

Inverse methods of Data Analysis in Neutron Scattering

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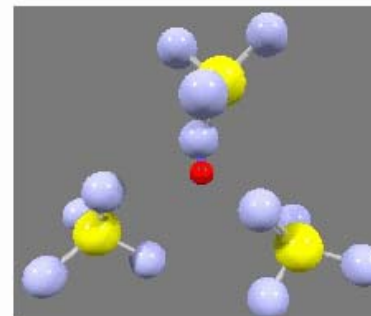
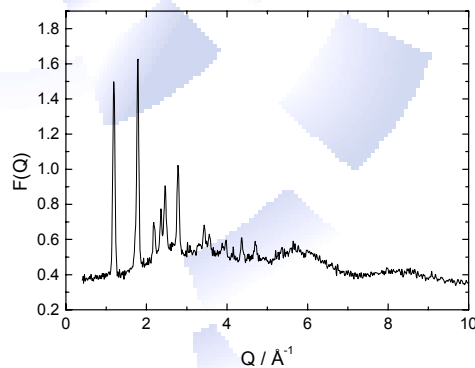


Inverse methods of Data Analysis in Neutron Scattering

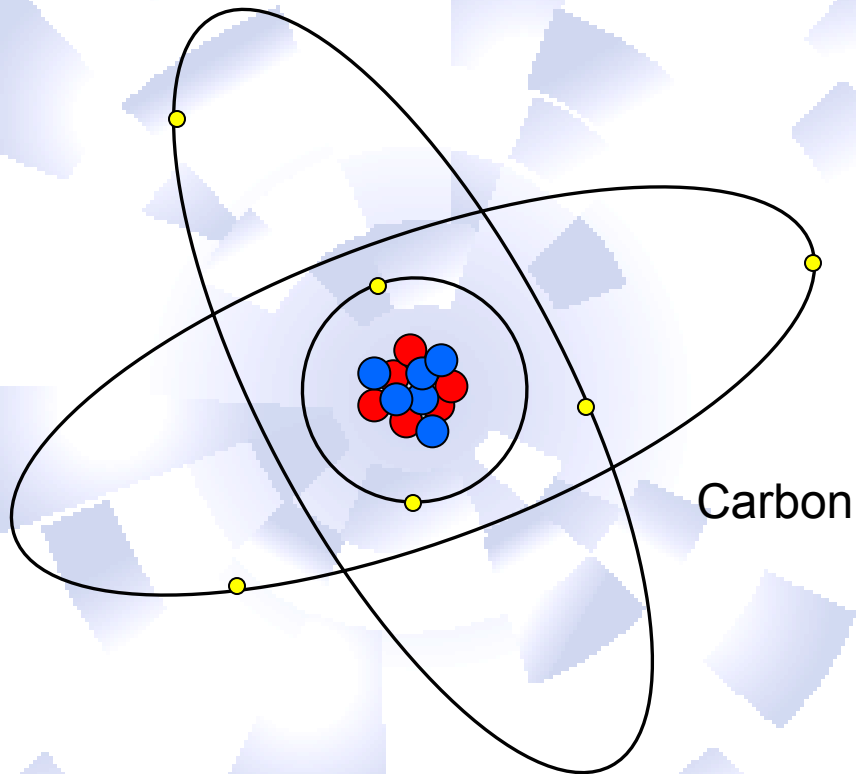
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From here to there



What is neutron scattering? A short introduction



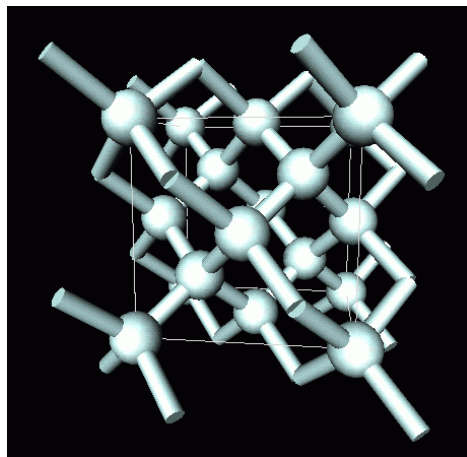
-  Proton +
-  Neutron
-  Electron -



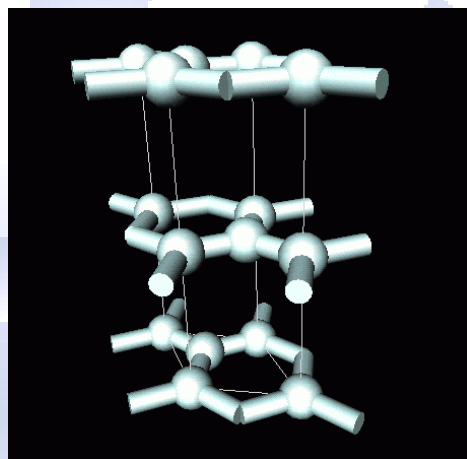
ISIS 

 CCLRC

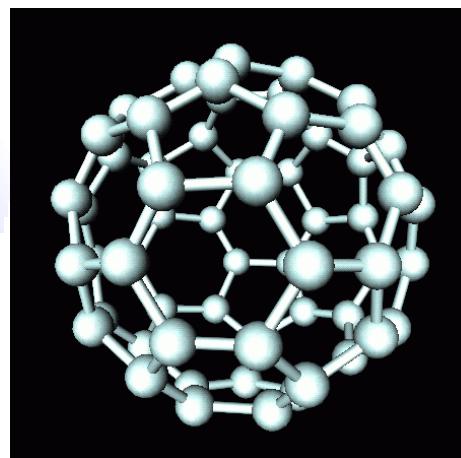
UCLA
12/11/2003



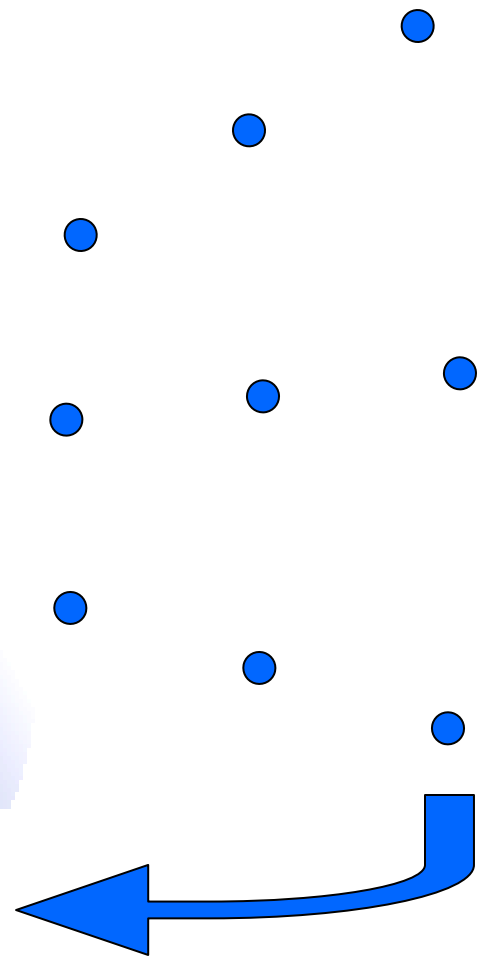
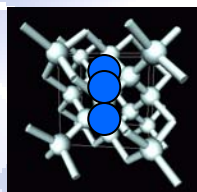
Diamond



