OF ENERGY

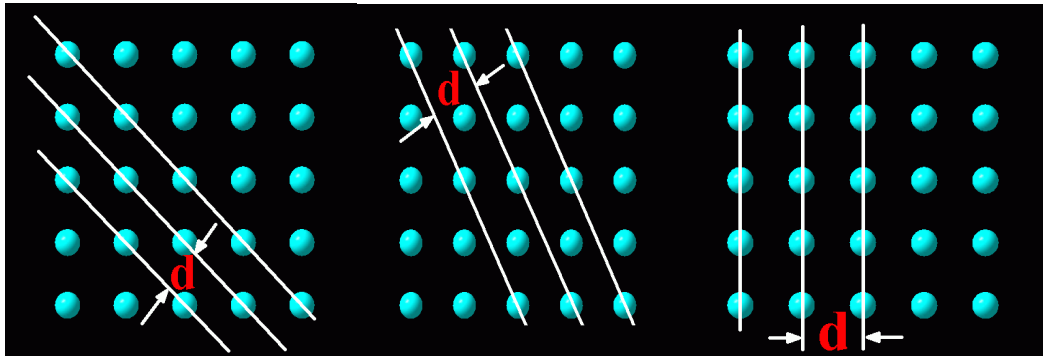
OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

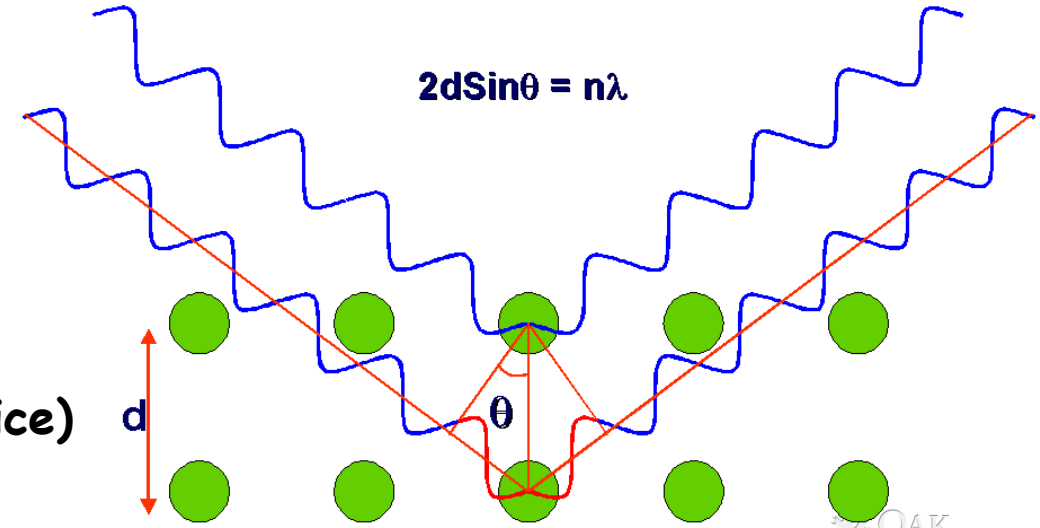
Bragg's law

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





Shared 1915 Nobel Prize

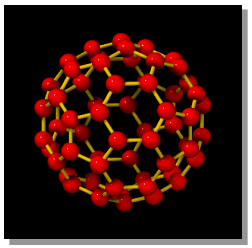


- Zinc Blend (fcc not sc)
- NaCl (not molecular)
- Diamond (two overlapping fcc lattice)

Where are the atoms?

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





X-ray:

(λ : 10^{-9}m - 10^{-11}m)

λ[Å] = 12.398/E_{ph}[keV]

Source:

- Lab diffractometers
- Synchrotron Sources

Neutron:

(thermal λ : 1-4Å)

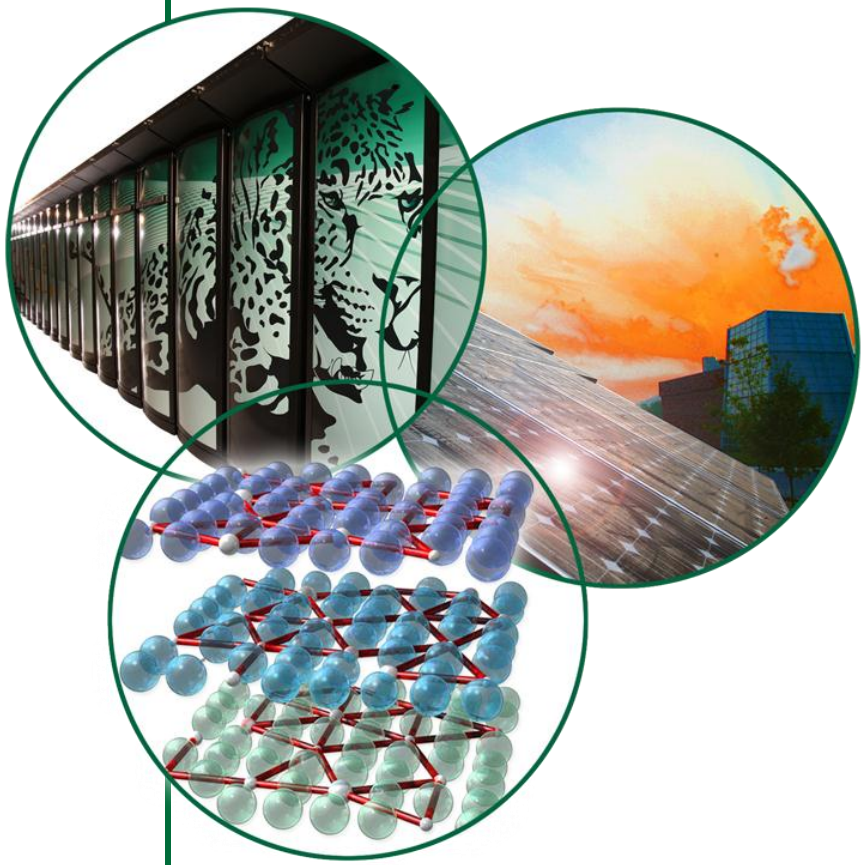
E_n[meV] =81.89/ λ^2[Å]

Source:

- Reactors (fission)
- Spallation Source

- ❑ **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**

Archeology

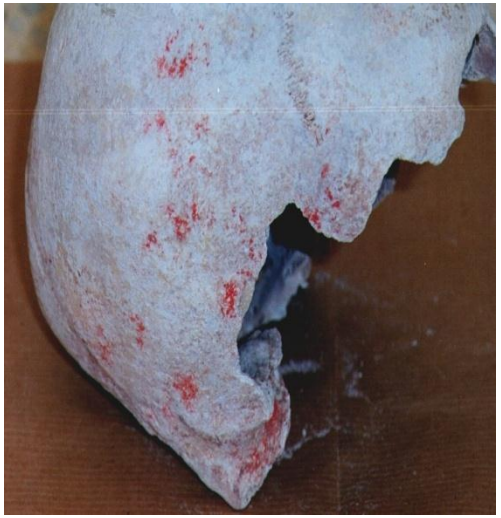


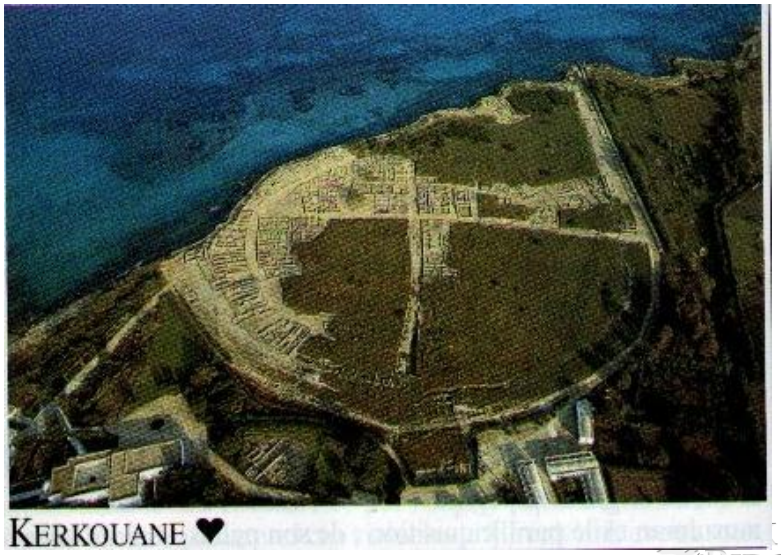
Phase ID: "Finger Printing"

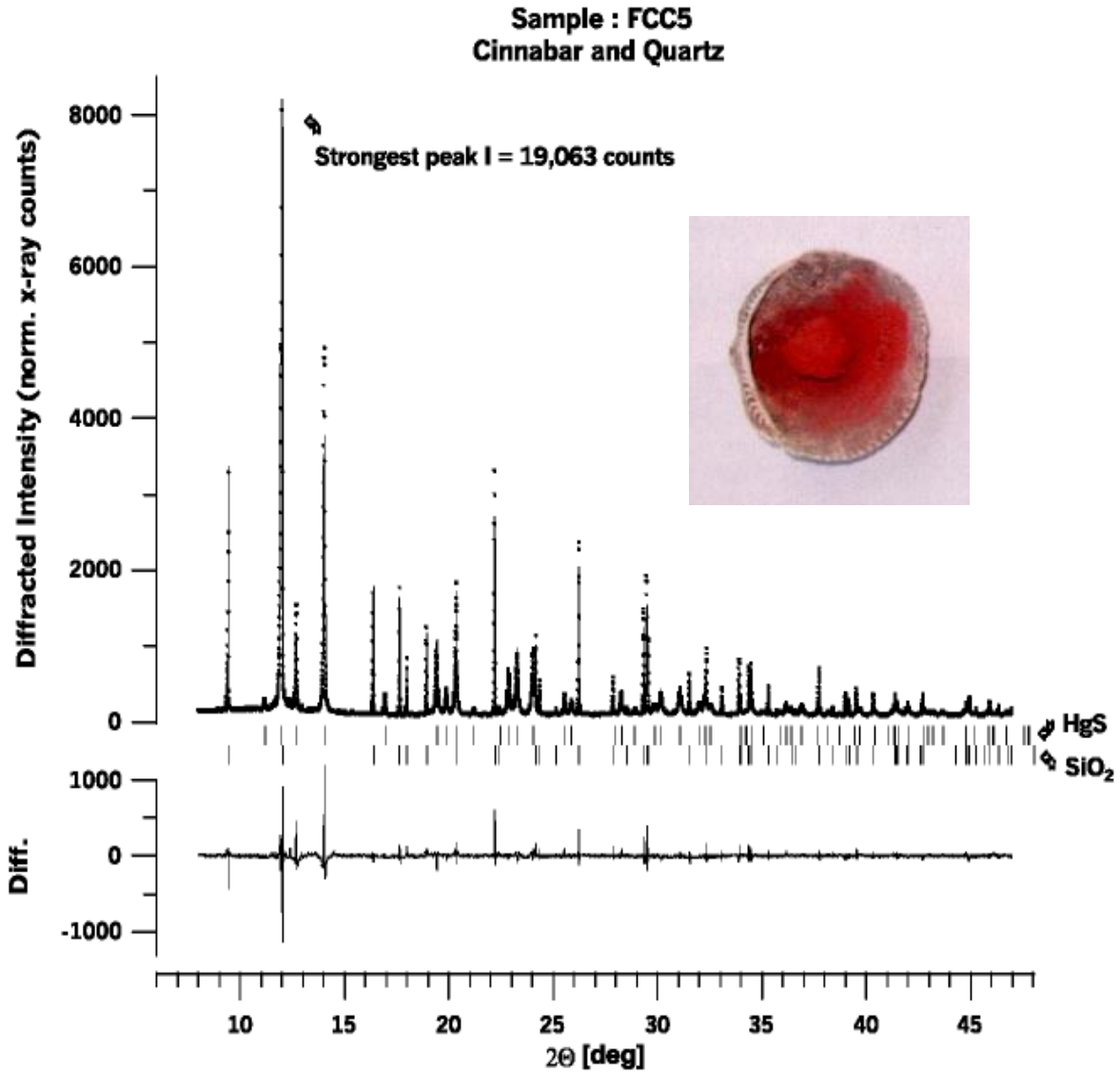
Huq et.al. Appl. Phys. A 83, 253 (2006)

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.

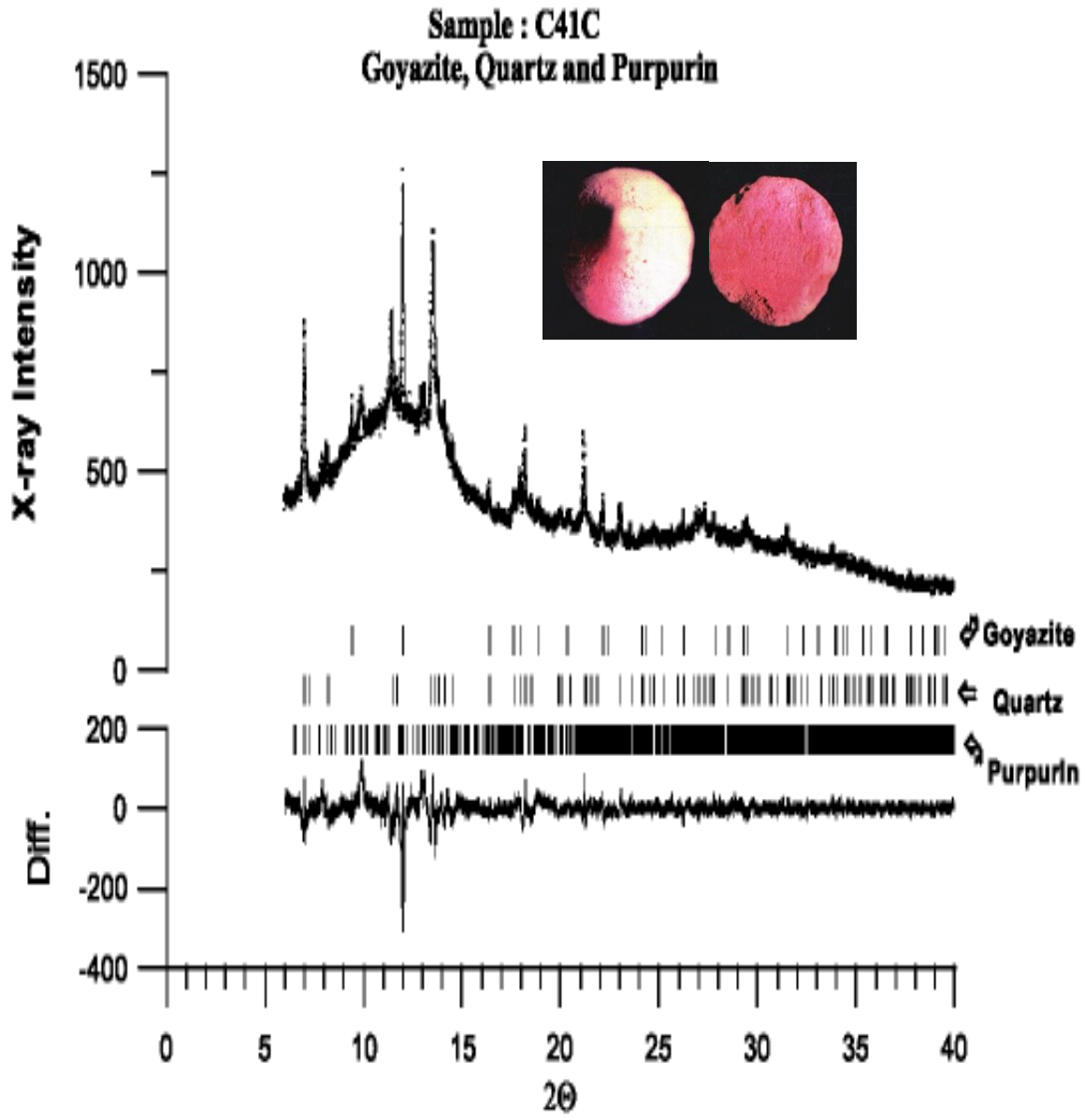
The pigments were discovered during different excavations in archaeological sites of Tunisia (Carthage, Kerkouane, Bekalta, Bouaarada and elsewhere).







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



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.

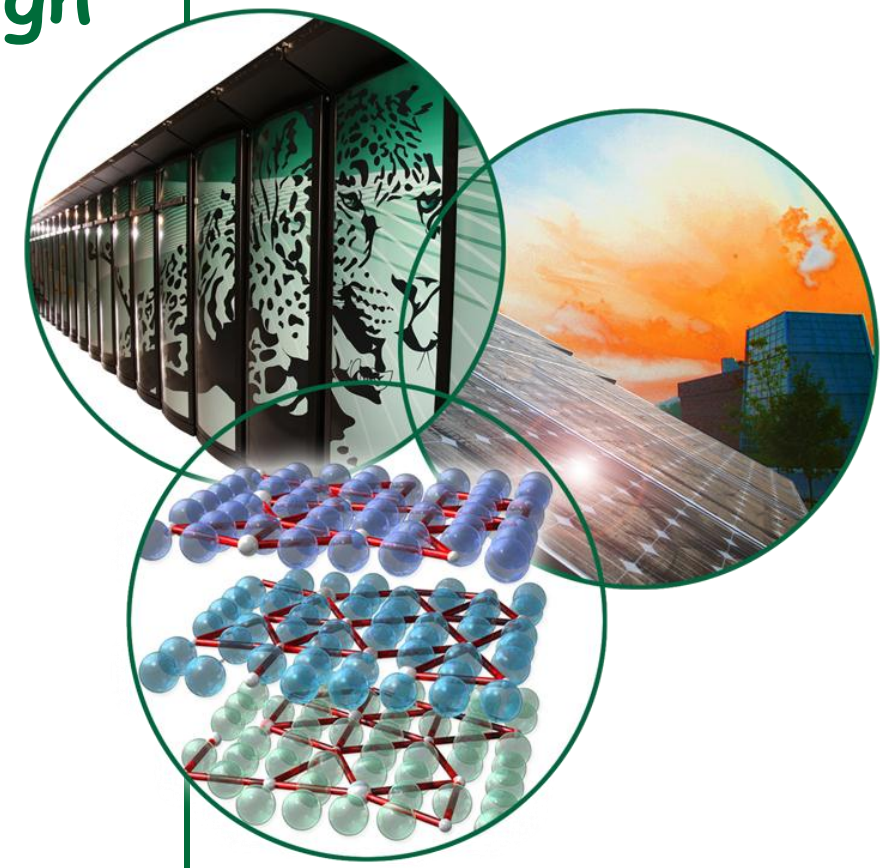
These results are similar to what would be obtained from raw materials indicating that these eight samples were not subject to any preparation by the Carthaginians. These eight samples were used as ritual make-up. However, the last two samples (FCC2 and C41C) showed an amorphous background, their preparation 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)

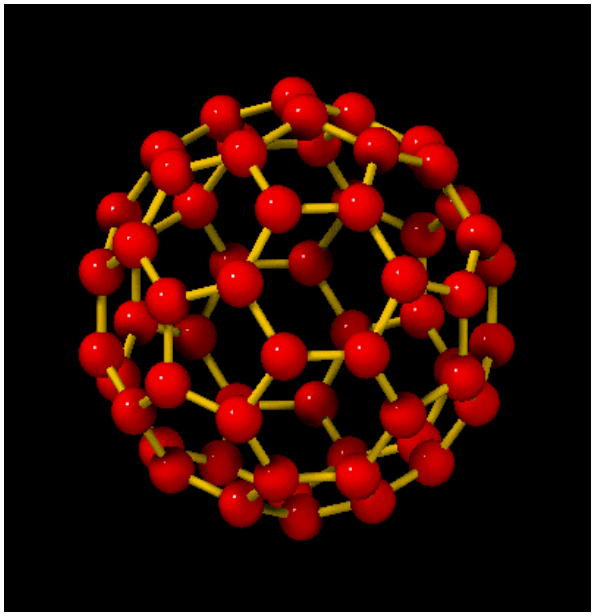
- **Powder diffraction file, maintained by ICDD**: **Release 2008 of the Powder Diffraction File contains 622,117 unique material data sets. Each data set contains diffraction, crystallographic and bibliographic data, as well as experimental, instrument and sampling conditions and select physical properties in a common standardized format.** http://www.icdd.com/products/overview.htm

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

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



Buckminsterfullerene

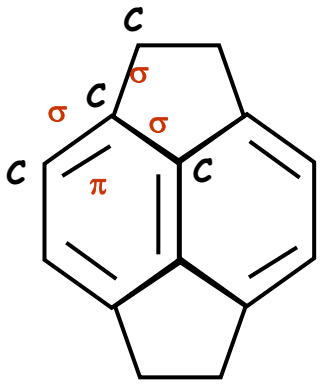


1985 : R.F Curt, H.W. Croto & R.E. Smalley discover C_{60}. They are awarded the Nobel prize in Chemistry in 1996.