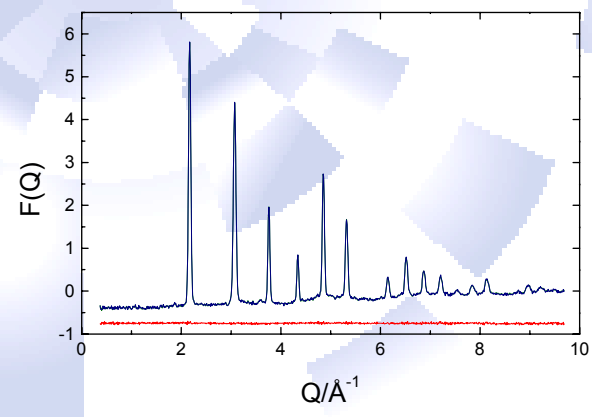
Graphite

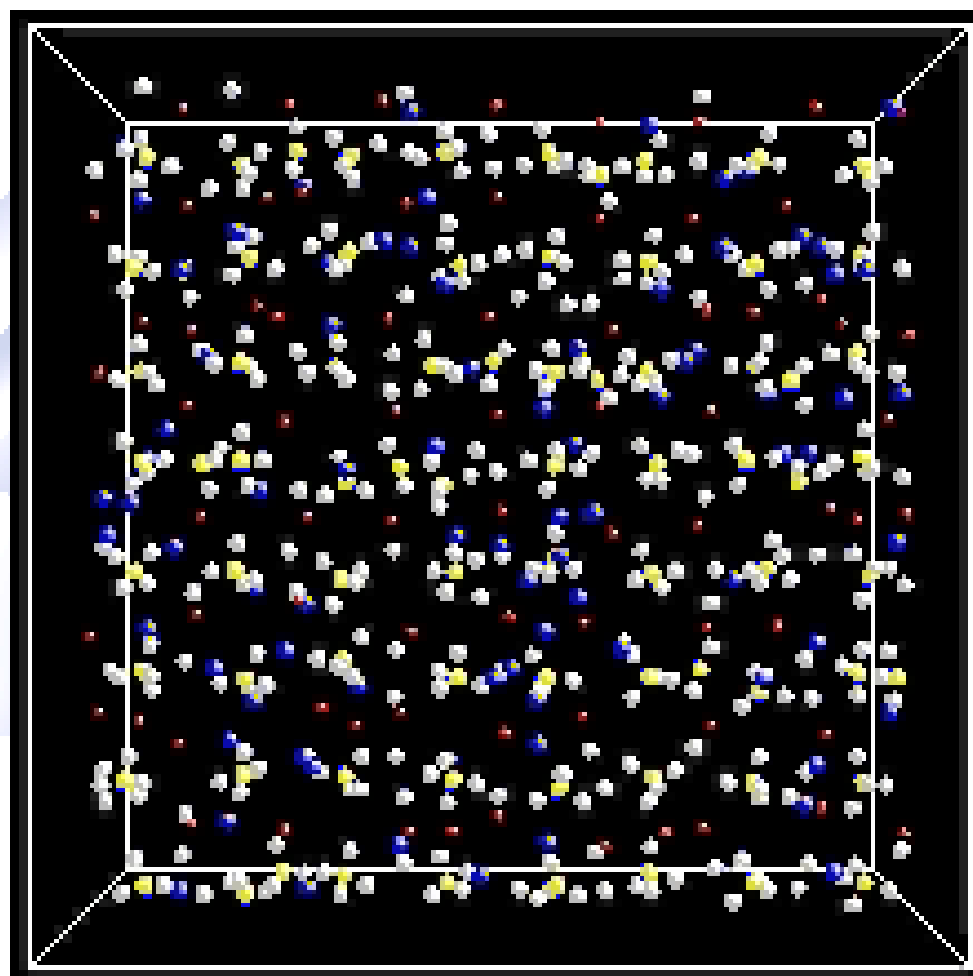


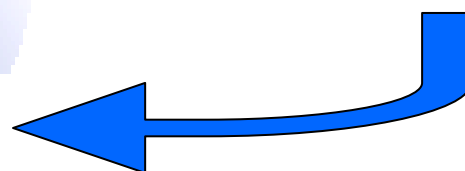
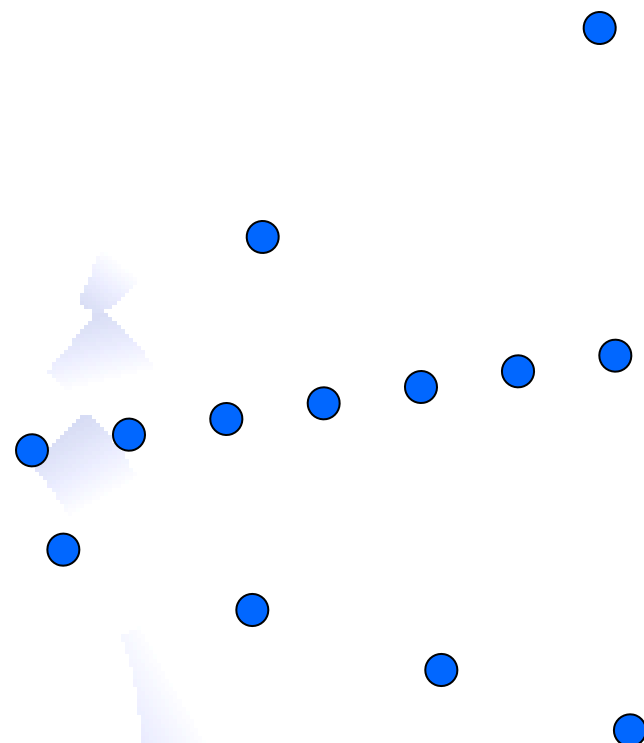
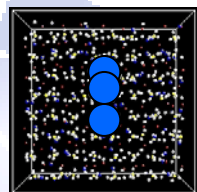
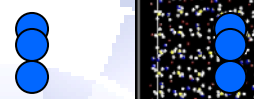
Fullerene



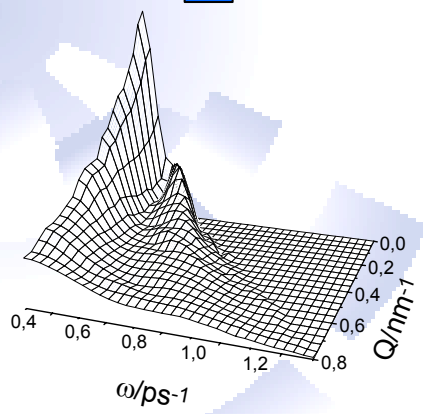
Neutron Diffraction







Inelastic Neutron Scattering



The Nobel Prize in Physics 1994

Neutrons behave as particles and as waves

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

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

Boris P. Bragg, McGill University, Montreal, Quebec, Canada, winner one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.

Neutrons reveal structure and dynamics

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

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

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

B Bragg made use of inelastic scattering (i.e. of neutrons which change both direction and energy when they collide with atoms. They then start to excite atomic oscillations in crystals and record neutrons in liquid and solids. Neutrons can also interact with spin waves in magnets.

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

Neutrons show where atoms are

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

When the neutron strikes with atoms in the sample material, the strong interaction just mentioned - elastic scattering.

Atoms in a crystalline sample

Research reactor

Scans spectrometer with neutron source and sensitive camera

Atoms in a liquid sample

When the neutrons penetrate the sample they start to excite vibrations in the atoms. If the neutrons excite phonons or magnons they demonstrate how the energy flows through the lattice.

Changes in the energy of the neutrons are first measured in an analyzer or filter.

Counted the neutrons that scattered in a detector

Neutrons see more than X-rays

It can be used for structural studies by itself, or in combination with X-rays. With X-rays it is easier to see atoms than neutrons. However, for example, it is able to determine in one go the positions of both of atoms and nuclei.

Neutrons reveal laser stresses

A bulk of material which is subjected to a stress will show a change in the spacing between the atoms. Neutrons can be used to measure this change in spacing.

Neutrons show what atoms vibrate

At their nuclei neutrons vibrate. They are constantly in motion or they are in a state of rest. The neutrons can be used to measure the energy of these vibrations.

There is a neutron source in the reactor. The neutrons are produced by the fission of uranium. The neutrons are then directed to the sample.

... have in question

Thousands of neutrons are sent working in the same manner through the world. They are used to study the structure of matter. They are used to study the dynamics of matter. They are used to study the structure of matter. They are used to study the dynamics of matter.

KUNGLIGA VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

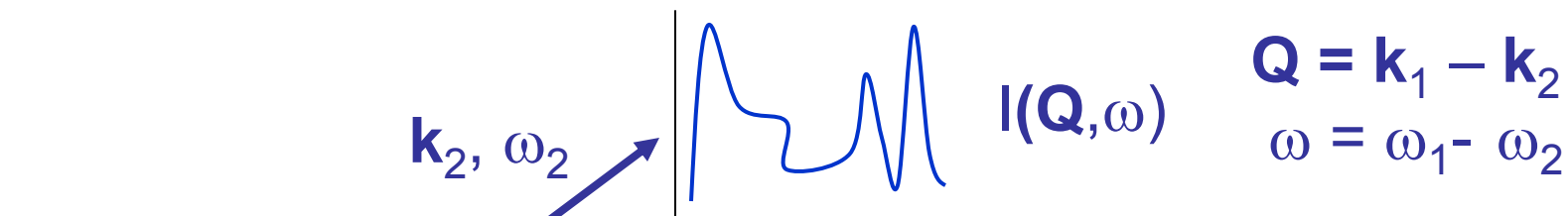
Further reading:

1. The Nobel Prize in Physics 1994. Stockholm: The Royal Swedish Academy of Sciences, 1994.

2. The Nobel Prize in Physics 1994. Stockholm: The Royal Swedish Academy of Sciences, 1994.

'Neutrons tell you where the atoms are and what the atoms do'

No they don't!



Measurement → Understanding

$I(\mathbf{Q}, \omega) \xrightarrow{\text{Corrections}} S(\mathbf{Q}, \omega) = \sum S_{AB}(\mathbf{Q}, \omega) \xrightarrow{\text{Separation}} G_{AB}(\mathbf{r}, t) \xrightarrow{\text{Transform}} r_i(t)$

Corrections

Separation

Transform

?

Constant b

Isotopic substitution

Wide (\mathbf{Q}, ω) range

Weak probe

Errors

Under defined
Poorly conditioned

Truncation

Phase problem

SO ...

Neutron scattering data analysis

is an

INVERSE

problem

$$I(\mathbf{Q}, \omega) \xrightarrow{\text{Corrections}} S(\mathbf{Q}, \omega) = \sum S_{AB}(\mathbf{Q}, \omega) \xrightarrow{\text{Separation}} G_{AB}(\mathbf{r}, t) \text{ --- } r_i(t)$$

Corrections

Separation

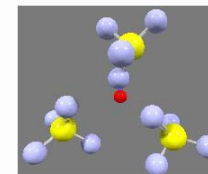
Transform

Errors

**Under defined
Poorly conditioned**

Truncation

Phase problem



$$I(\mathbf{Q}, \omega) \longrightarrow S(\mathbf{Q}, \omega) = \sum S_{AB}(\mathbf{Q}, \omega) \longrightarrow G_{AB}(\mathbf{r}, t) \text{ --- } r_i(t)$$

Corrections

Separation

Transform

Errors

**Under defined
Poorly conditioned**

Truncation

Phase problem

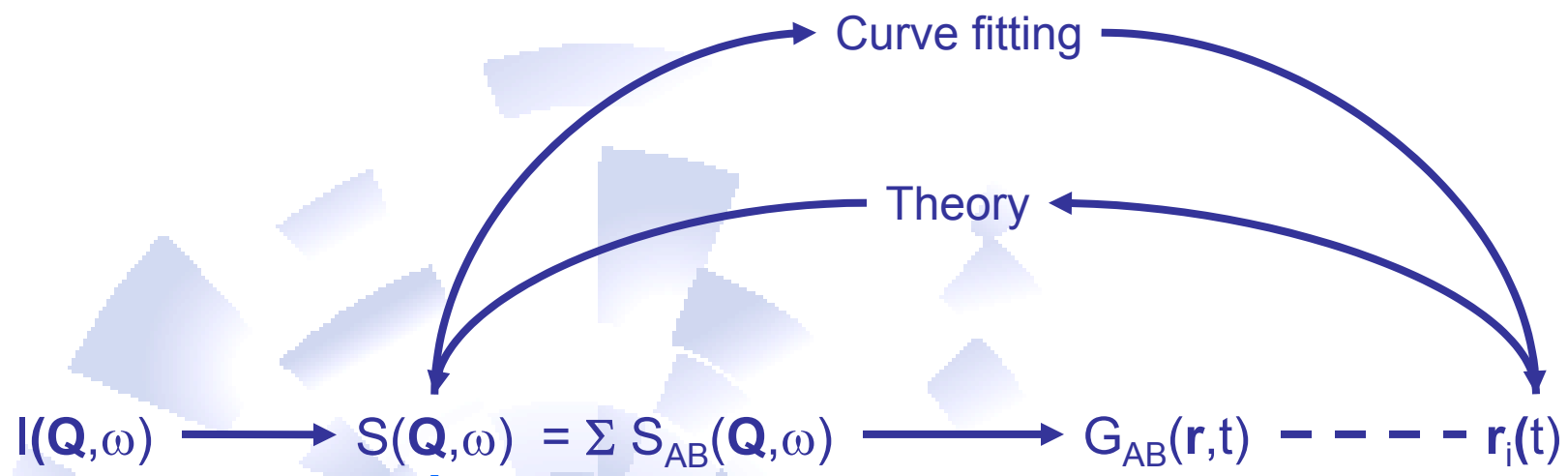
$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} S(\mathbf{Q}, t) dt \quad S(\mathbf{Q}, t) = \int e^{i\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, t) d\mathbf{r}$$

$$S(\mathbf{Q}) = S(\mathbf{Q}, \omega = 0) = \int S(\mathbf{Q}, t) dt = \frac{1}{N} \sum_{j, j'} \int \langle e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{Q} \cdot \mathbf{R}_{j'}(t)} \rangle dt$$

$$S(\mathbf{Q}) = \frac{1}{N_c} e^{-WQ^2} \left| \sum_k e^{-i\mathbf{Q} \cdot \langle \mathbf{R}_k(t) \rangle} \right|^2$$

$$I(\theta) \propto F(\mathbf{Q}) = \int_{-\infty}^{\infty} S(\mathbf{Q}, \omega) d\omega = S(\mathbf{Q}, t = 0) = \int e^{i\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, t = 0) d\mathbf{r}$$

$$= \frac{1}{N} \sum_{j, j'} \langle e^{-i\mathbf{Q} \cdot (\mathbf{R}_j(0) - \mathbf{R}_{j'}(0))} \rangle = \frac{1}{N} \left| \sum_j e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} \right|^2$$



Corrections

Separation

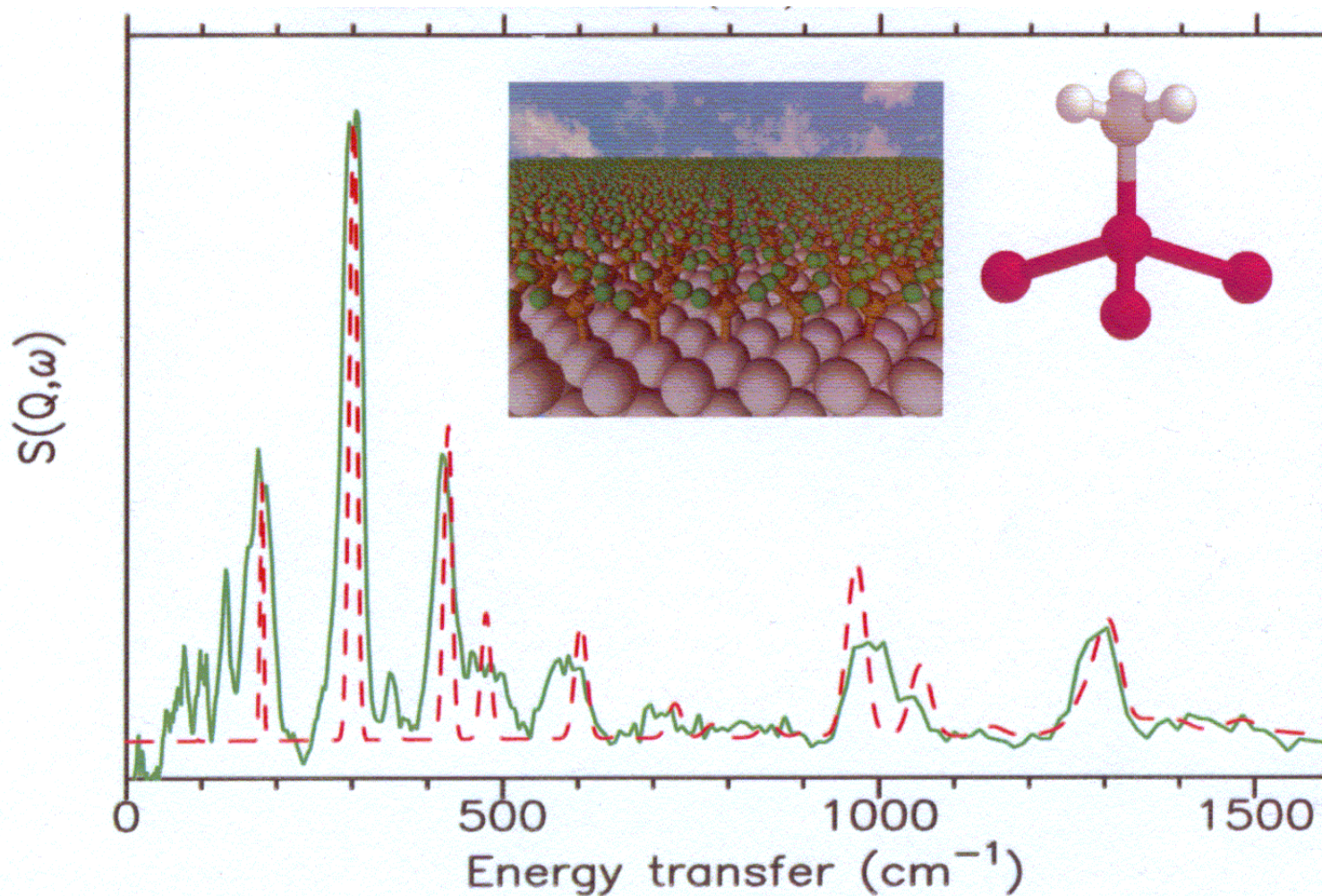
Transform

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Truncation

Phase problem



$$S(\omega) = \left[A_0 \delta(\omega) + \sum_{j=1}^N A_j \frac{\alpha_j}{\omega^2 + \alpha_j^2} \right] \otimes R(\omega) + \beta(\omega) + \gamma(\omega)$$

What is N ?