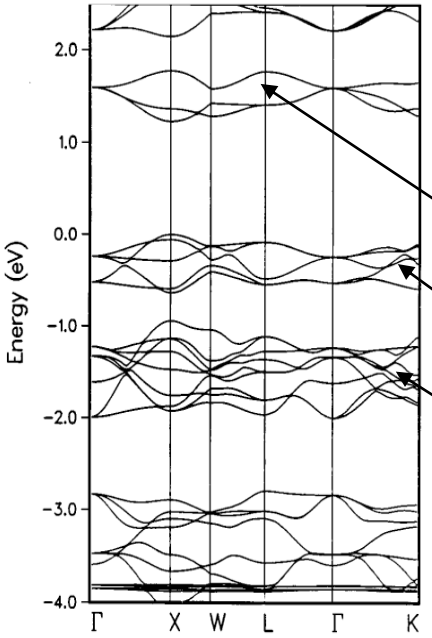
1990 : W. Kratchmer and D.R. Huffman produces isolable quantities of C_{60}.

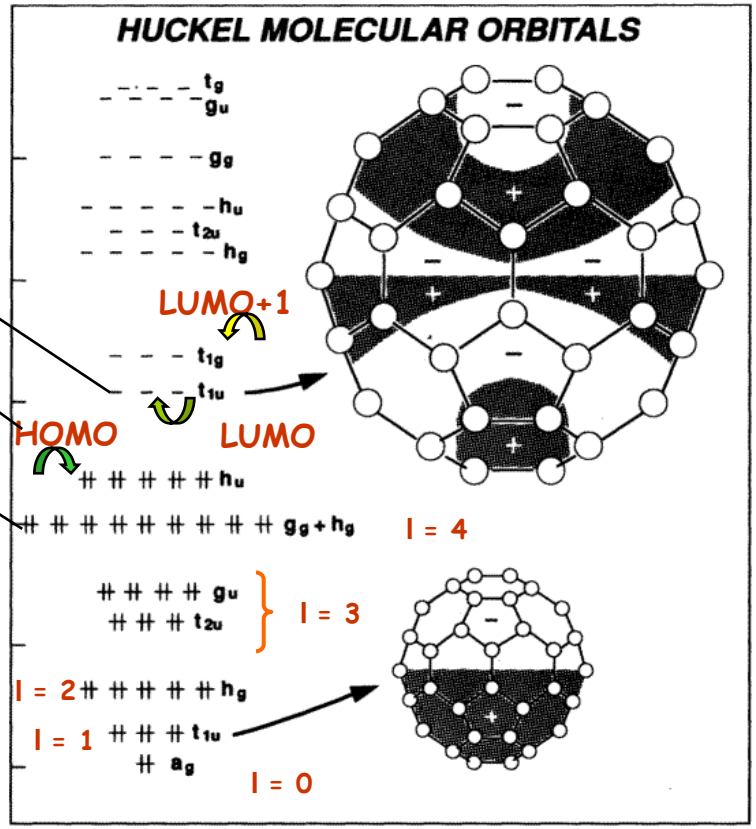
1991 : A group at AT&T Bell labs, finds superconductivity in alkali doped C_{60} with Tc=18K for K_3C_{60}. Later Tc=28K is observed for Rb_3C_{60}

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





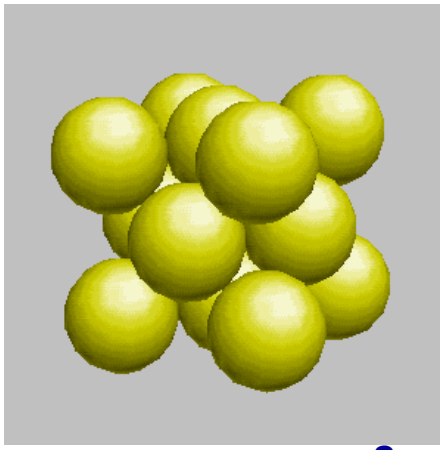
sub bands around E_F of solid C_{60}. (Erwin 1993)

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

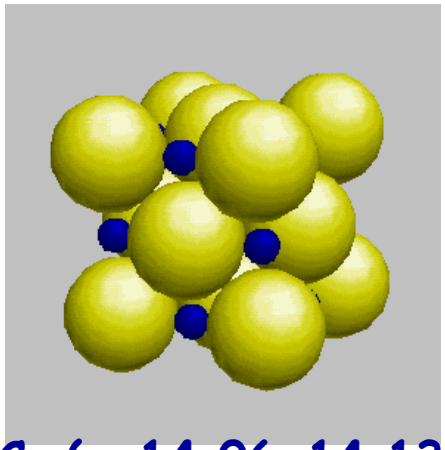
Single bond ~1.45Å
Double bond ~1.39Å

HOMO – LUMO ~2ev

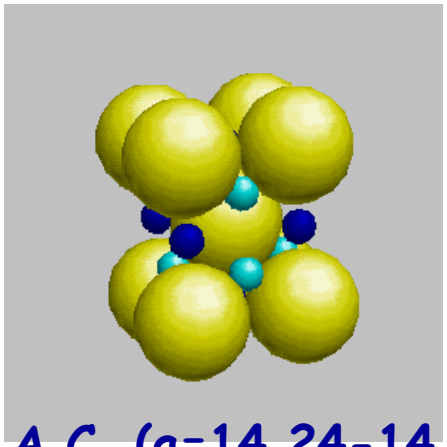
Alkali(K,Rb,Cs) doped C_{60}



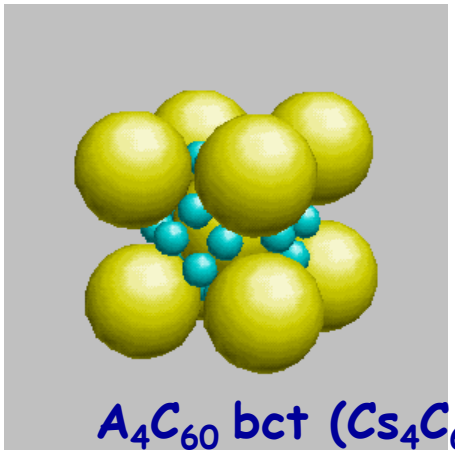
fcc C_{60}(a=14.17Å)



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

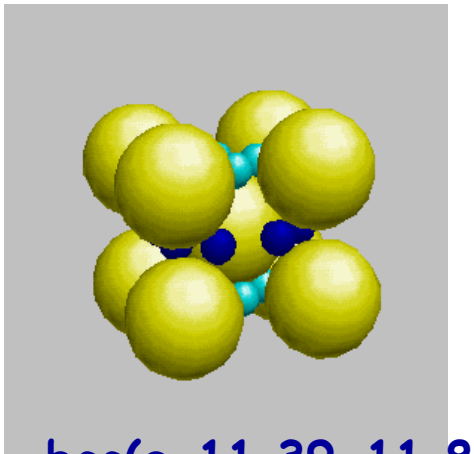


A_3C_{60}(a=14.24-14.44)
A in both tetrahedral
And octahedral site



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)

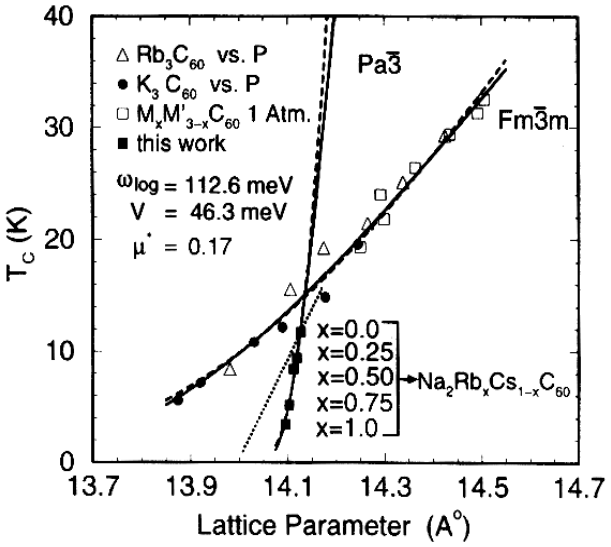
C_{60} base Superconductors:

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 $N(E_F)$.

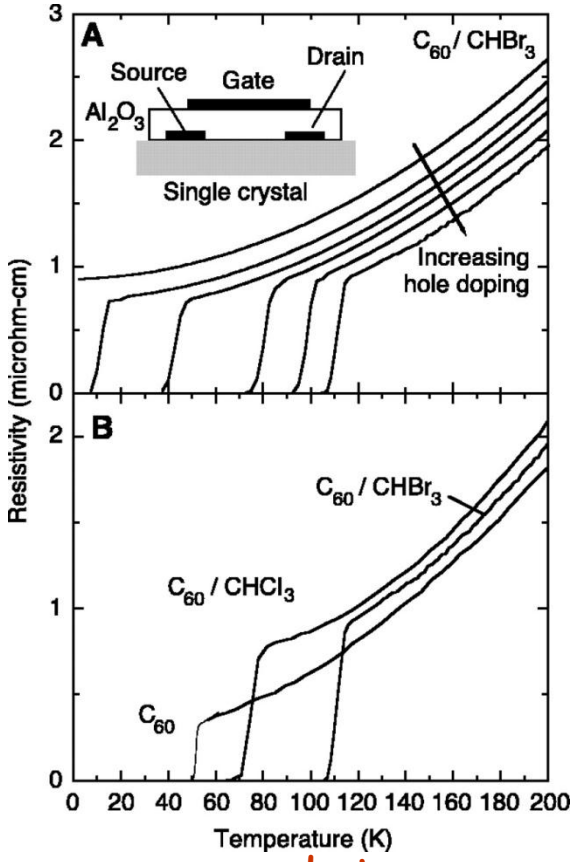
According to BCS theory

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

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



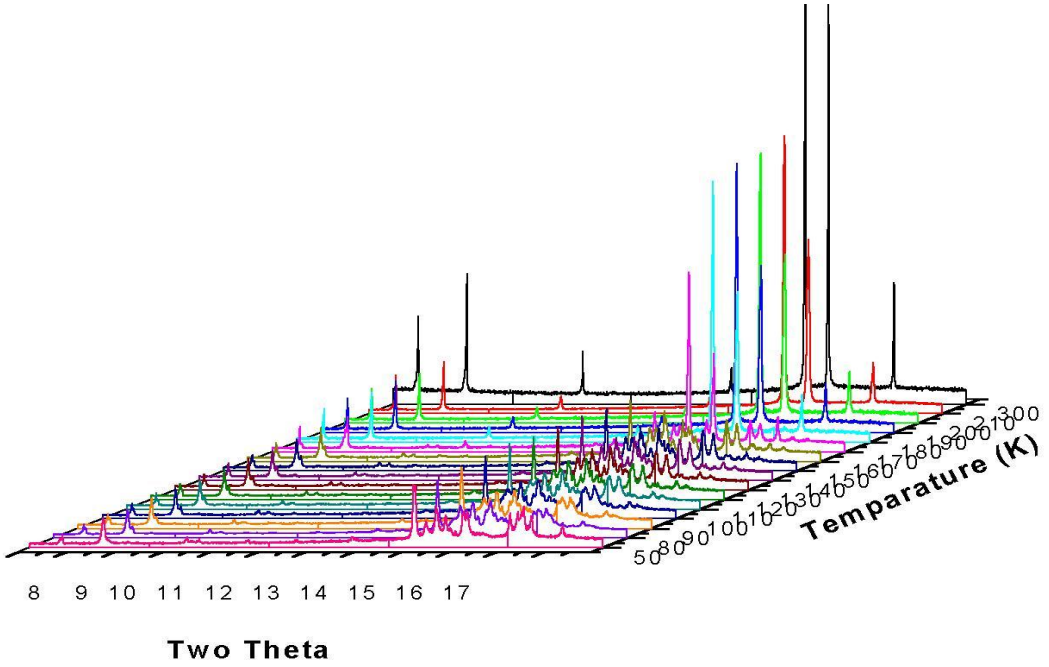
*Yildrim T et. al., 1995, Solid State Commun. 93 269-74



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).

What happens to the crystal structure as we decrease T ?



Hexagonal

↓

Monoclinic

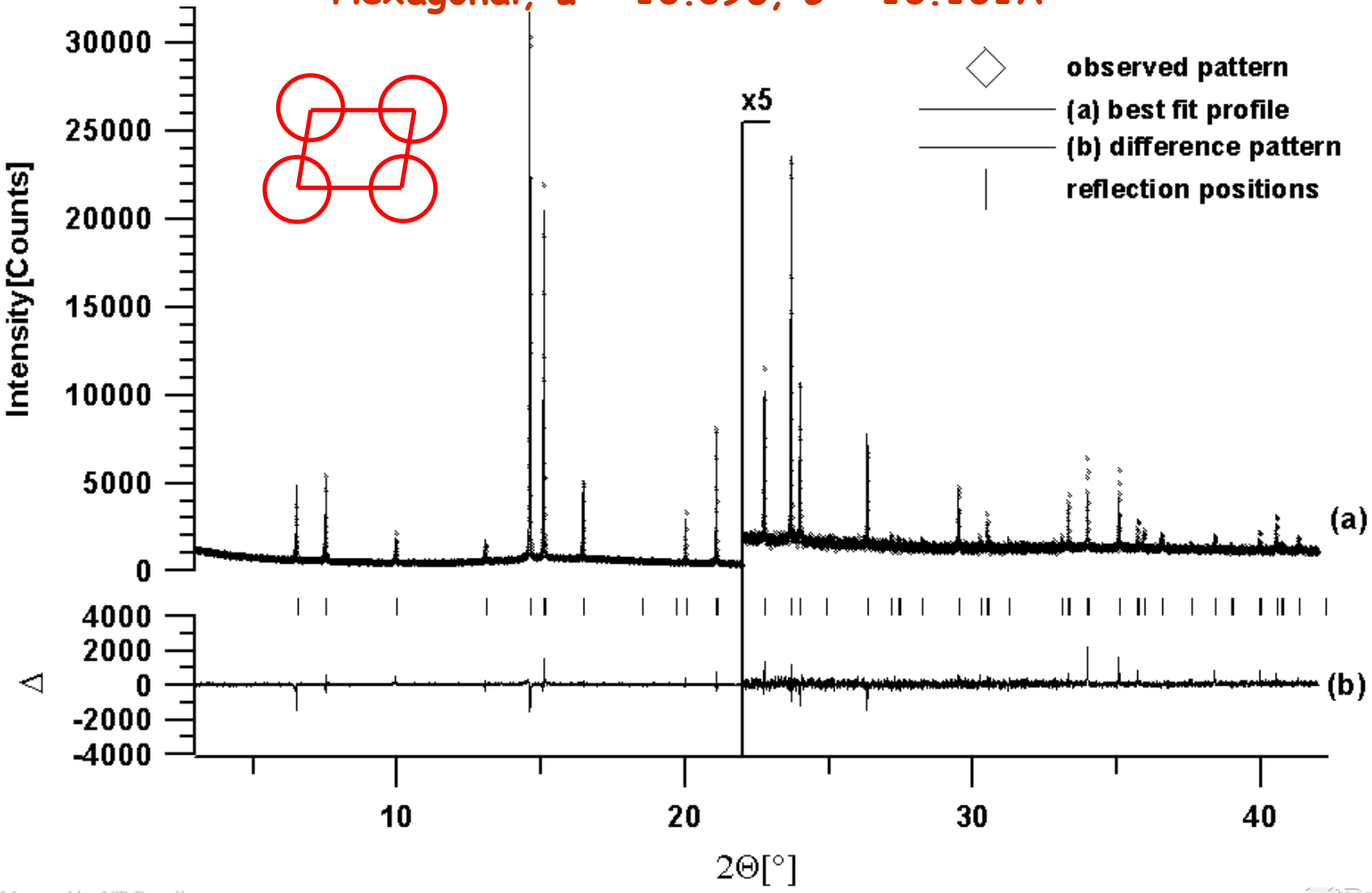
↓

Triclinic

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

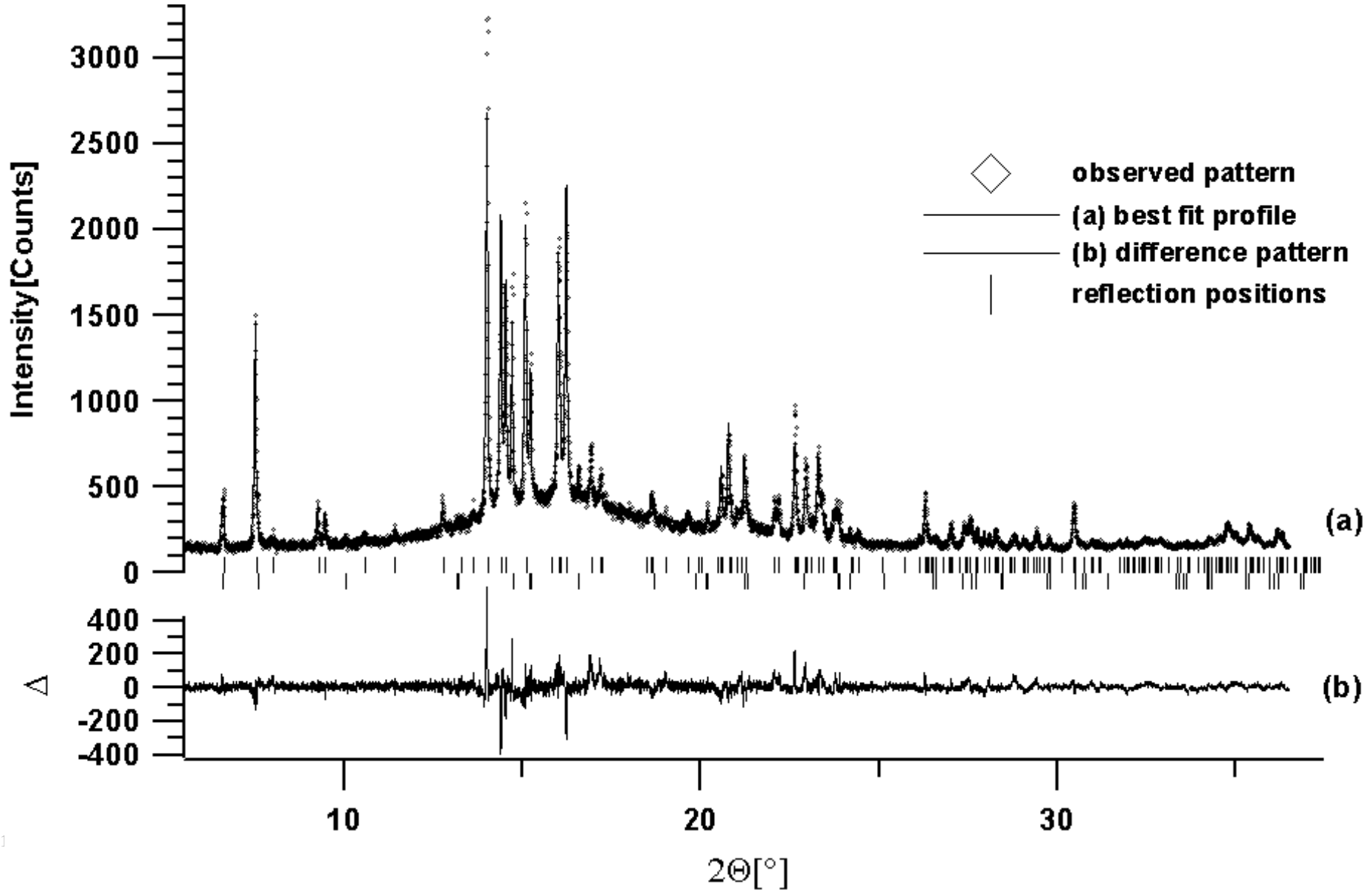
$C_{60} \cdot 2CHCl_3$ at room temp.