How big can we justifiably make N on the basis of the data?

D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992

Bayes theorem

$$\text{prob}(A_0, A_j, \alpha_j | N, d) \propto \text{prob}(d | A_0, A_j, \alpha_j, N) \times \text{prob}(A_0, A_j, \alpha_j | N)$$

Posterior

Likelihood function

Prior

If we assume a uniform prior (i.e. we don't know anything about the answer beforehand) and independent data (uncorrelated errors) then the most probable 'posterior' is just the 'best fit'.

But to fit we need to know N ...

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$$\text{prob}(N|d) \propto \text{prob}(d|N) \times \text{prob}(N)$$

$$\text{prob}(d|N) \propto \int \dots \int \text{prob}(d, A_0, A_j, \alpha_j | N) \partial A_0 \partial^N A_j \partial^N \alpha_j$$

$$\text{prob}(d|N) \propto \int \dots \int \text{prob}(d | A_0, A_j, \alpha_j, N) \times \text{prob}(A_0, A_j, \alpha_j | N) \partial A_0 \partial^N A_j \partial^N \alpha_j$$

If we assume no knowledge of N then

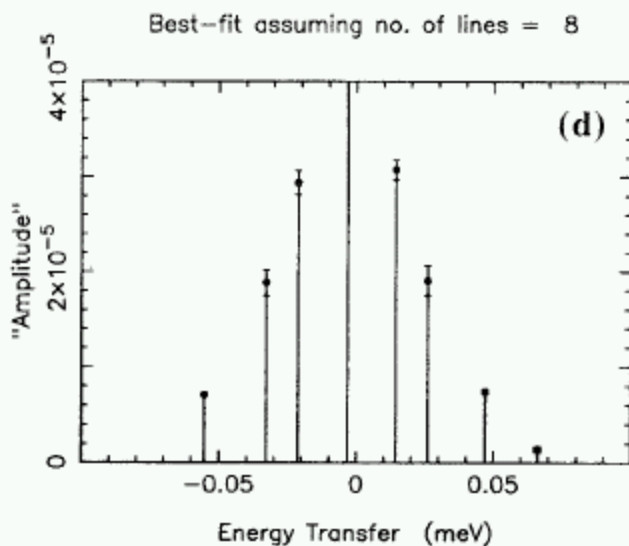
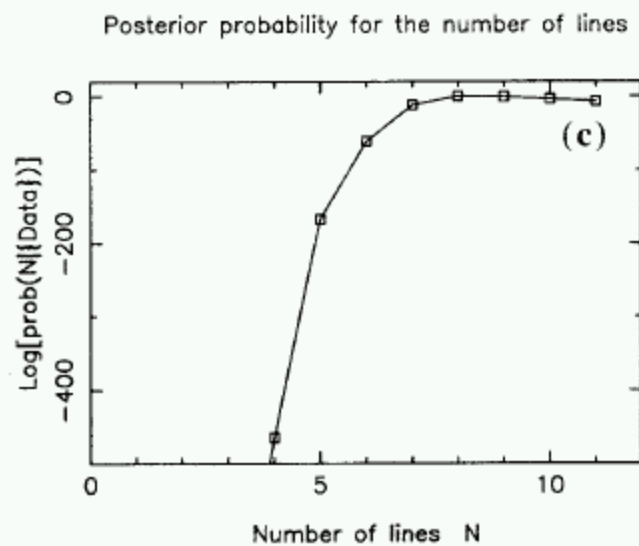
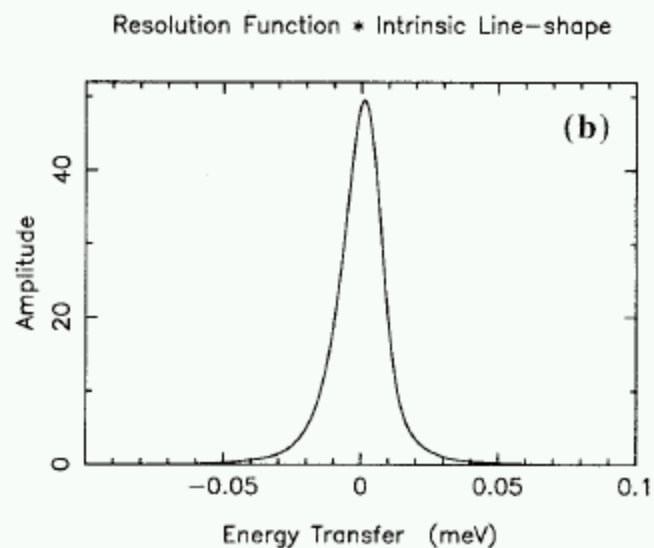
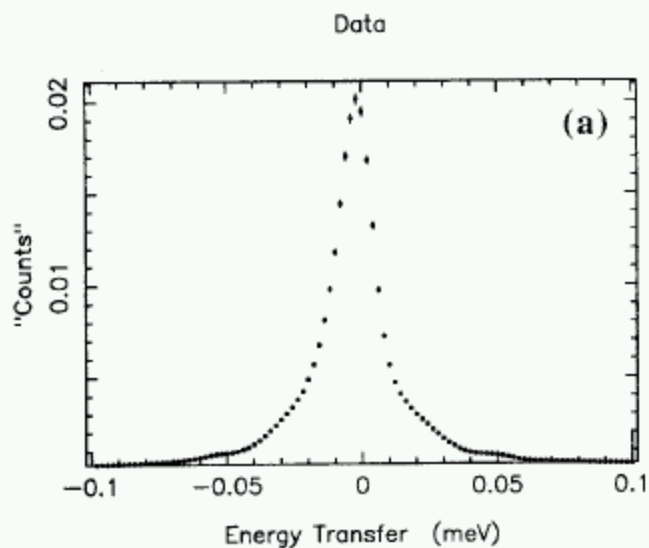
$$\text{prob}(N|d) \propto \text{prob}(d|N)$$

so

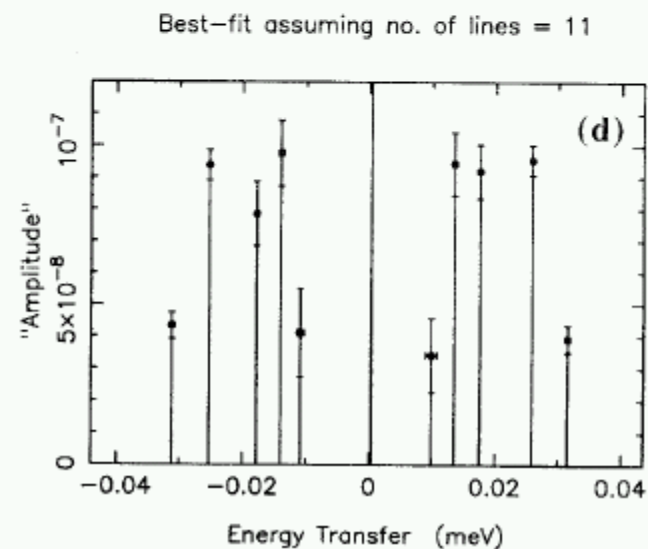
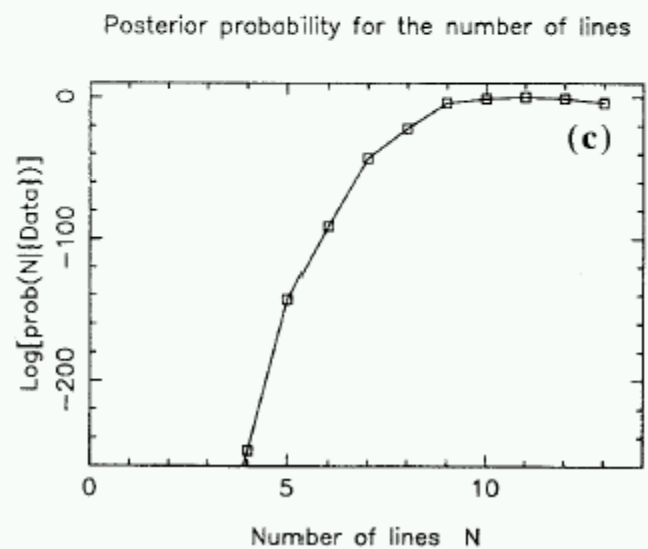
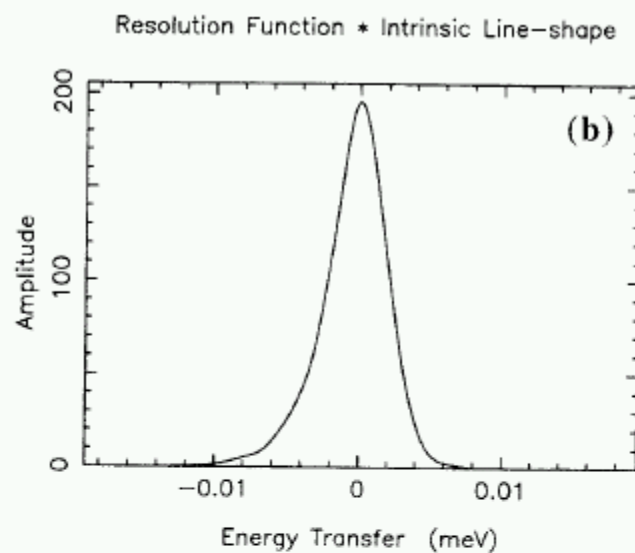
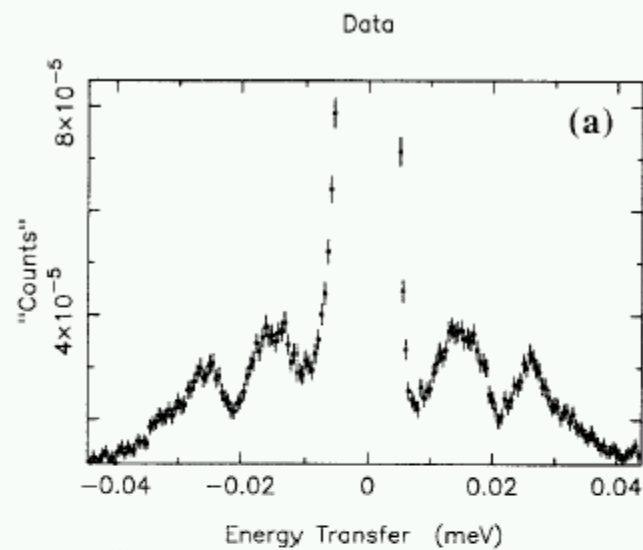
$$\text{prob}(N) = \text{uniform}$$