Hexagonal, a = 10.096, c = 10.101Å



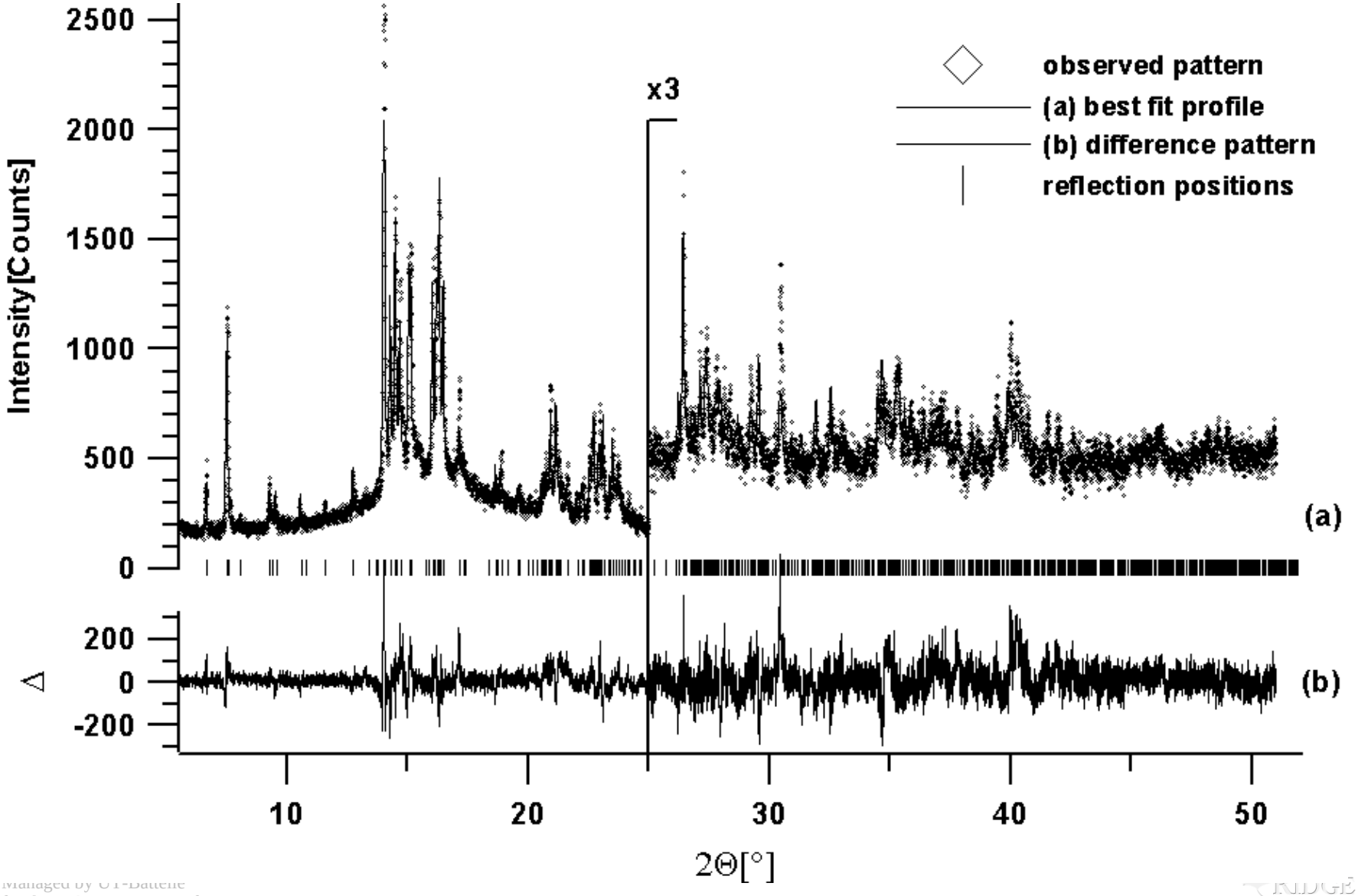
$C_{60} \cdot 2CHCl_3$ at 170K

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°)

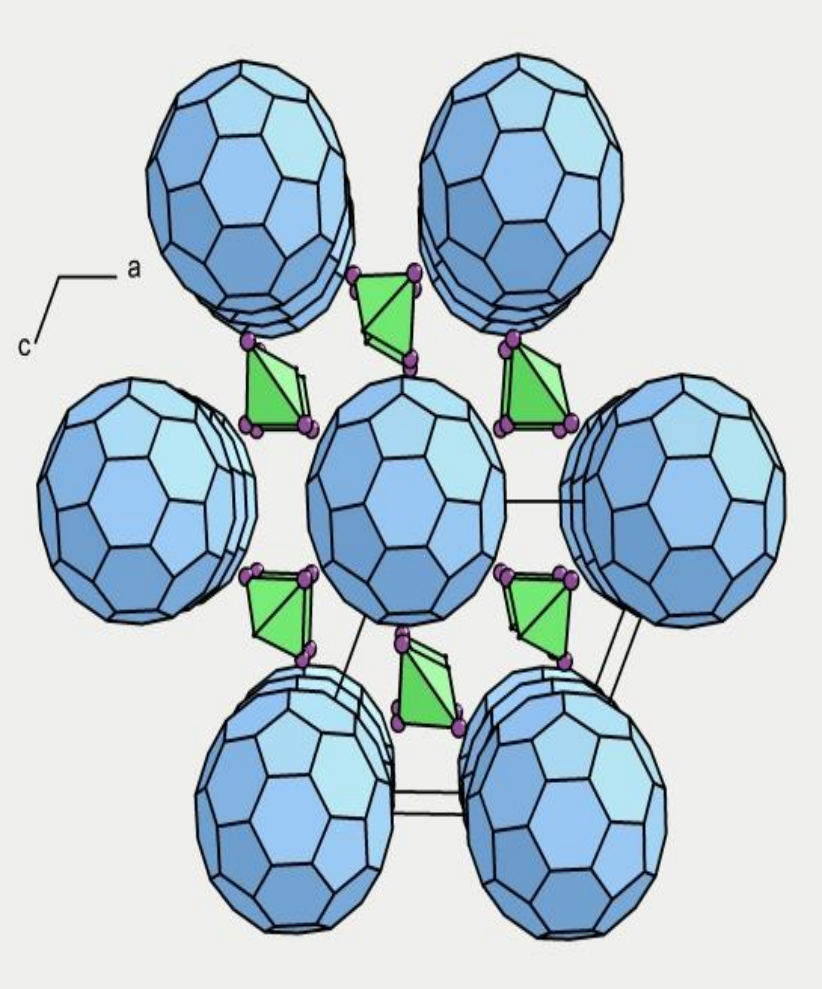


The crystal structure of C_{60} intercalated with $CHCl_3$/$CHBr_3$ is not fcc but hcp. More over when it is cooled it undergoes a phase transition and at ~150K they are converted into a fully order triclinic phase.

	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)



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.

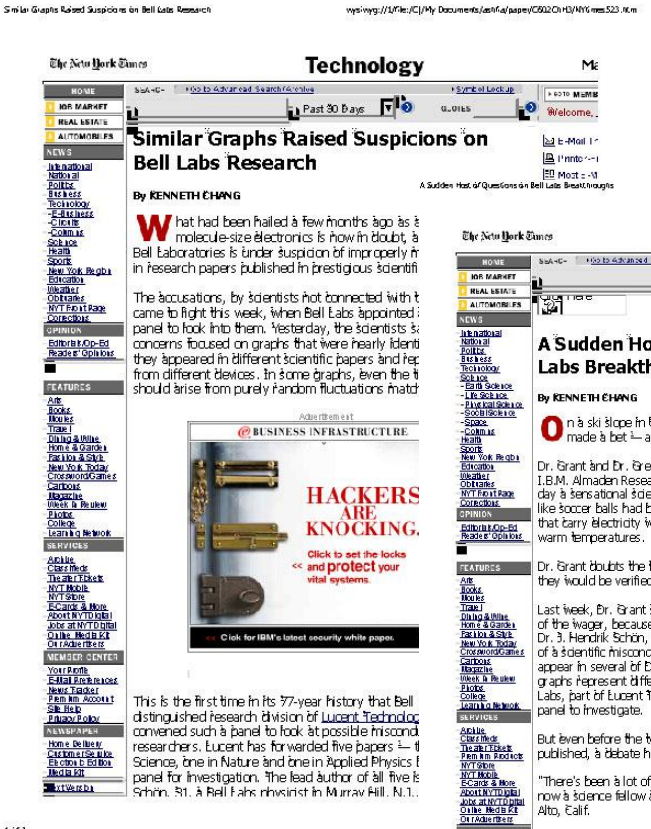
Evidence against lattice expansion as the sole explanation for T_c increase in chloroform- and bromoform- doped C_{60}

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

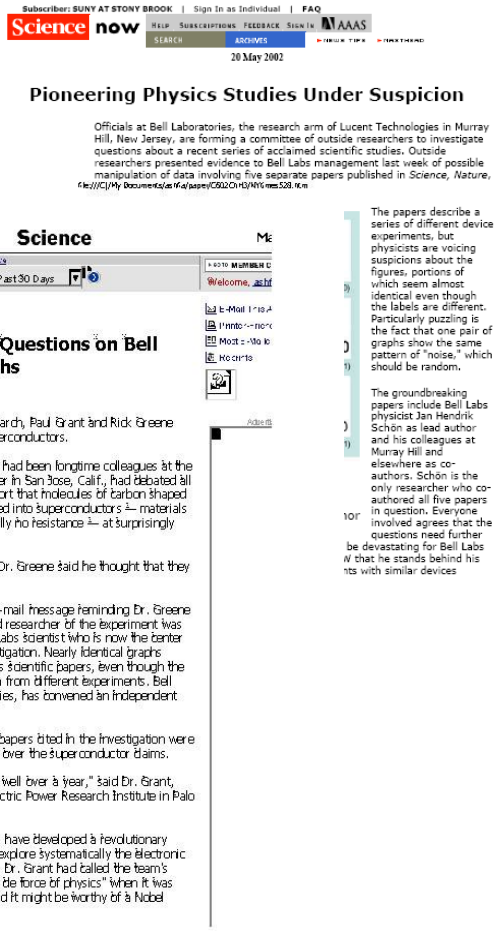
Similar Graphs Raised Suspicions on Bell Labs Research

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 in research papers published in prestigious scientifi

The accusations, by scientists not connected with t came to fight this week, when Bell Labs appointed panel to look into them. Yesterday, the scientists s concerns focused on graphs that were nearly identi they appeared in different scientific papers and rep from different devices. In some graphs, even the ti 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 misconduct researchers. Lucent has forwarded five papers — t Science, one in Nature and one in Applied Physics L 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 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.

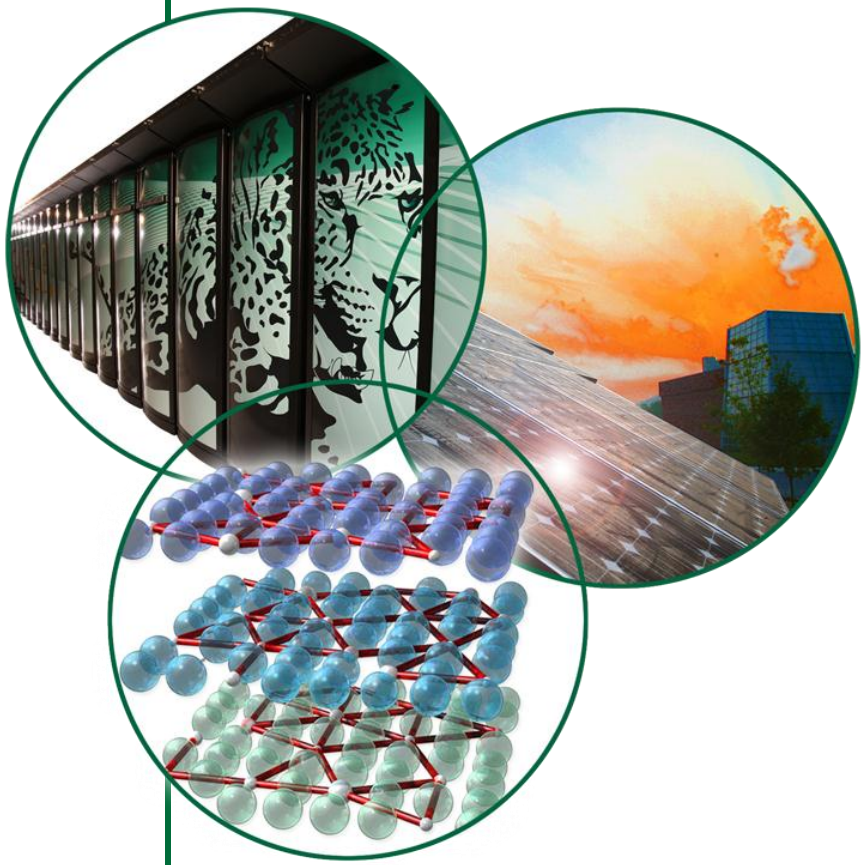
The papers describe a series of different device experiments, but physicists are voicing suspicions about the figures, portions of which seem almost identical even though the labels are different. Particularly puzzling is the fact that one pair of graphs show the same pattern of "noise," which should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

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

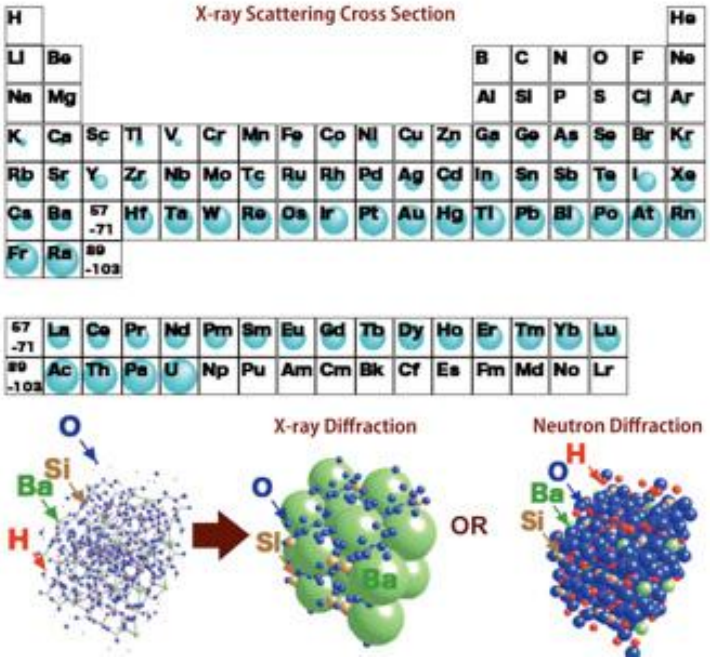
On October 31, 2002, *Science* withdrew eight papers written by Schön. On December 20, 2002, the *Physical Review journals* withdrew six papers written by Schön. On March 5, 2003, *Nature* withdrew seven papers written by Schön.

Neutron Powder Diffraction

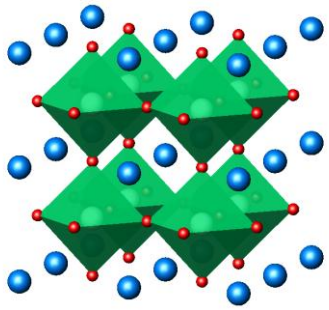


Why Neutrons ?

- 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.

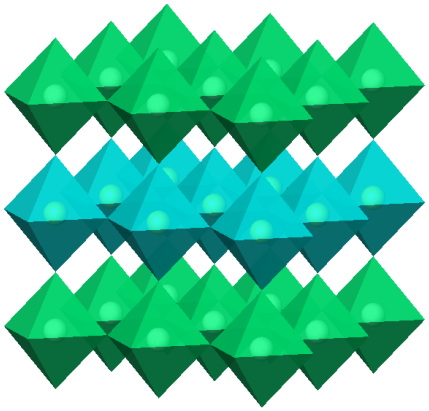


Ba_2CuWO_6: An Ordered Tetragonal Perovskite

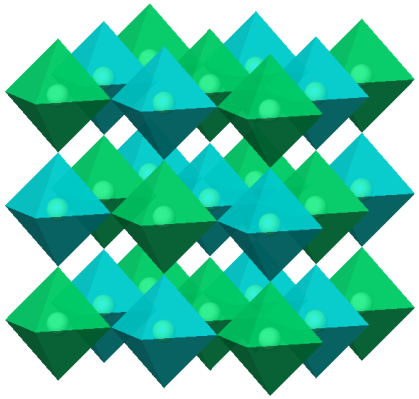


Simple cubic AMX_3 perovskite: a = 3.8045.

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



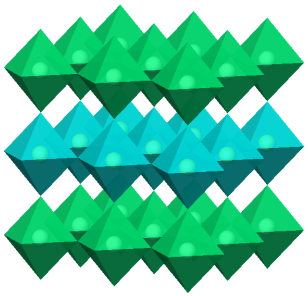
Model #1: Ordered alternation of MO_6 and $M'O_6$octahedra in one direction, leading to formation of layered perovskite.



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

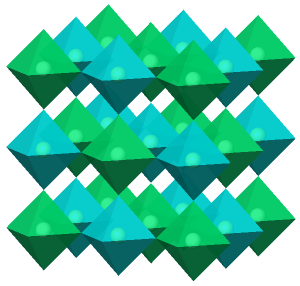
Model #1 – Layered Ordering:

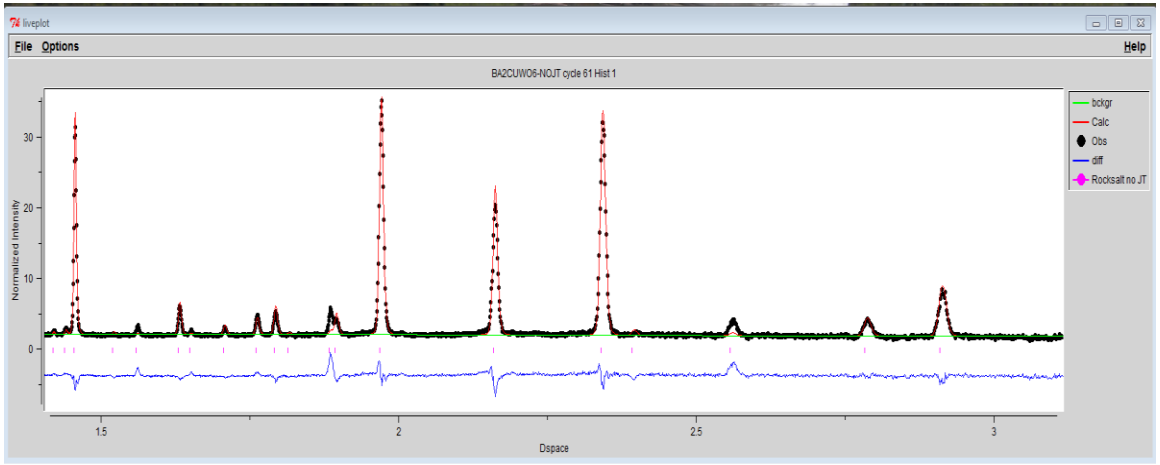
Space Group	*P4/mmm*			
Lattice	*a* = 3.94 Å; *c* = 8.64 Å			
Atom	*x*	*y*	*z*	Occupancy
Ba	¼	¼	½	1
Cu	0	0	0	1
W	0	0	0	1
O(1)	0	0	¼	1
O(2)	½	0	0	1
O(3)	½	0	½	1