so calculate the integral above and then maximise

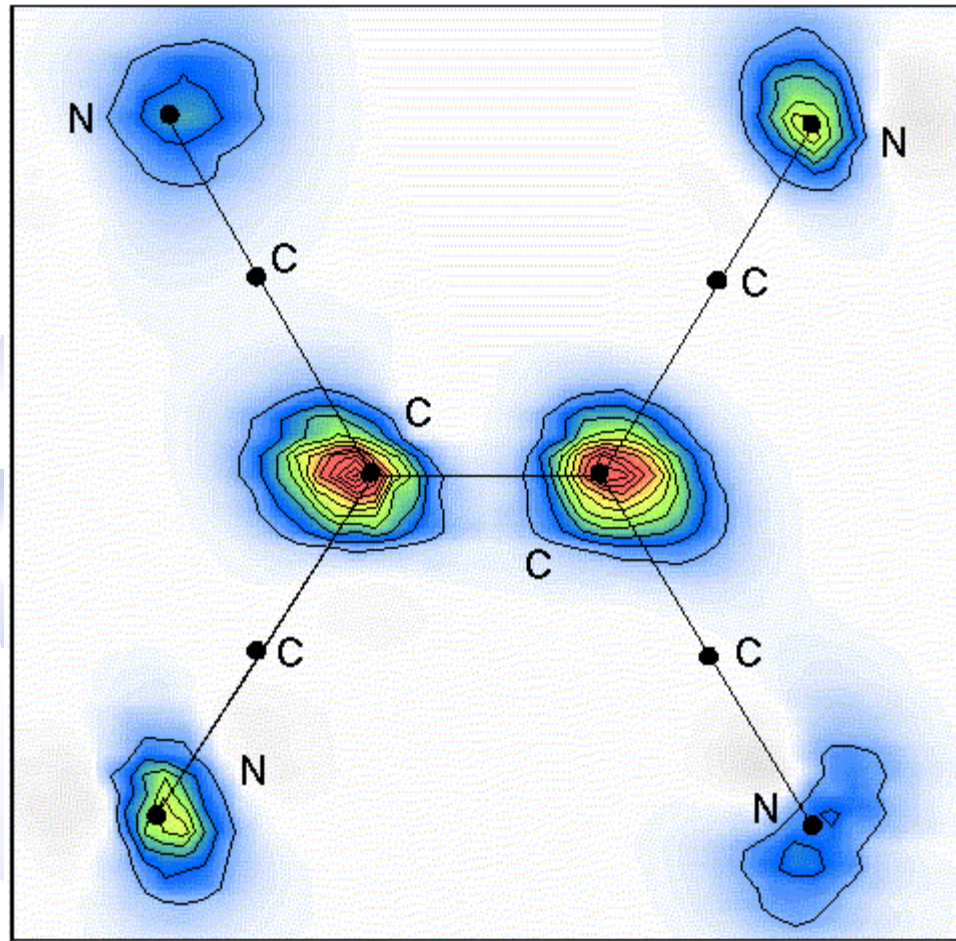
$$\text{prob}(N|d)$$



D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992

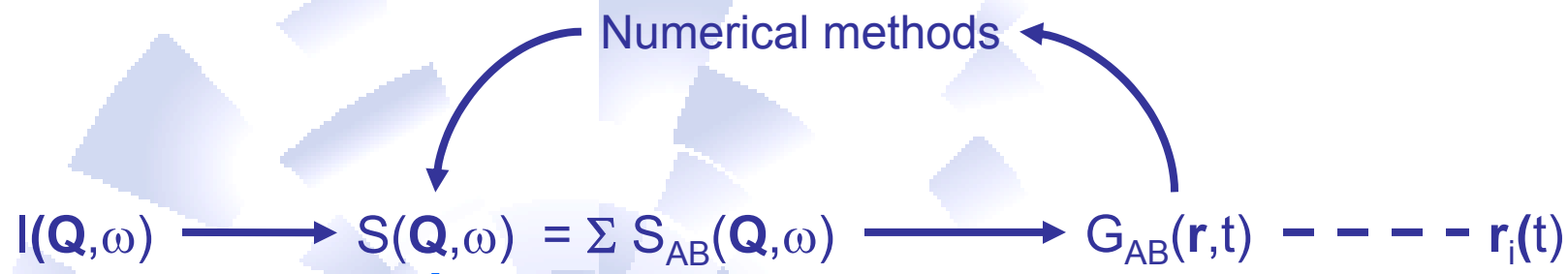


D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992



What not to do

Choose the prior to get the answer you want



Corrections

Separation

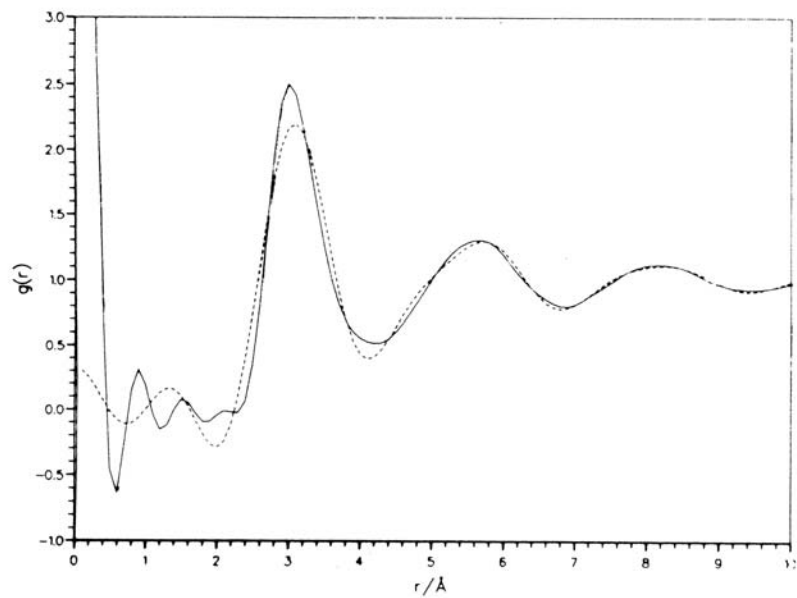
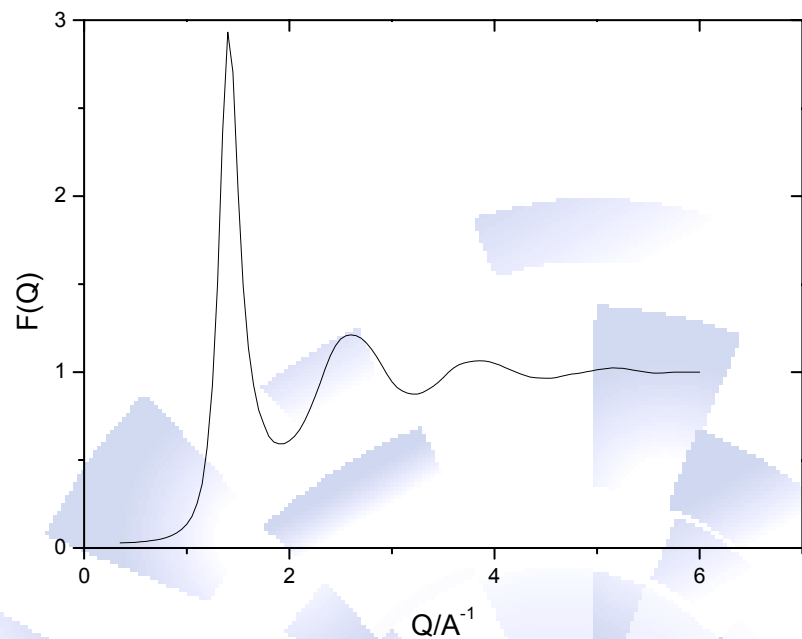
Transform

Errors

**Under defined
Poorly conditioned**

Truncation

Phase problem



Truncation
(limited data range)

'Smoothing'

$$n(r) = 4\pi r^2 \rho g(r)$$

$$H = -\sum n(r) \ln(n(r) / p(r))$$

'Flattest' (Max. Ent.)

$$H' = \sum w(r) d''(r)$$

$$d(r) = n(r) - p(r)$$

'Least noisy'

$$I = \int (1 + d'^2(r))^{1/2} \partial r$$

'Shortest line'

$$I(\mathbf{Q}, \omega) \xrightarrow{\text{Corrections}} S(\mathbf{Q}, \omega) = \sum S_{AB}(\mathbf{Q}, \omega) \xrightarrow{\text{Separation}} G_{AB}(\mathbf{r}, t) \text{ --- } r_i(t)$$

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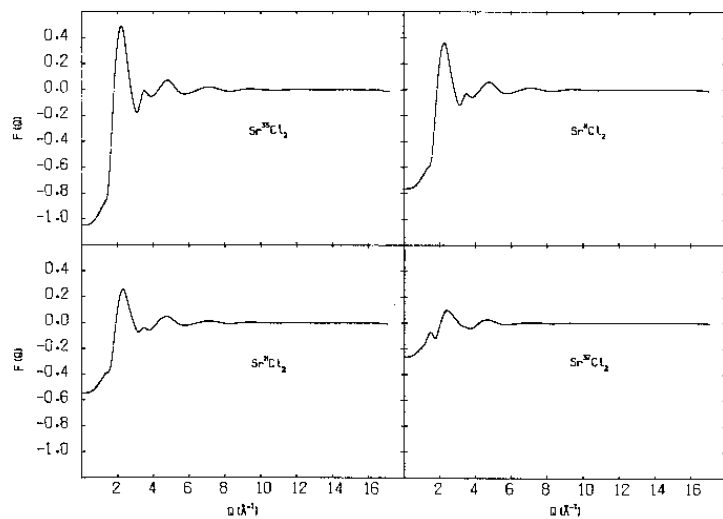
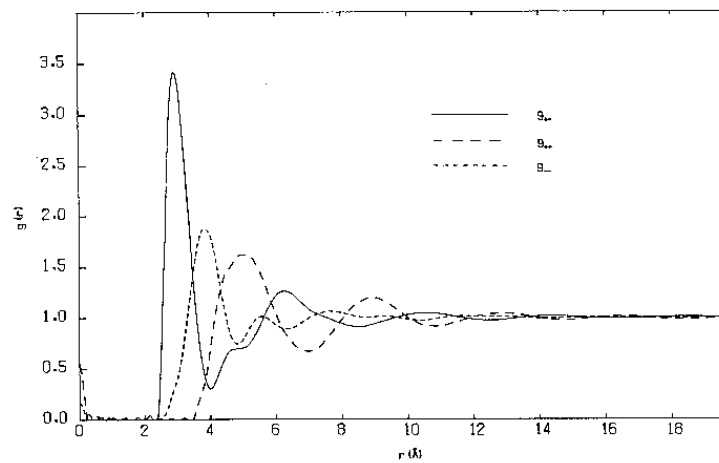
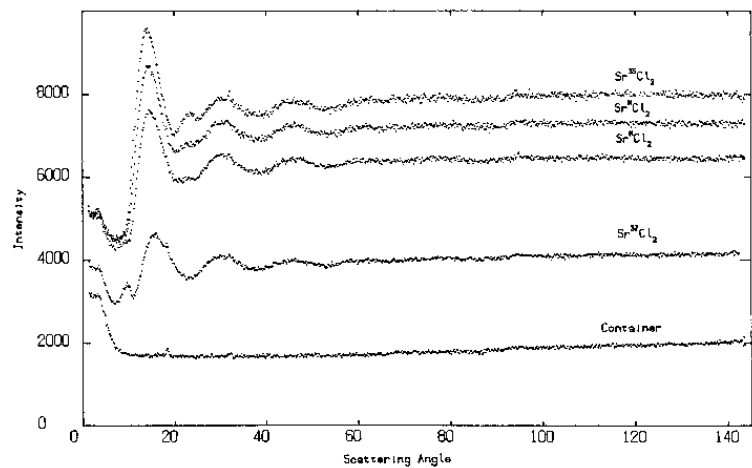
$$F^{(k)}(Q) = \sum_{\alpha} \sum_{\beta} c_{\alpha\beta}^{(k)} (A_{\alpha\beta}(Q) - 1)$$

$$\vec{F} = \mathbf{C} \vec{A} \quad \vec{A} = \mathbf{C}^{-1} \vec{F}$$

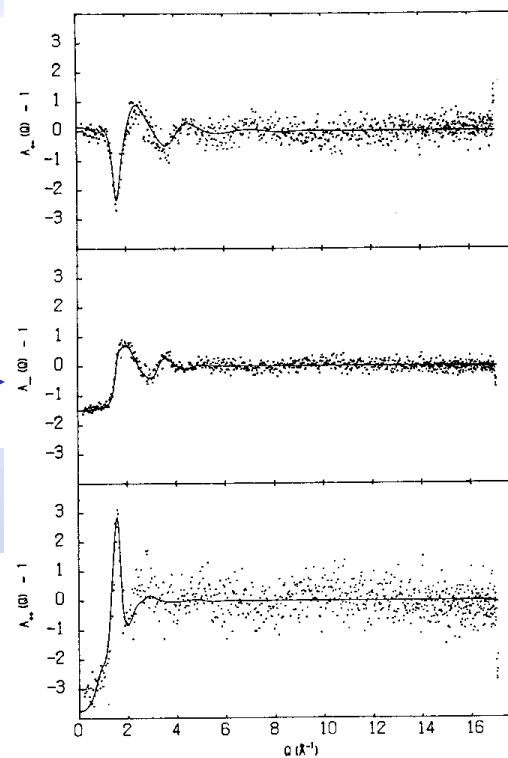
Make a set of measurements with varying coefficients $c_{\alpha\beta}^{(k)}$ (isotopic substitution, anomalous scattering, EXAFS) and solve

\mathbf{C} is poorly conditioned (nearly singular), so small errors in F lead to large errors in A

The Turing M conditioning number is a measure of the conditioning of matrix \mathbf{C}



M=35

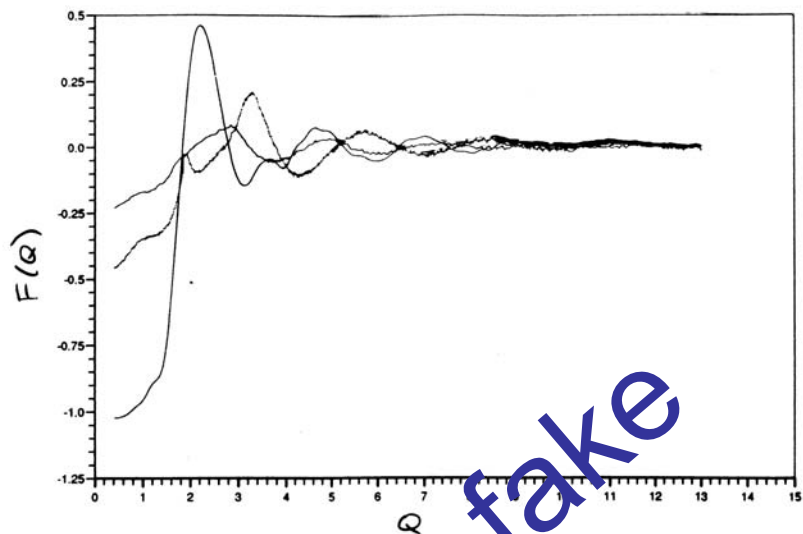


0.136538 0.200896 0.168601
 0.754507 0.657018 0.704565
 0.641932 0.726614 0.68932

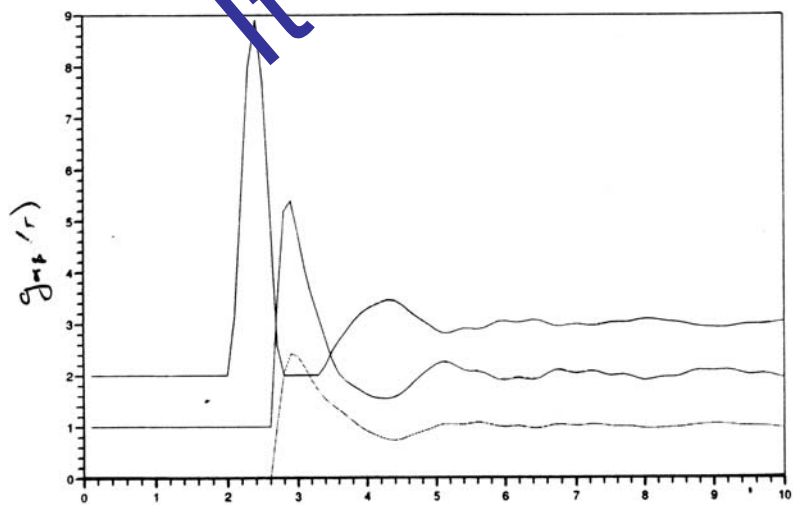
162.8921 44.0622 -84.87856571
 187.0622 38.92702 -85.54158763
 -348.8769 -82.06621 170.6639011