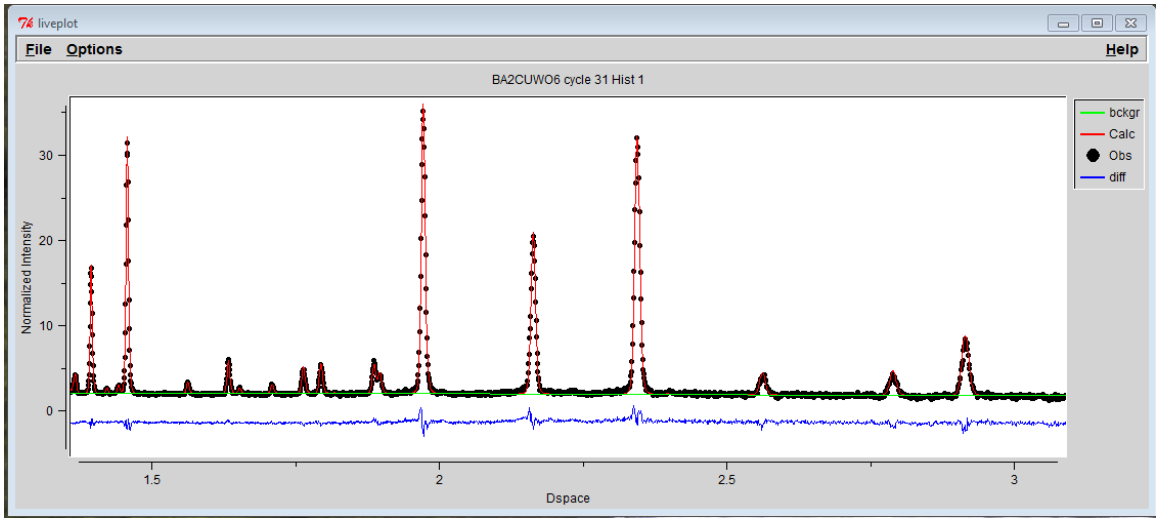
Model #2 – Rock Salt Type Ordering:

Space Group	*I4/m*			
Lattice	*a* = 5.57 Å; *c* = 8.64 Å			
Atom	*x*	*y*	*z*	Occupancy
Ba	0	½	¼	1
Cu	0	0	0	1
W	0	0	0	1
O(1)	0	0	0.25	1
O(2)	0.25	0.25	0	1





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

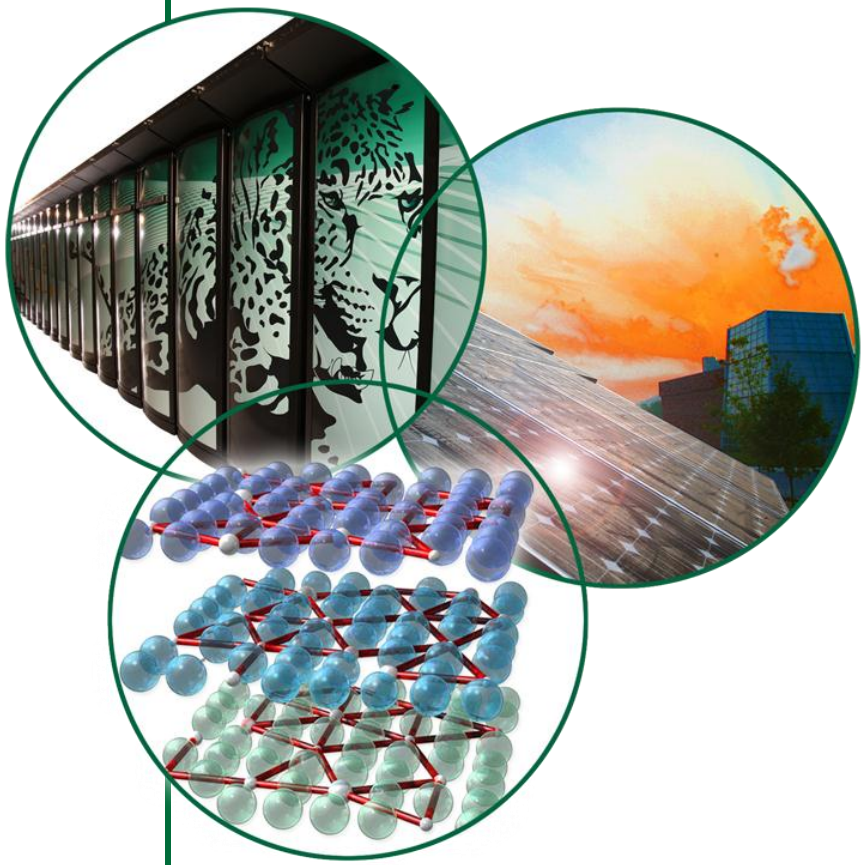


So in fact CuO_6 octahedra are elongated along the c axis. The e_g orbital is split into

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

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

Magnetism & Powder Diffraction

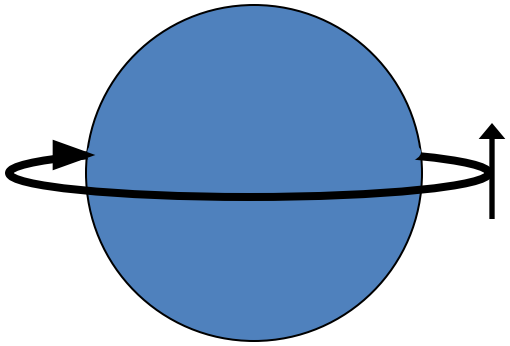


Introduction to Magnetism

- **Origin of magnetism – electrons.**

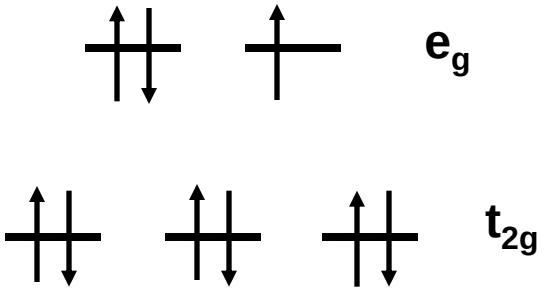
Electrons have a magnetic moment (dipole; μ_S). Magnetic moments arise from two properties of an electron:

- **Motion around the nucleus (gyromagnetic ratio)**
- **Total spin quantum number ($S = \Sigma s$; $s = \pm ½$)**



- **Dipole unit – Bohr magnetons (μ_B). $1\ \mu_B = 9.2742 \times 10^{-24}$ J/T**

- **Ions with magnetic properties have unpaired electrons. Materials that contain magnetic ions have magnetic properties.**
- **Examples – Cu^{2+} and low spin Co^{3+} in an octahedral ligand field:**



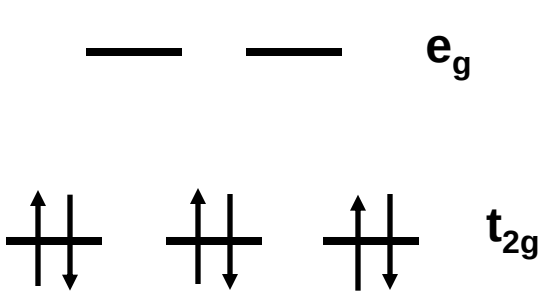
Cu^{2+}

d^9 ion

$S = {}^1/_2$

$\mu = 1.9\text{-}2.1\ \mu_B$

Paramagnetic ion



Co^{3+} (low spin)

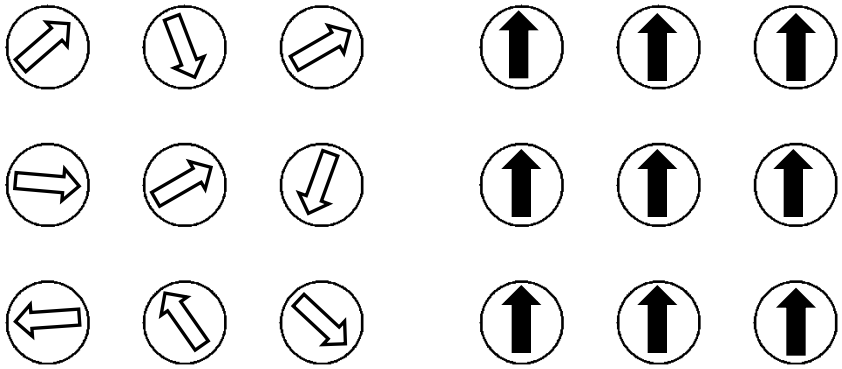
d^6 ion

$S = 0$

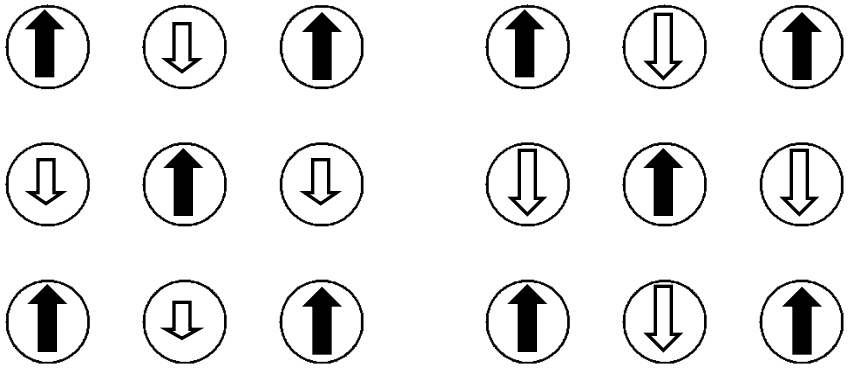
No magnetic moment

Diamagnetic ion

Magnetic Ordering Types



Paramagnetic (PM) Ferromagnetic (FM)

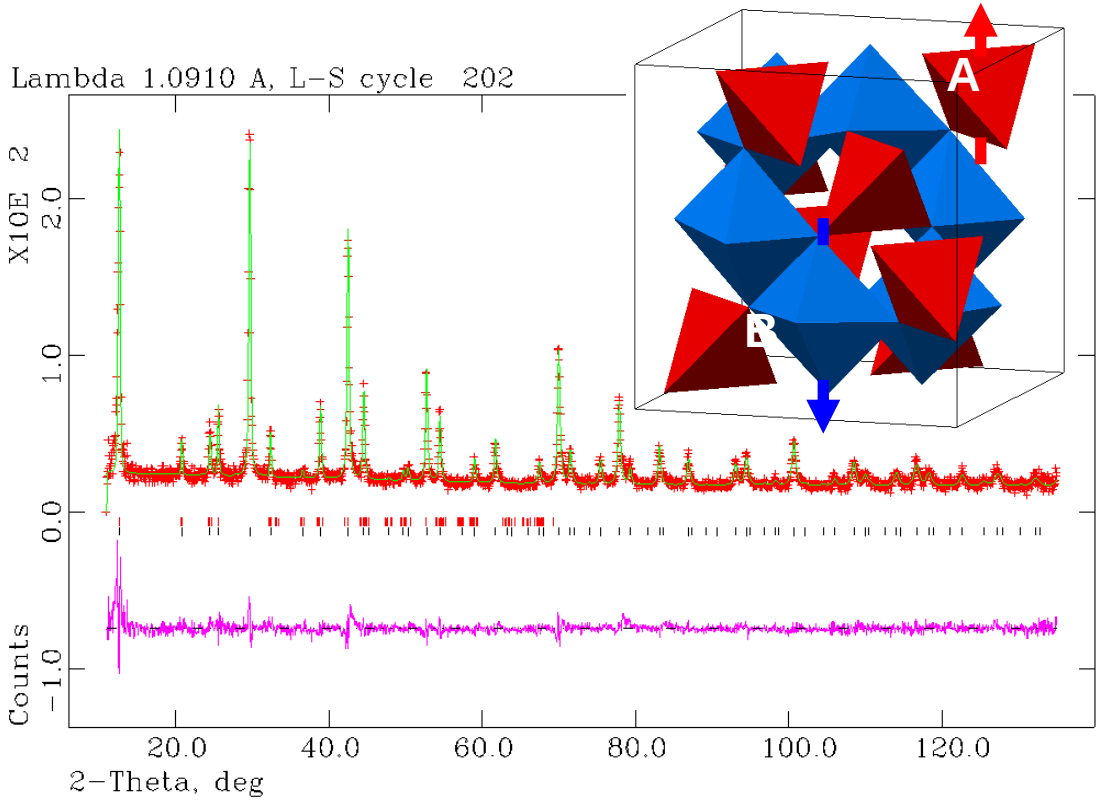


Ferrimagnetic Antiferromagnetic (AFM)

FERRIMAGNETIC AB_2O_4 SPINEL STRUCTURE

$(Mn_{0.81}Fe_{0.19})(Fe_{0.80}Mn_{0.20})_2O_4$

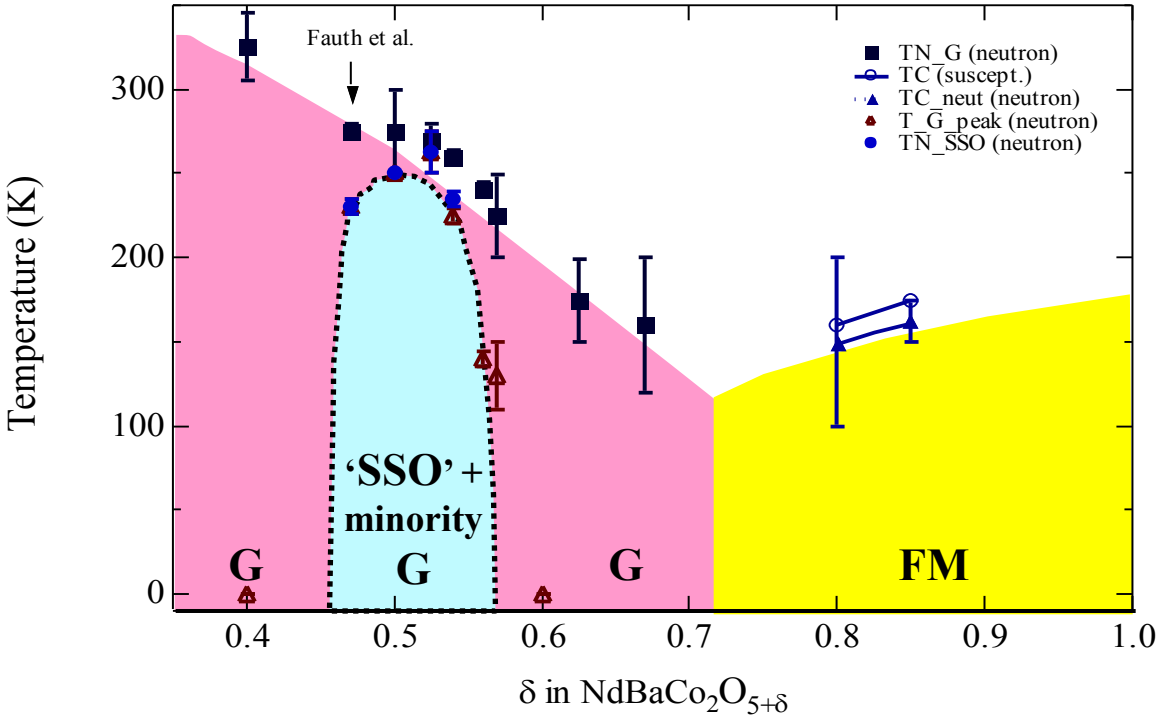
- lattice parameter
- oxygen position
- distribution of Mn/Fe on T and O sites
- atomic displacement parameters
- magnetic moments on the T and O sites (e.g., -2.9 and 2.0 m_B)



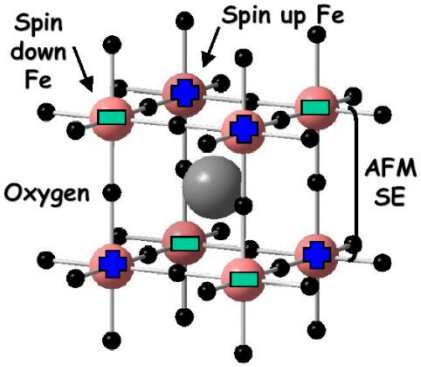
2-phase refinement
nuclear + magnetic structure

Zhang ZJ et. al. JACS, 120 1800 (1998)

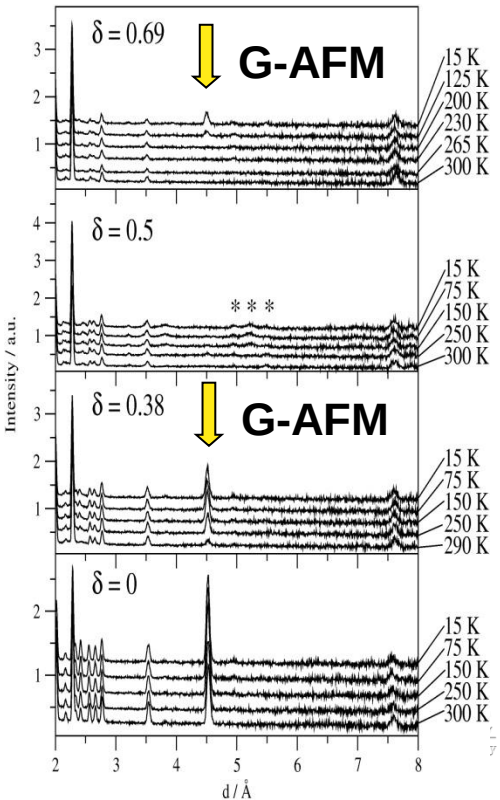
Magnetic Ordering: Oxygen-deficient A-site Layered Perovskite $NdBaCo_2O_{5+d}$



Magnetic phase diagram

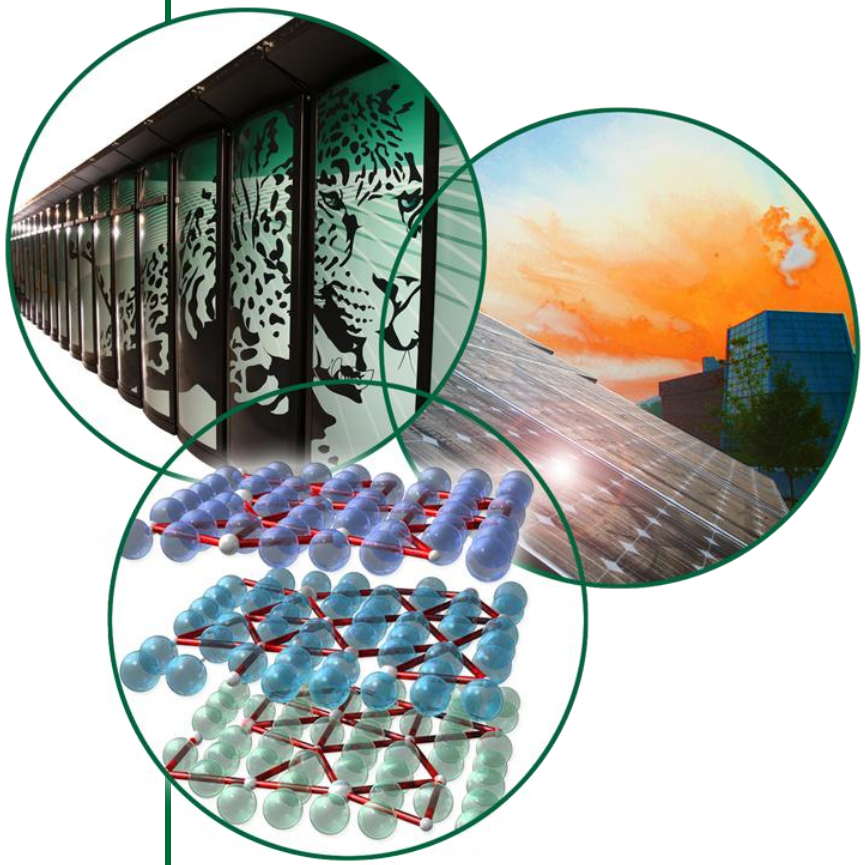


G type AF ordering in a simple perovskite

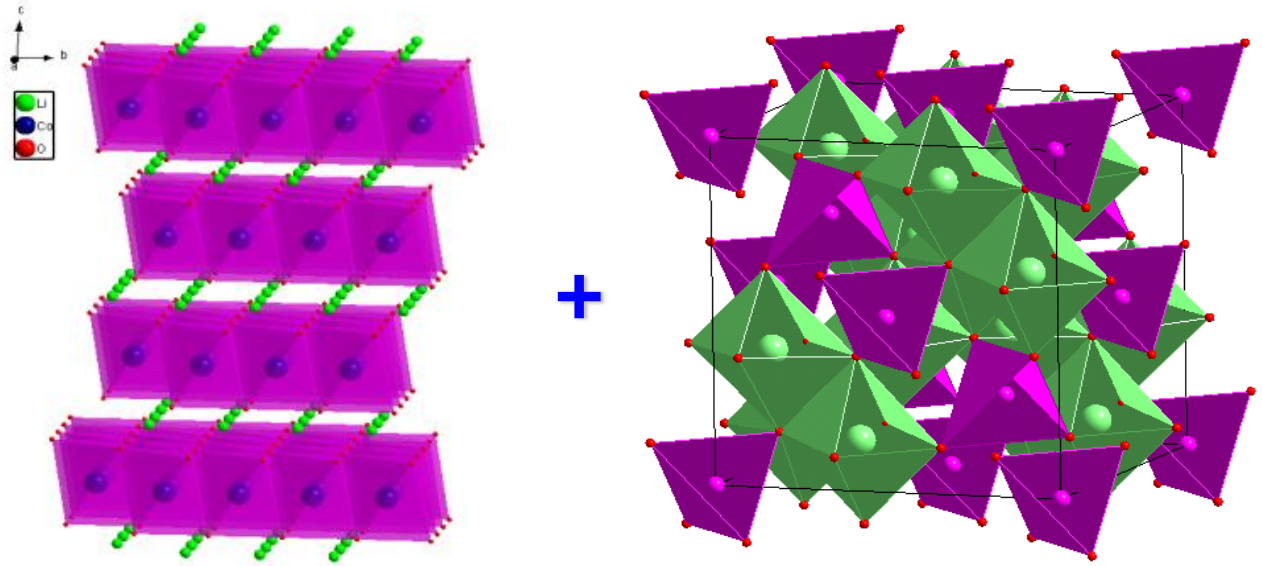


Burley et. al. J. Solid State. Chem. 170, 339 (2003)

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



HIGH-VOLTAGE, HIGH-ENERGY LAYERED-SPINEL COMPOSITE CATHODES



Eun-Sung Lee, Ashfia Huq, Hong-Young Chang, and Arumugam Manthiram, "High-voltage, High-energy Layered-Spinel Composite Cathodes with Superior Cycle Life for Lithium-ion Batteries", Chemistry of Materials 24, 600-612 (2012)

Cathodes for Li-ION Battery

Materials Consideration:

1. Readily reducible/oxidizable ion (TM)
2. Reaction with Li : reversible
3. High free energy
4. Rapid insertion and removal of Li
5. Good electronic conductor : preferably metal
6. Structural stability during charge and discharge
7. Low cost
8. Environmentally friendly

History:

1. Goodenough suggested $LiCoO_2$ in 1980, commercialized by SONY with a carbon anode. However, Co is expensive and thus usage is limited to small cells.
2. 1990-present : Second-Generation Li Batteries
   - Spinels
   - Other mixed TM layered oxides :

     $Li\,(Ni_{1-y-z}Mn_yCo_z)O_2$

     $Li_{1+x}(TM)_{1-x}O_2$

Candidates:

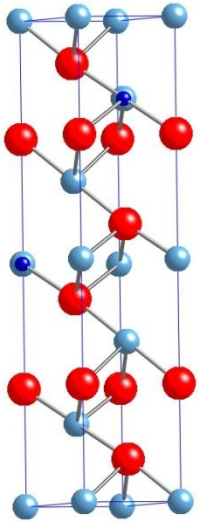
1. Layered structure with anion closed pack lattice, alternate layers in between anion sheets are redox-active TM and Li in remaining empty layeres. Spinels are special case where the TM are ordered in all the layers.
2. More open structures such as V oxide, Mn oxide, TM phosphates such as the olivine $LiFePO_4$.

Roles of different TM:

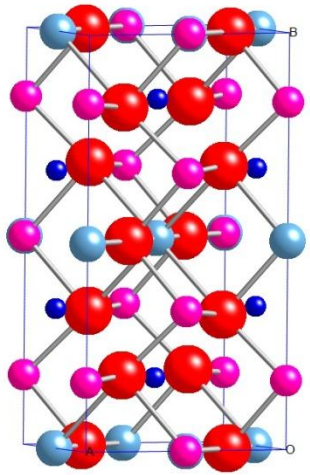
- ❑ Mn: Stabilizes the lattice
- ❑ Ni: Electrochemically active
- ❑ Co: Ordering the TM, increasing rate capability and the conductivity.
- ❑ Li: Increasing capacity

Structural Consideration

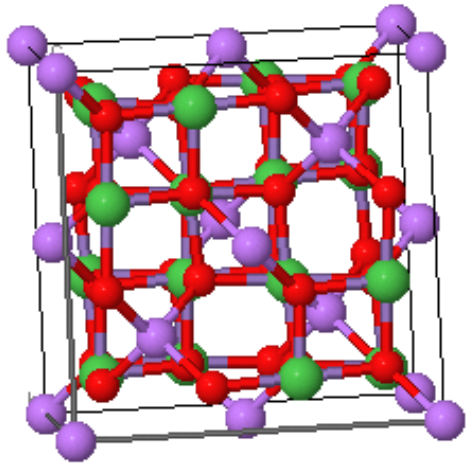
Elements	Neutron scattering length : b	Atomic Number : Z
Li (natural)	-1.9	3
Mn	-3.73	25
Co	2.49	27
Ni	10.3	28



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

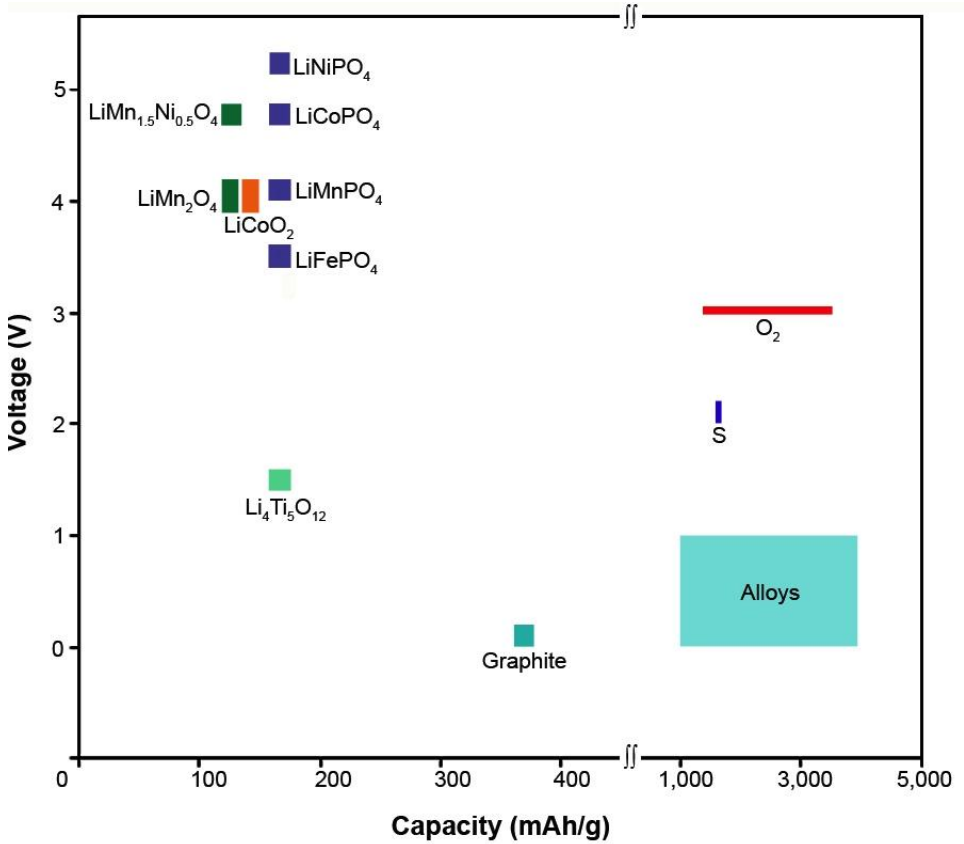


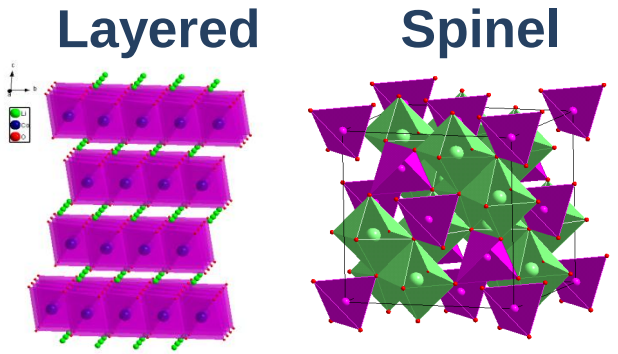
Space Group : C 2/m
a=4.94,b=8.55, c = 5.04, β =109.3
$Li(Li_{0.2}Ni_{0.17}Mn_{0.6}Co_{0.03})O_2$

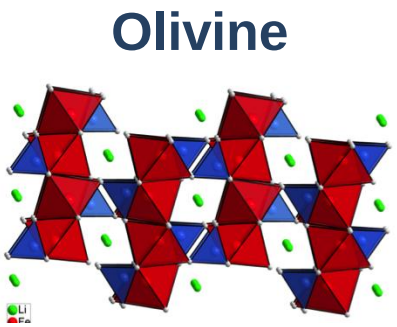


Space Group : F d 3 m
a = 8.17
$Li(Ni_{0.425}Mn_{1.5}Co_{0.075})O_2$

ELECTRODE MATERIALS FOR LITHIUM BATTERIES







A. Manthiram, *J. Phys. Chem. Lett.*, **2011**, **2 (3)**, 176.

Energy density of the current lithium-ion technology is limited by the cathode materials, and there is immense interest to develop new cathodes with higher capacity or higher operating voltages

$xLi[Li_{0.2}Mn_{0.6}Ni_{0.17}Co_{0.03}]O_2 \cdot (1-x)LiMn_{1.5}Ni_{0.425}Co_{0.075}O_4$: COMPOSITE

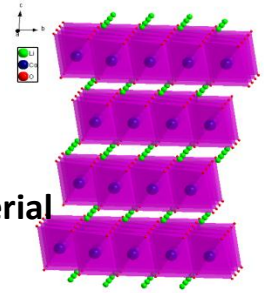
- $Li[Li,Mn,Ni,Co]O_2$ and $LiMn_{1.5}Ni_{0.5}O_4$ are candidates for Li-ion battery cathodes

Cathode	Structure	Advantage	Disadvantage
$Li[Li,Mn,Ni,Co]O_2$	Layered (*R*-3*m*)	High energy density	Large IRC at 1st cycle Poor rate capability
$LiMn_{1.5}Ni_{0.5}O_4$	Spinel (*Fd*-3*m*)	High power density	Low energy density

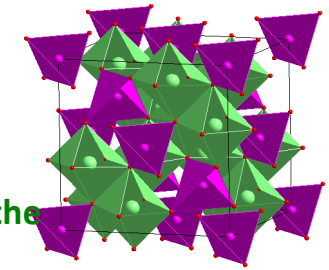
- The cubic-close packed oxygen arrays in both structures are structurally compatible

- A combination of high energy and power density might be possible to use composite material

Layered



Spinel



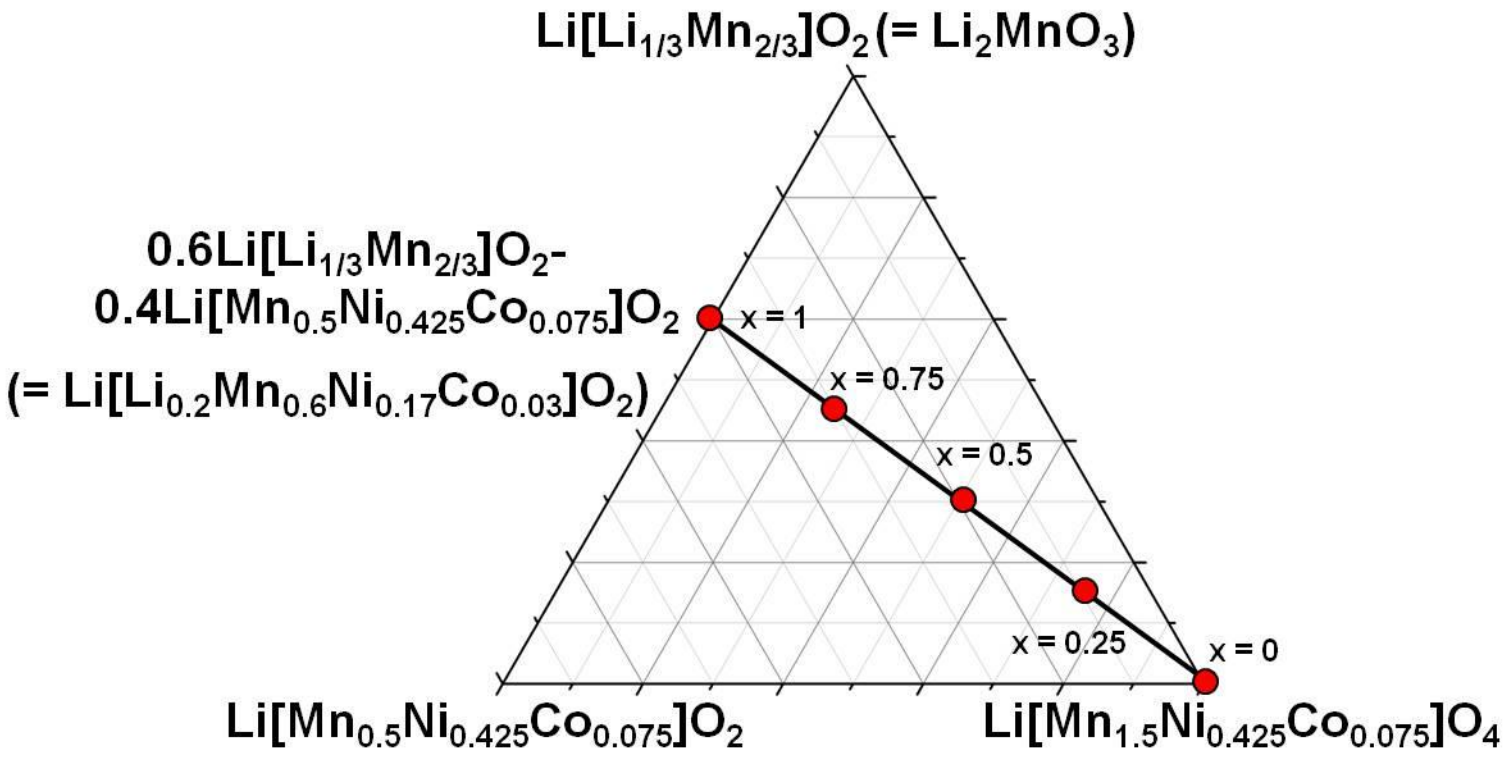
  - Two systems have been reported in the literature:

    (1) $xLi_2MnO_3 \cdot (1-x)Li_{1+\delta}Mn_{2-\delta}O_4$ $(0 \le \delta \le 1/3)$

    (2) $xLi[Li_{0.2}Mn_{0.6}Ni_{0.2}]O_2 \cdot (1-x)Li[Mn_{1.5}Ni_{0.5}]O_4$

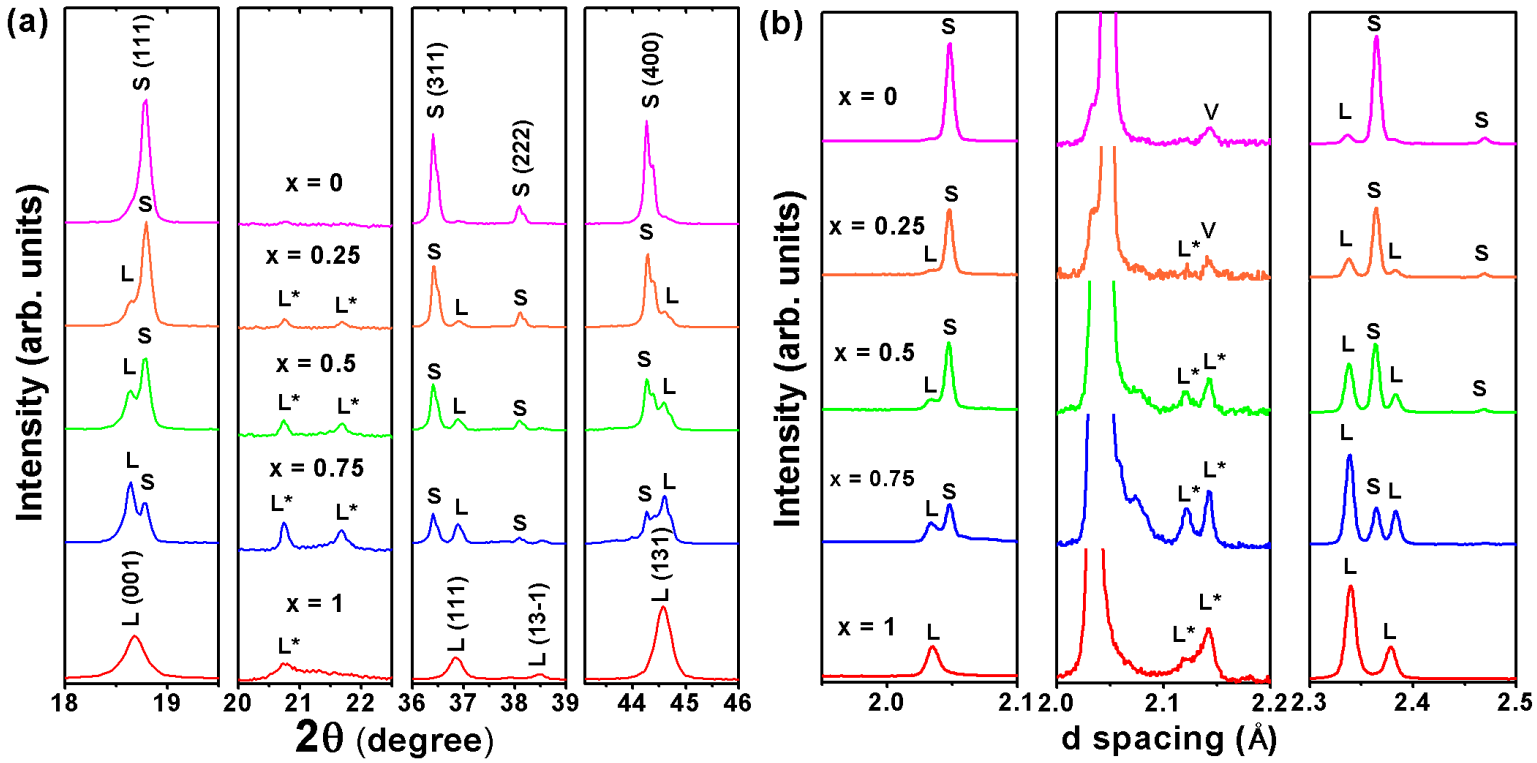
  - Synthesis of the composite material that includes Co could increase the capacity due to the overlap of the Co^{3+} 3d band with top of the O^{2-} 2p band.

Synthesis of $xLi[Li_{0.2}Mn_{0.6}Ni_{0.17}Co_{0.03}]O_2 \cdot (1-x)LiMn_{1.5}Ni_{0.425}Co_{0.075}O_4$



- Synthesized by firing the co-precipitated hydroxides of Ni, Mn, and Co with LiOH in air at 600 - 900 °C
- Li/M ratios are 0.5, 0.62, 0.79, 1.05, and 1.5 for x = 0, 0.25, 0.5, 0.75, and 1

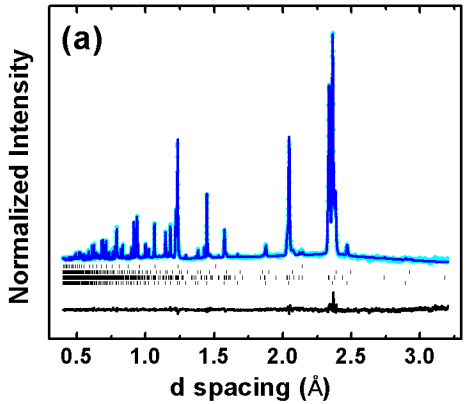
Pristine ND and XRD

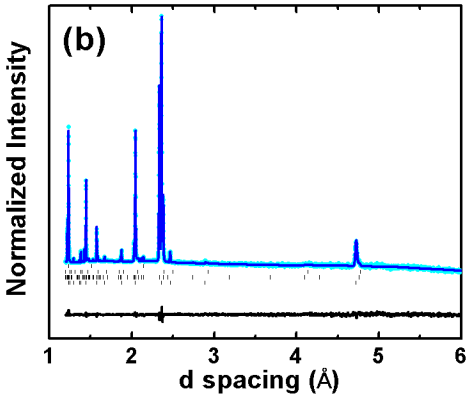


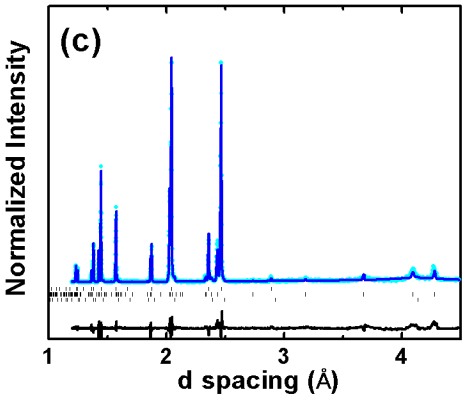
Synthesized at 800°C

- **Strong superstructure peaks imply that there is higher Li^+ content in TM layer**
- **Higher Li^+ contents in TM layer is the reason for the low layered capacity at first cycle**

Rietveld Refinements

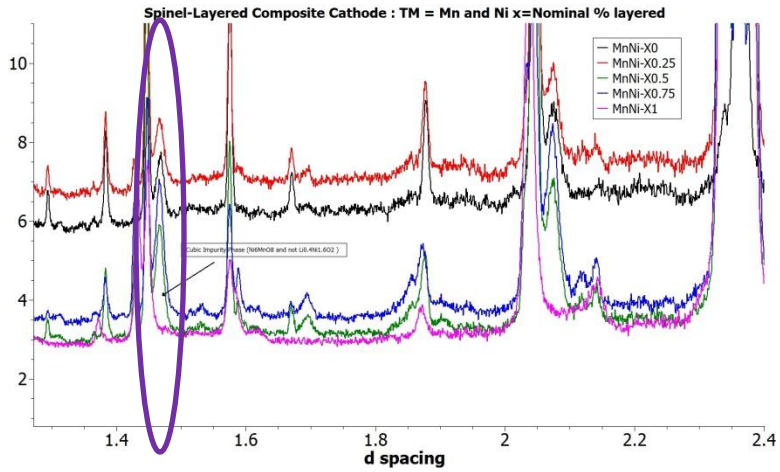






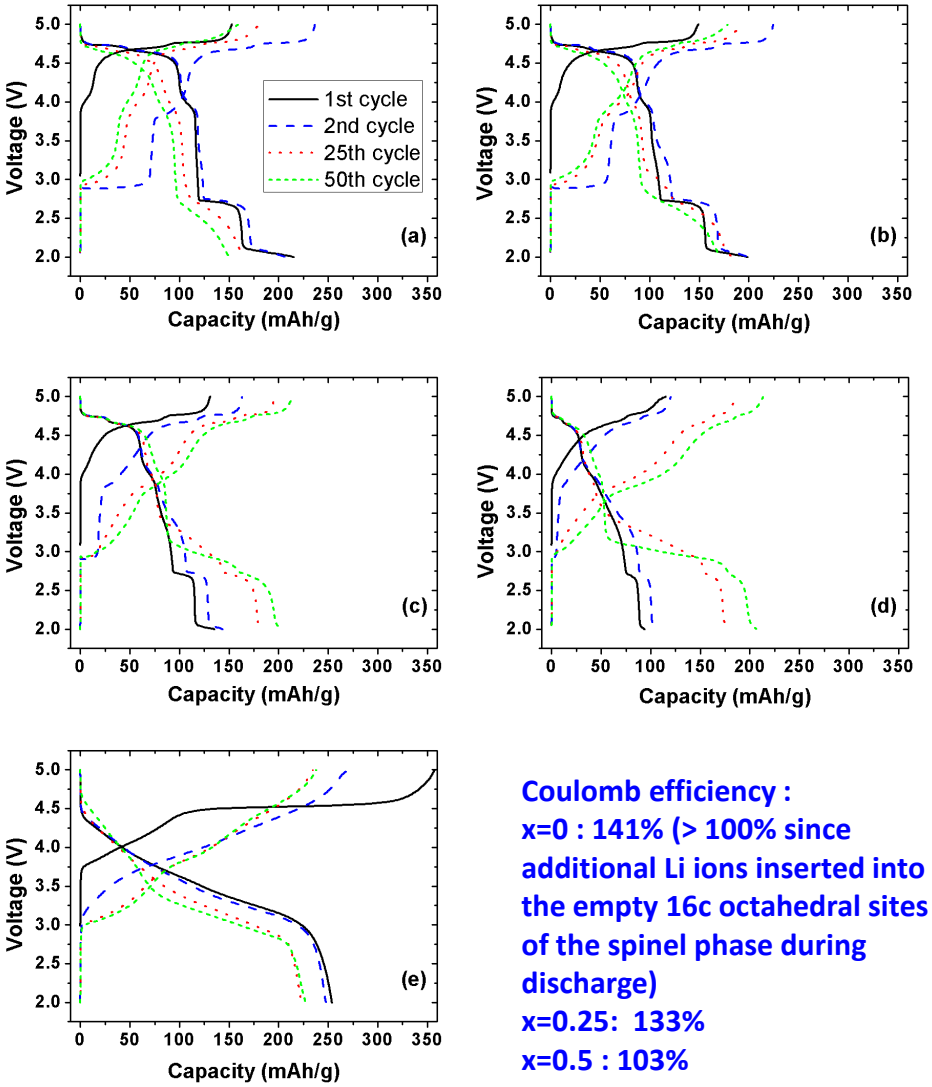
x	Chemical composition			Weight %			Li / [Mn+Ni+Co]
	Atom	Spinel (*Fd*-3*m*)	Layered (*C*2/*m*)	Spinel (*Fd*-3*m*)	Layered (*C*2/*m*)	Cubic	
0	Li	1	1.20	89.67	10.54		0.59
	Mn	1.5000(9)	0.60				
	Ni	0.3750(9)	0.17				
	Co	0.1235(9)	0.03				
0.25	Li	1	1.19(2)	81.34	18.28	0.40	0.69
	Mn	1.500(1)	0.67(2)				
	Ni	0.402(1)	0.05(1)				
	Co	0.099(1)	0.01(1)				
0.50	Li	1	1.26(1)	63.86	34.86	1.30	0.93
	Mn	1.500(1)	0.60(1)				
	Ni	0.441(1)	0.051(5)				
	Co	0.059(1)	0.005(5)				
0.75	Li	1	1.31(1)	37.26	59.59	3.1	1.05
	Mn	1.500(2)	0.56(1)				
	Ni	0.489(2)	0.046(4)				
	Co	0.011(2)	0.012(4)				
1.00	Li	1	1.185(2)	3.89	96.11		1.64
	Mn	1.5	0.620(2)				
	Ni	0.425	0.115(5)				
	Co	0.075	0.006(5)				

Electrochemistry



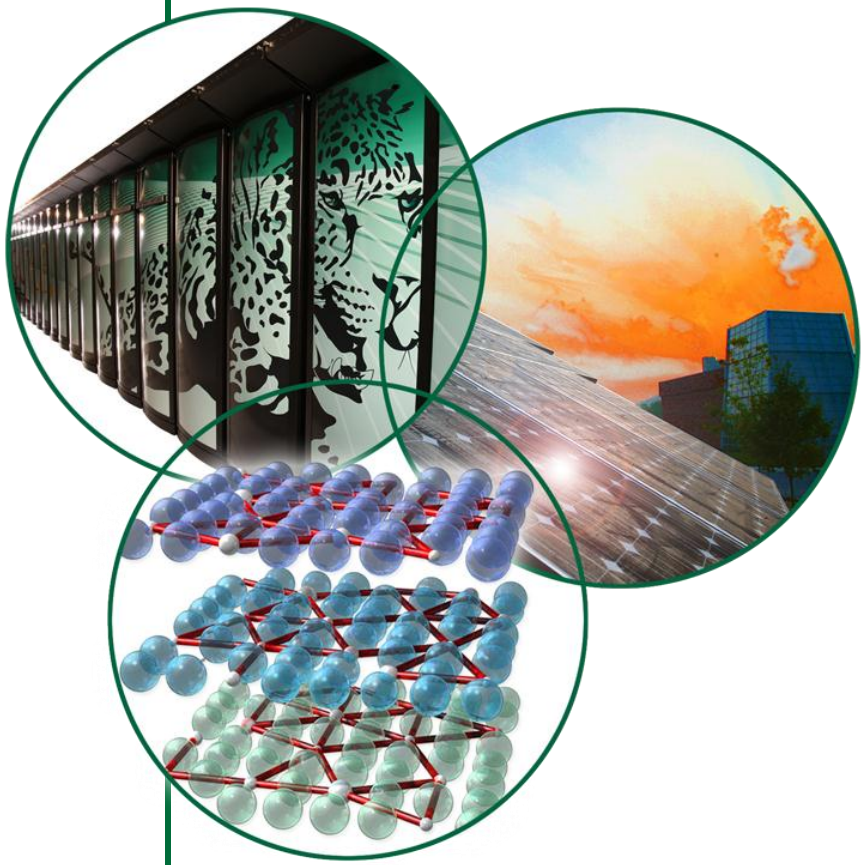
- High res and high intensity data helped identify this phase as Ni rich doubled cubic phase Ni_6MoO_8 instead of Li Nickelate phase.

- 2c and 4h site almost entirely Li
  Mn shows clear preference to 4g site
  Ni prefers 2b site.



Coulomb efficiency :
x=0 : 141% (> 100% since additional Li ions inserted into the empty 16c octahedral sites of the spinel phase during discharge)
x=0.25: 133%
x=0.5 : 103%
x=0.75 : 82%
x=1 : 71%

In situ studies of Solid Oxide Fuel Cell materials

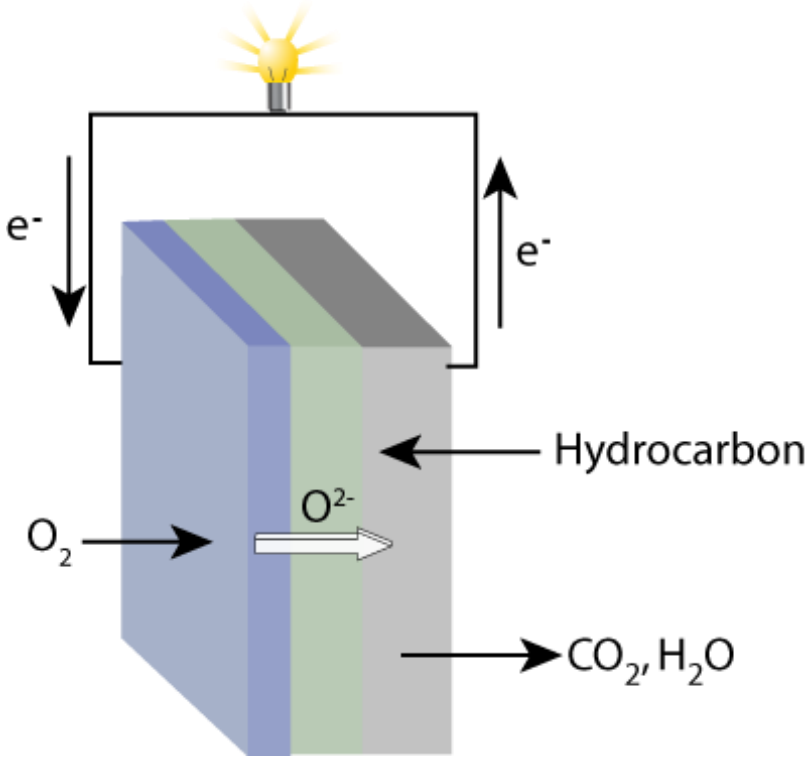


U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Solid Oxide Fuel Cell (SOFC)



- 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.**

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

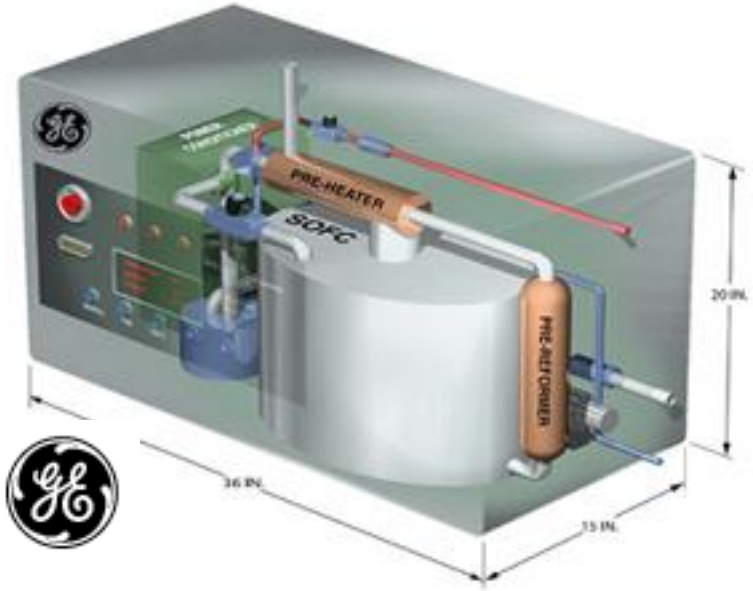
- **Current cells have a reformer to generate CO/H_2 fuels from hydrocarbons.**

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

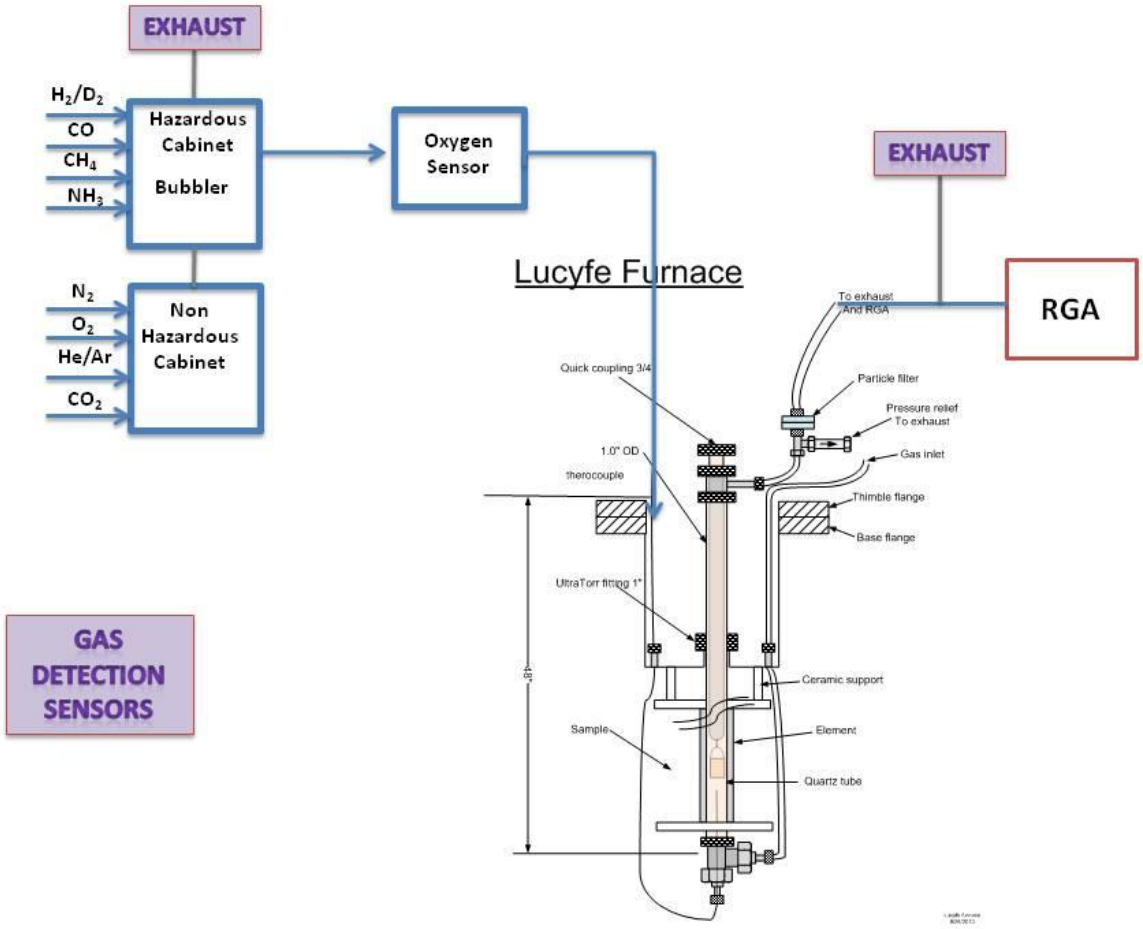
- **Ideally we can utilize hydrocarbons directly:**

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

Industrial SOFC Development

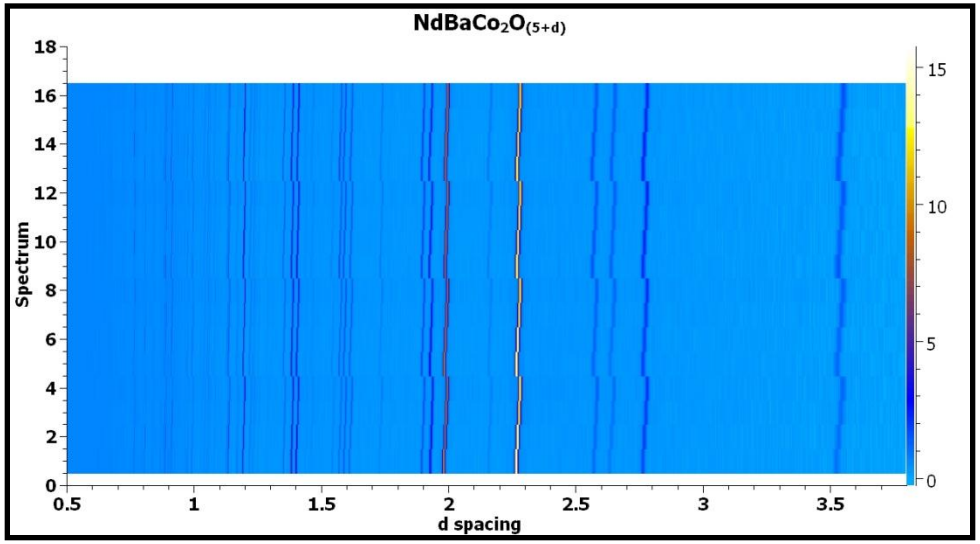


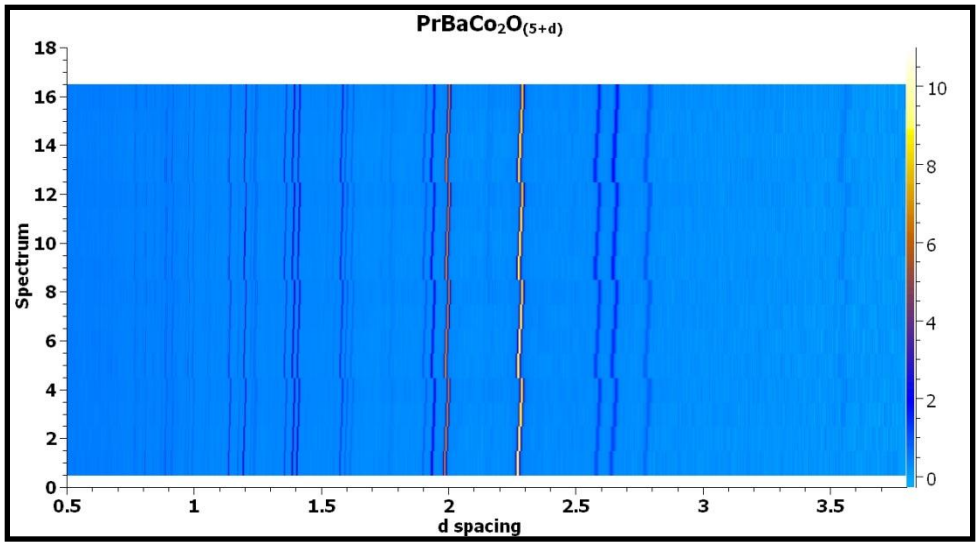
An integrated sample environment that includes a high temperature furnace, a gas flow insert, a pO_2 sensor and Residual Gas Analyzer (RGA) makes it possible to study Solid Oxide Fuel Cell (SOFC) materials among other things under operational condition.



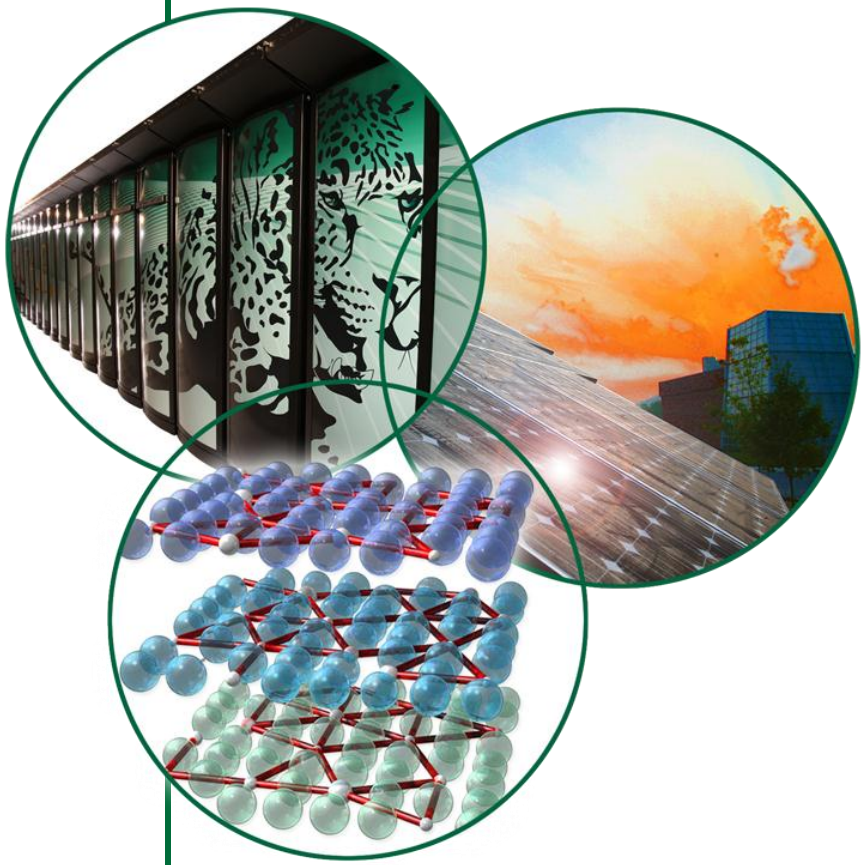
$REBaCo_2O_{5\pm d}$: cathode materials for SOFC

- 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.





Ab-initio Structure Solution from Powder Diffraction



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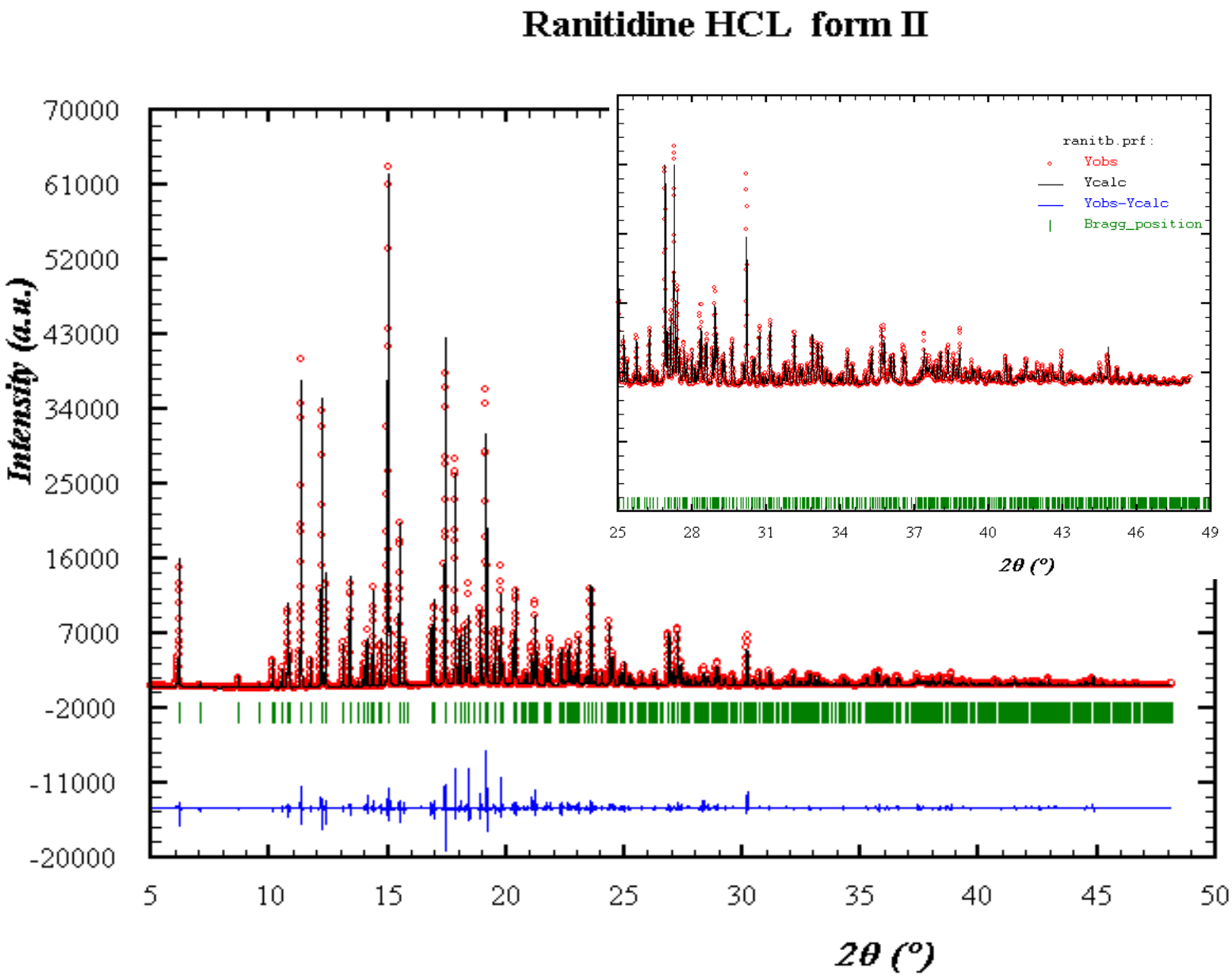
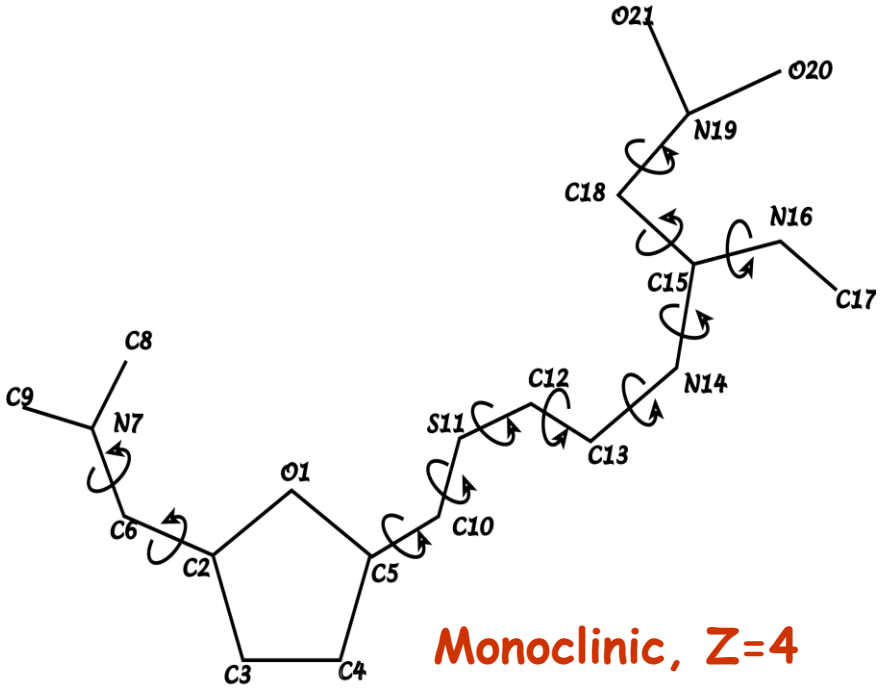
Undertake a project like this with very good data



Ranitidine HCl (Zantac®) is a very widely used drug for ulcers, excess production of stomach acid. There is an interesting subtlety in its crystal structure. Huq et. al. J. Pharm. Sci. 92, 244 (2003)



Space Group : P $2_1/n$

3 spatial coordinates : position

3 Eulerian angles : orientation

11 torsions.

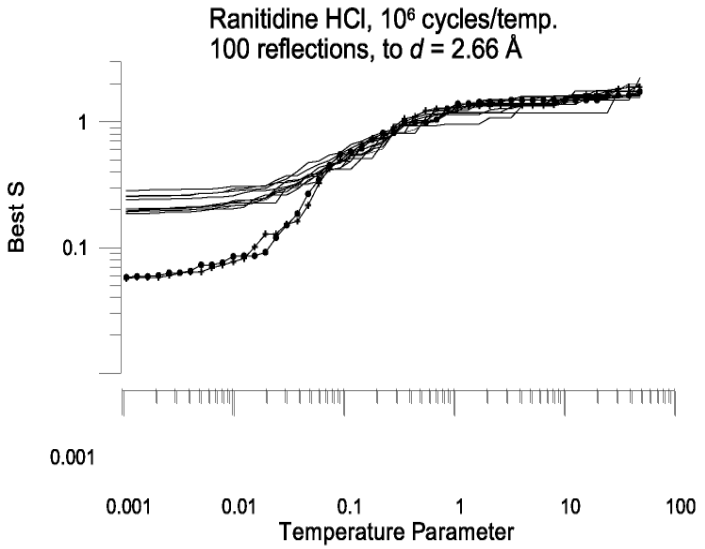
Monoclinic, Z=4

a=18.808Å,

b=12.981Å,

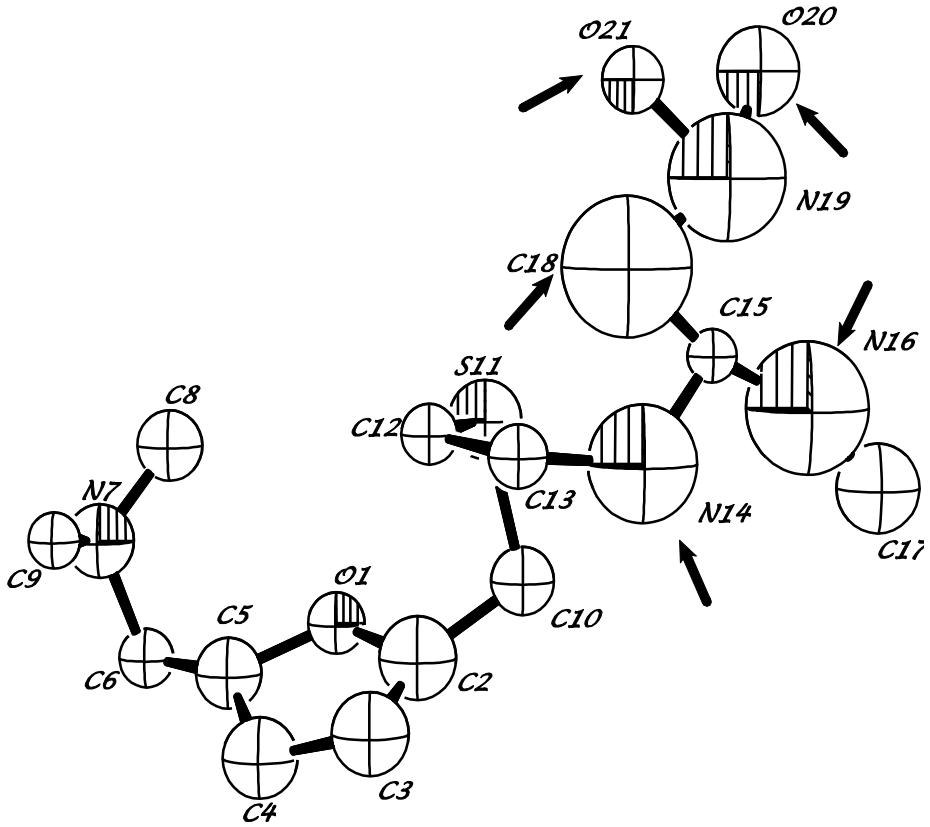
c=7.211Å

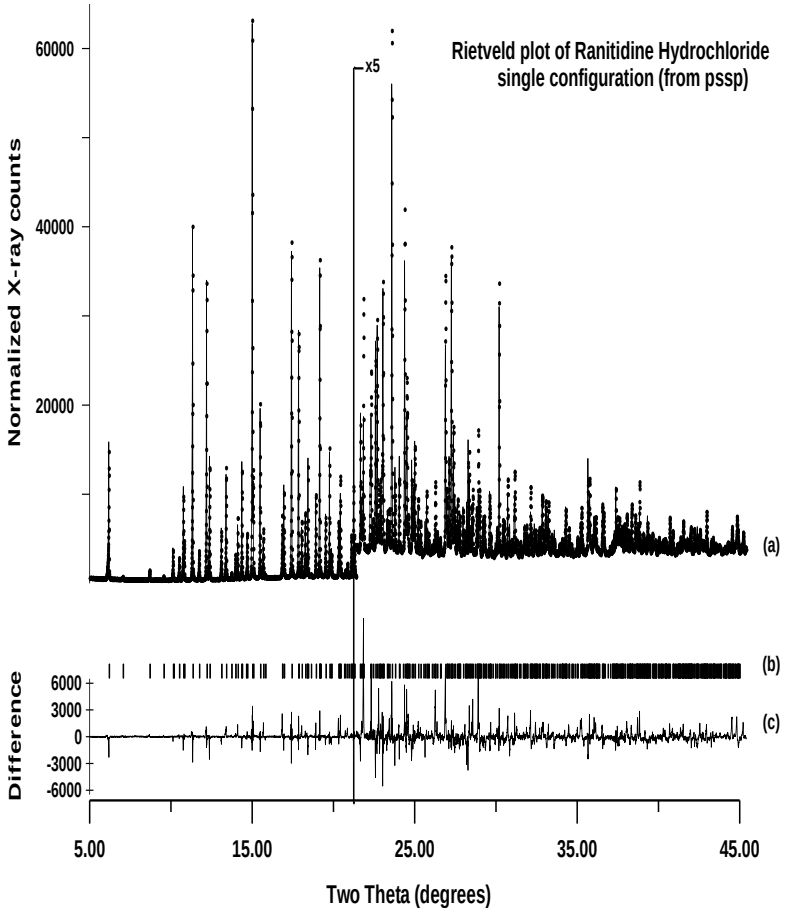
β=95.057°,

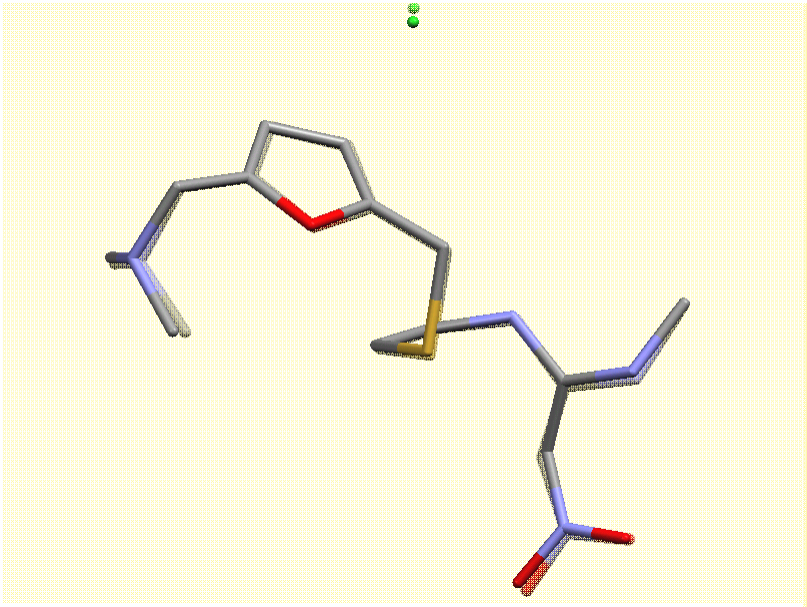


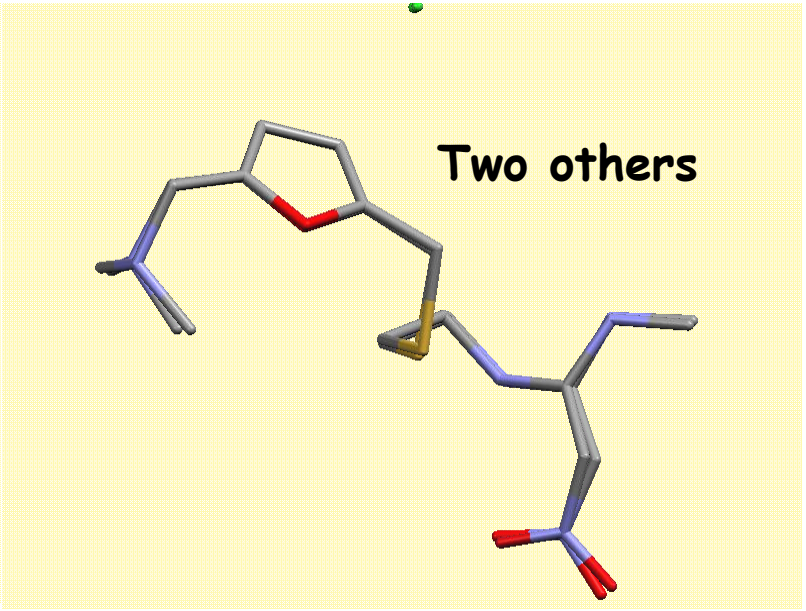
Atomic structure of our best Rietveld refinement of a single molecule. Essentially independent of which solution we start from.

R_{wp} = 11.12%, χ^2 = 10.56

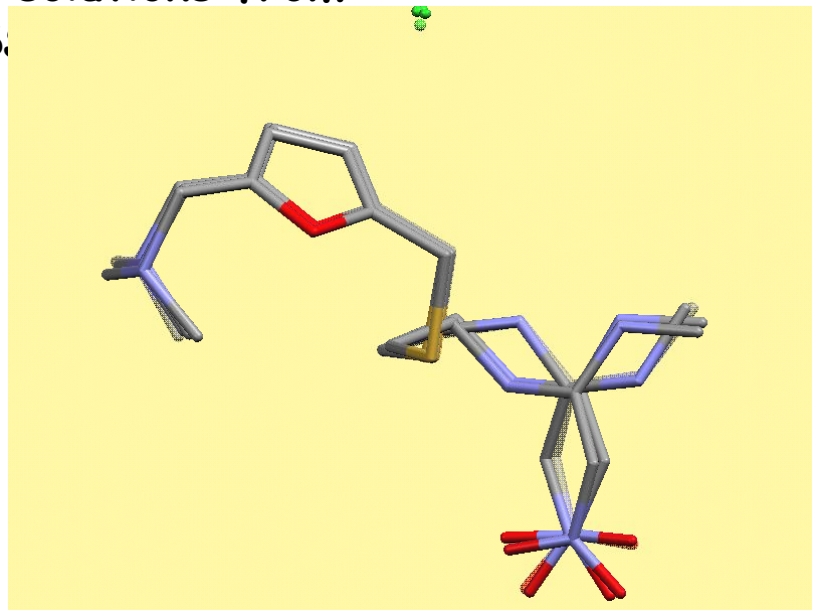








Two candidate solutions from PS



All four, superimposed.

Disorder,

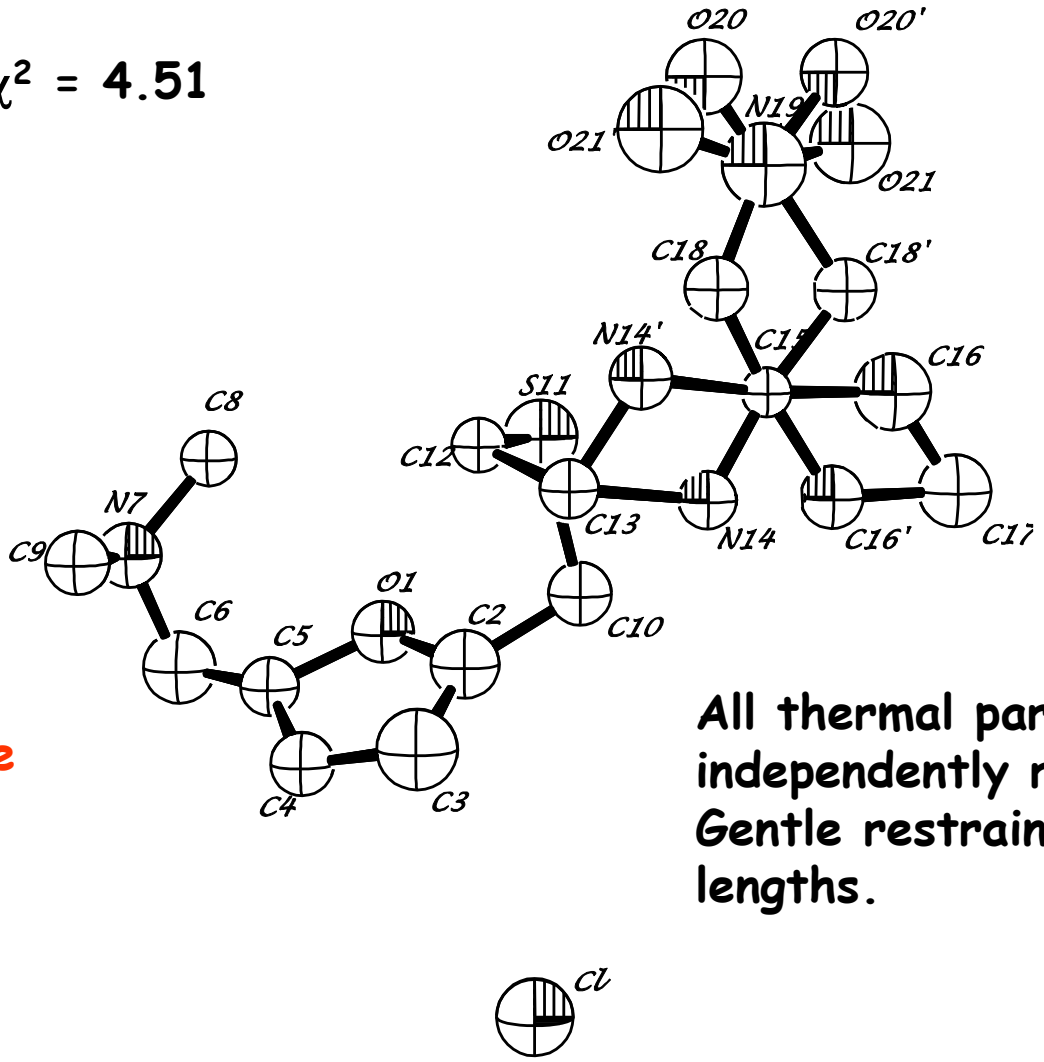
or inability of powder

data to distinguish

a few of the atoms?

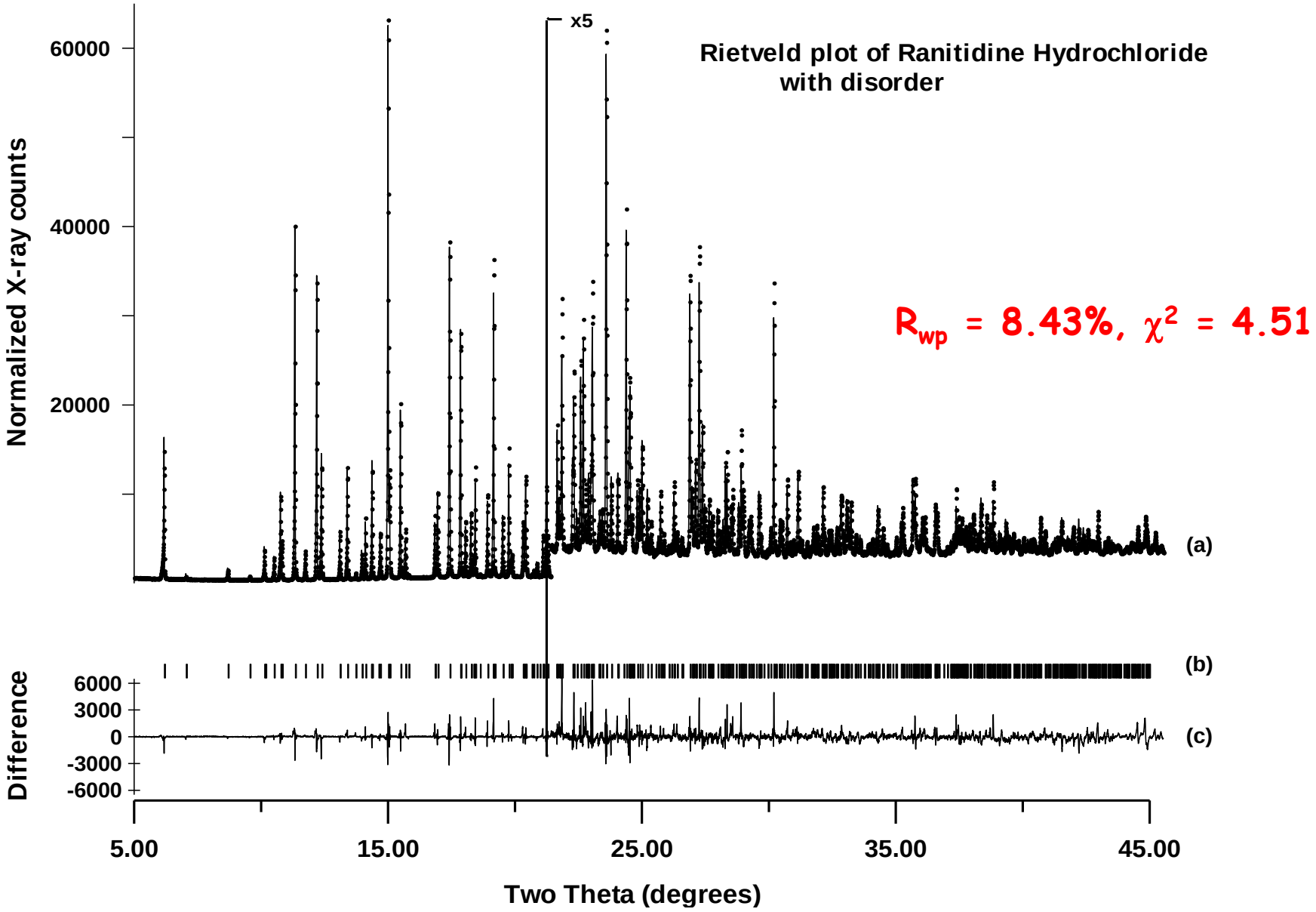
Refinement incorporating disorder. 50% occupancy of each of two sites for N14, C16, C18, O20, and O21.

R_{wp} =8.39%, χ^2 = 4.51

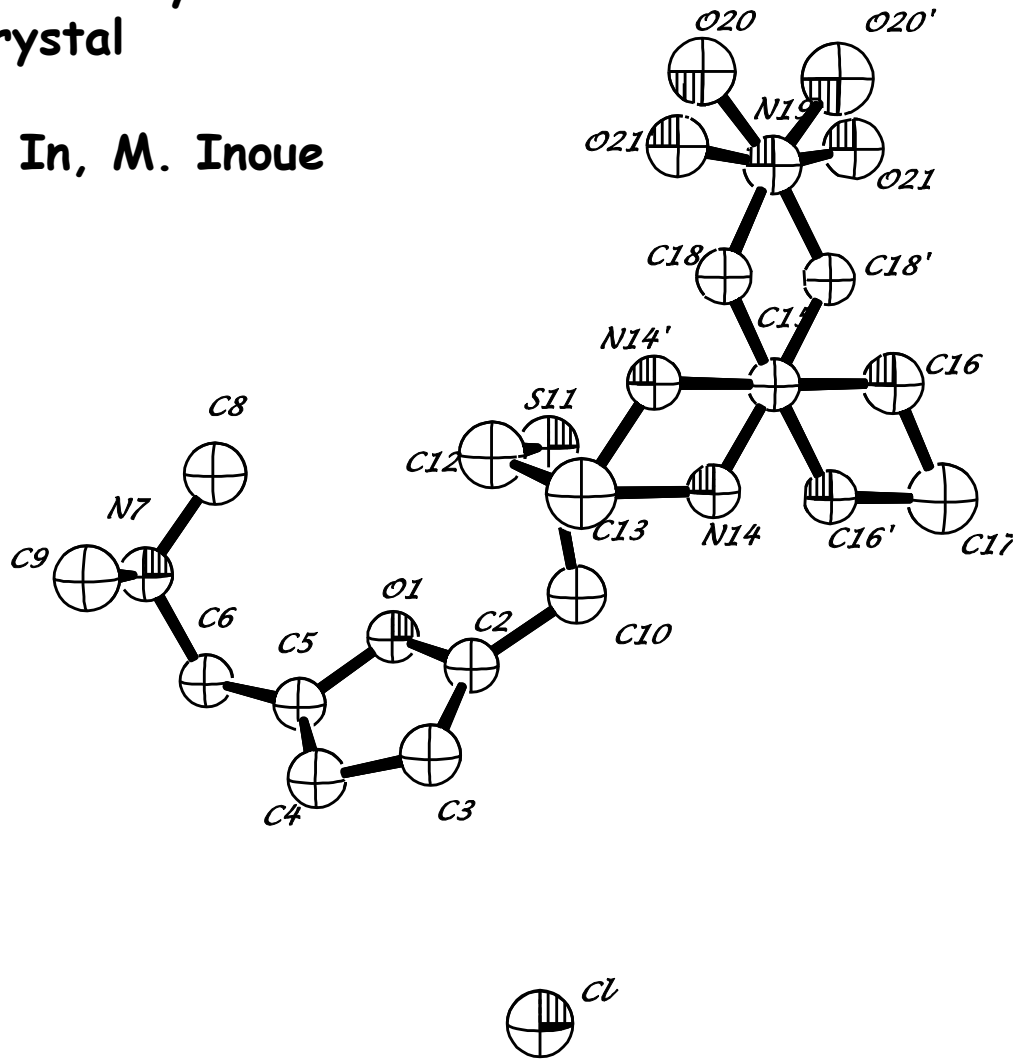


This is clearly the correct solution, which includes molecular disorder.

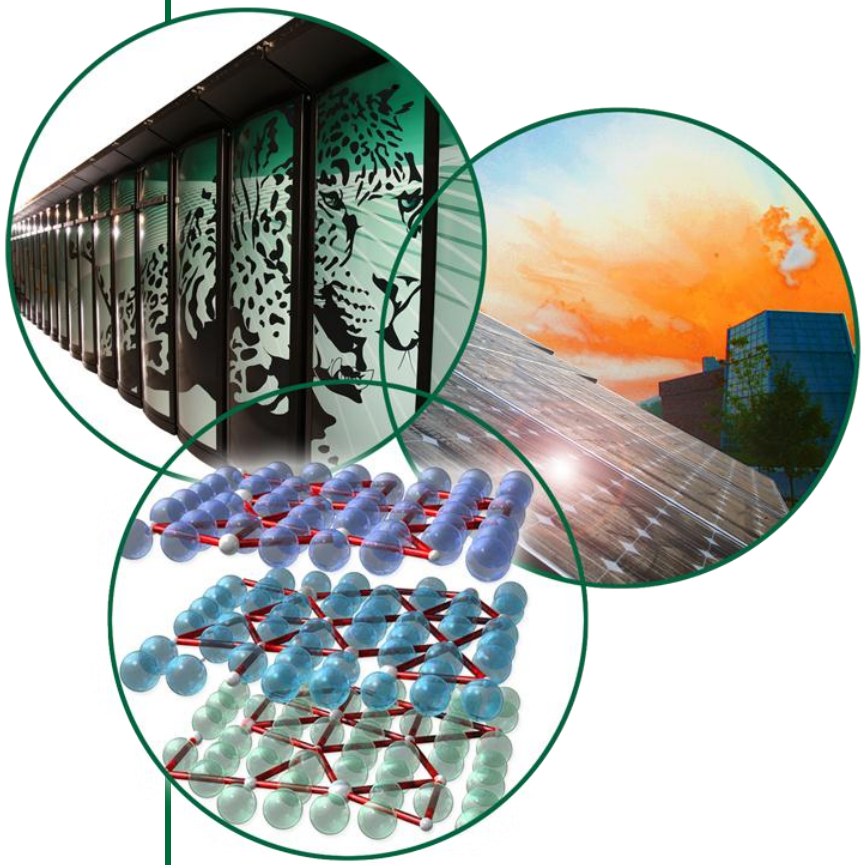
All thermal parameters independently refined! Gentle restraints on bond lengths.



The answer, including disorder, was already known from single crystal experiment.
T. Ishida, Y. In, M. Inoue (1990)



Proteins and Powder Diffraction



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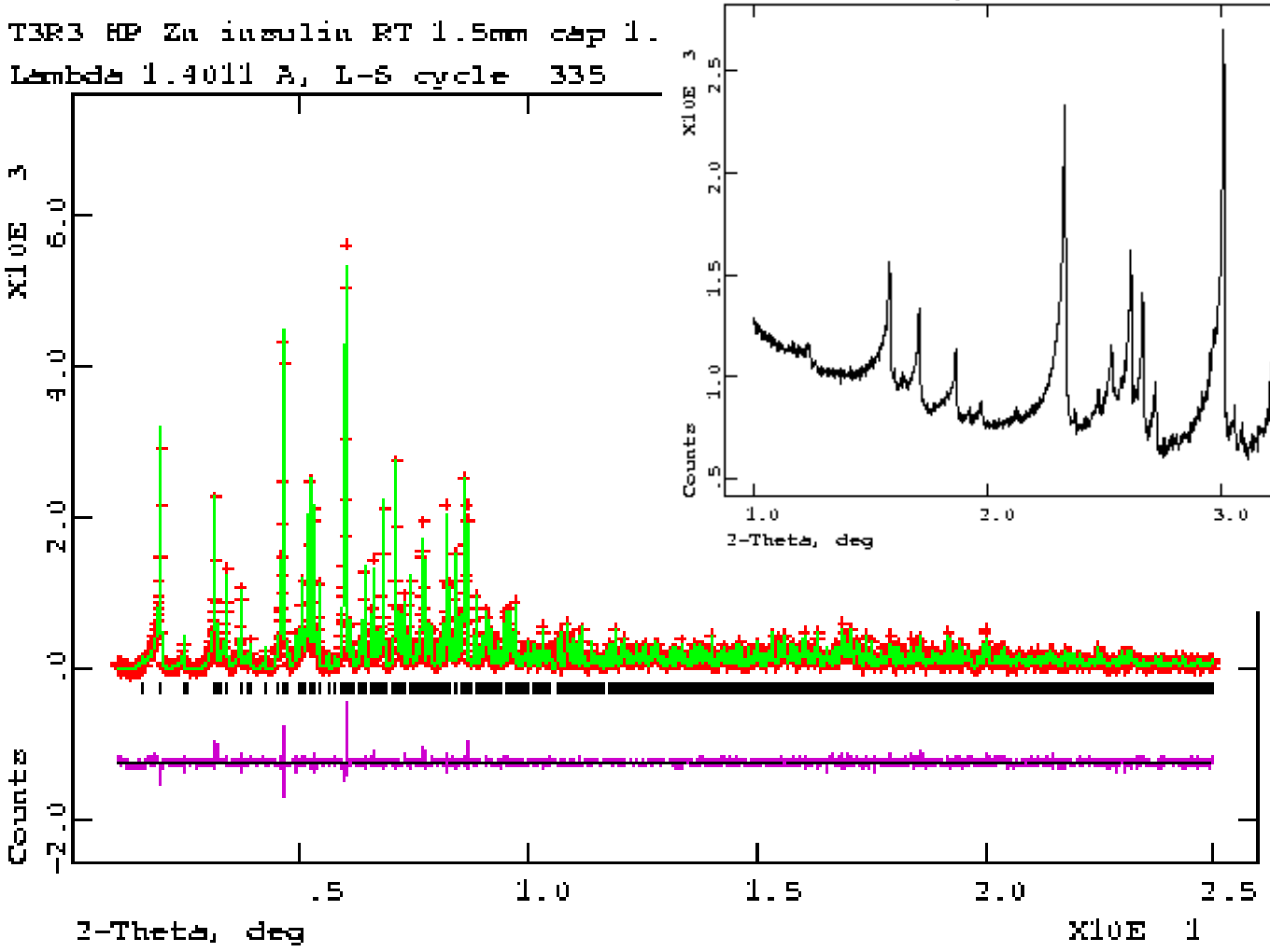
Extreme limit: Proteins

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.



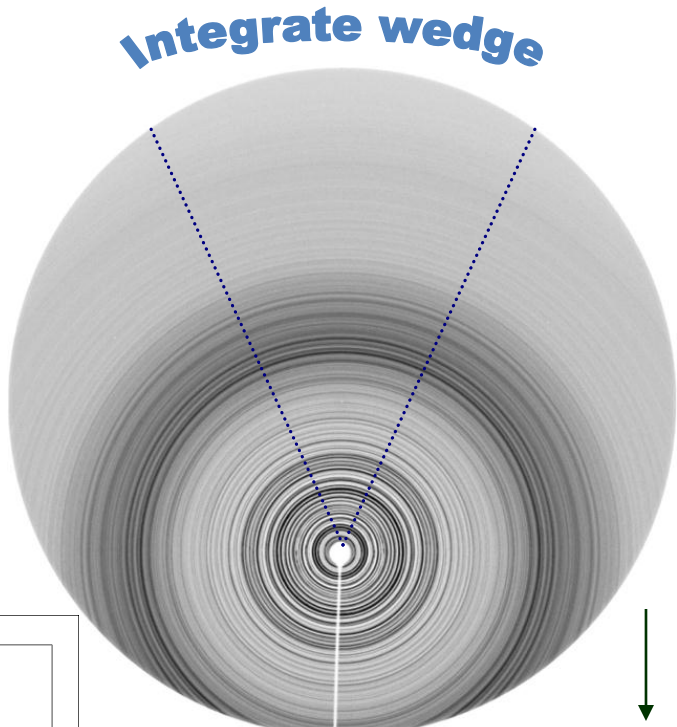
Structure solved from powder data & Rietveld refinement

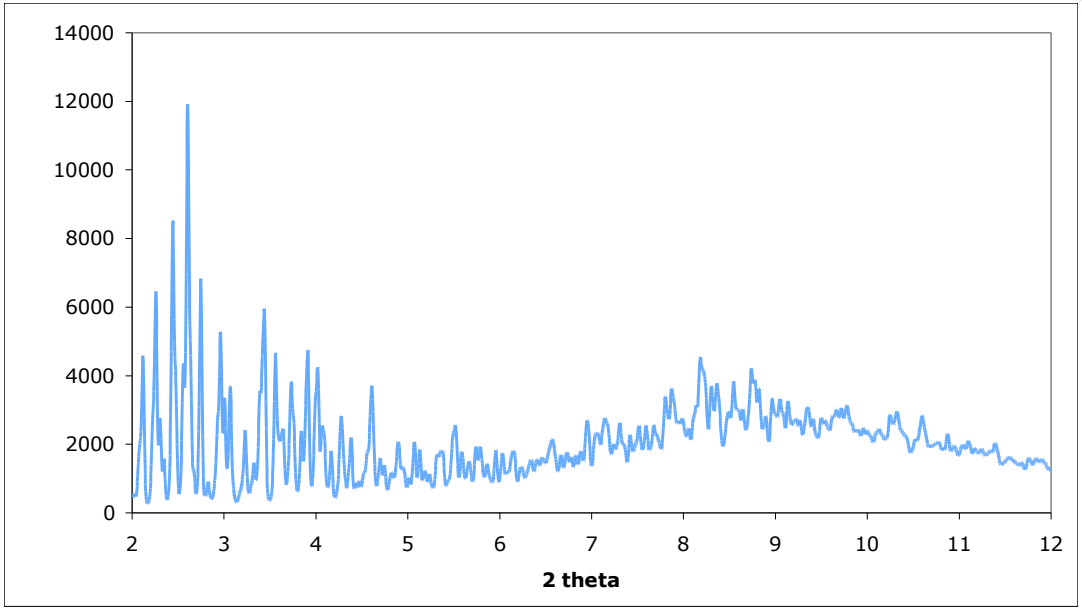
Human Insulin Zn complex

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).

Current work at APS: Structure solution via molecular replacement





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.