841.7145

TITLE: QF1,F2,F3
 PLOTTED: 13-AUG-1992 140332 by process Robert
 FILE: qf3.dat

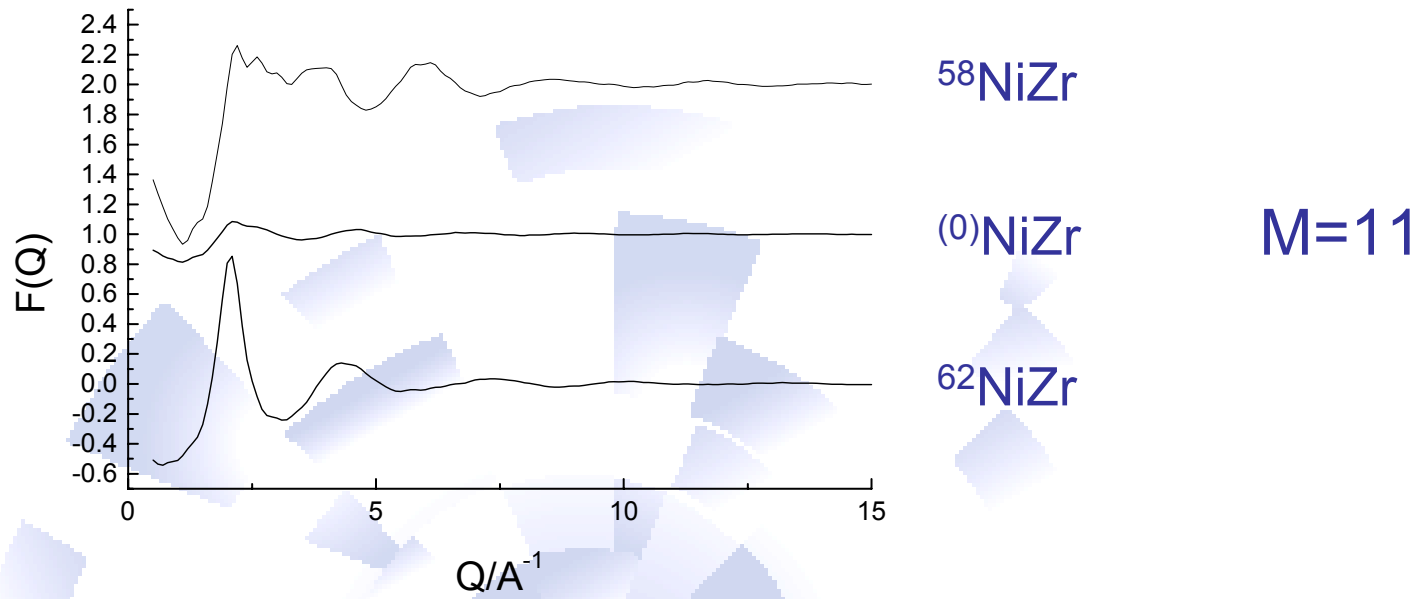


TITLE: ~~g(r)~~
 PLOTTED: 13-AUG-1992 140408 by process Robert
 FILE: g12.dat

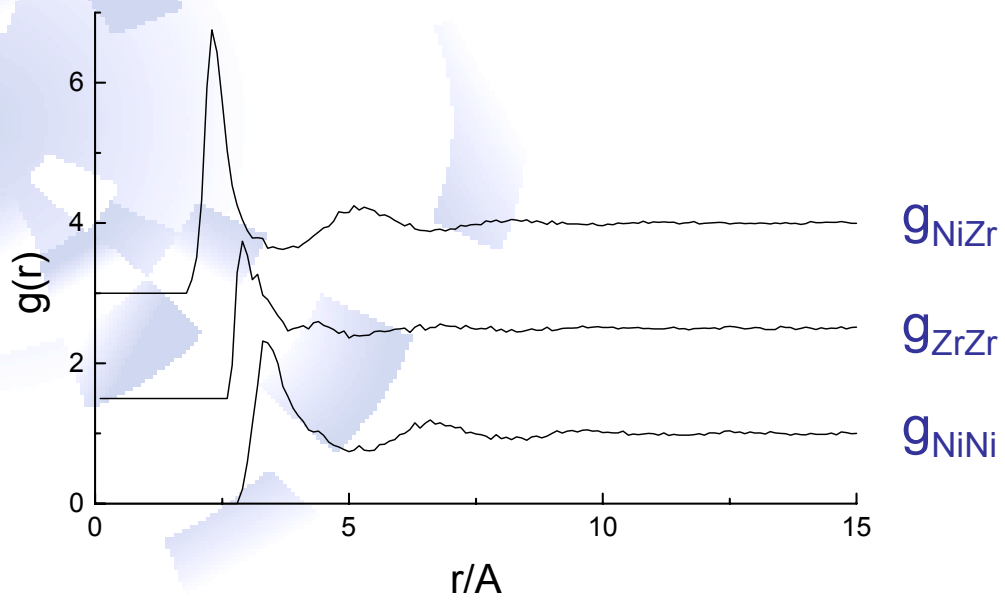


It's a fake

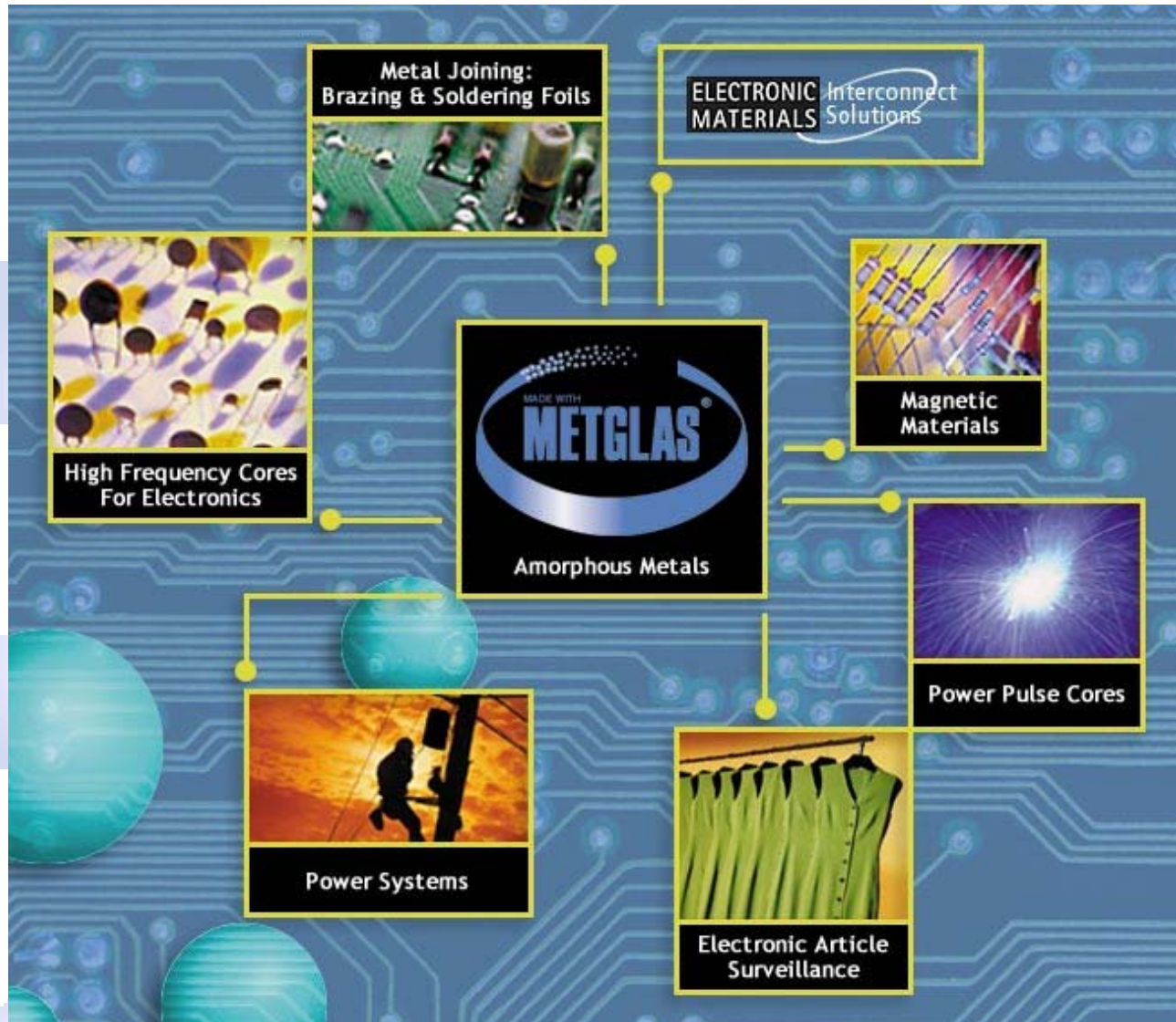
Metallic glass: NiZr



M=11



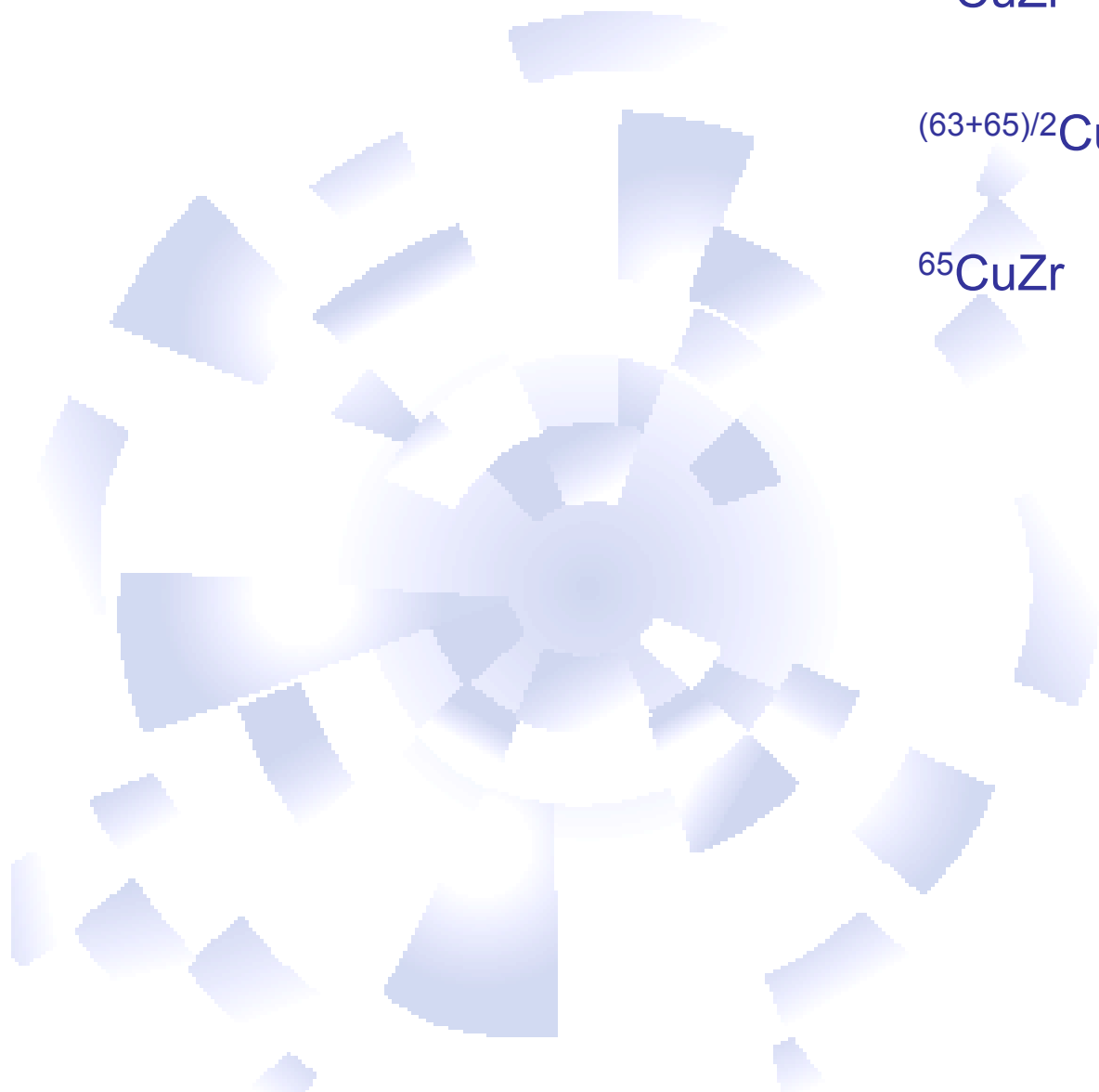
Metallic glasses



Metallic glasses



Metallic glass: CuZr



$^{63}\text{CuZr}$

$(^{63}+^{65})/2\text{CuZr}$

$M=286$

$^{65}\text{CuZr}$

$$c^{(k)} = \begin{pmatrix} c_{11} \\ c_{12} \\ \cdot \\ \cdot \\ c_{nn} \end{pmatrix}$$

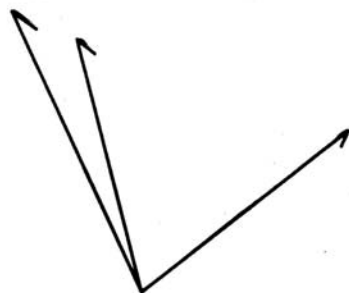
$$\hat{c}^{(k)} = c^{(k)} / \sum c_{\alpha\beta}^2$$

$$\theta_{jk} = \cos^{-1}(\hat{c}^{(j)} \cdot \hat{c}^{(k)})$$

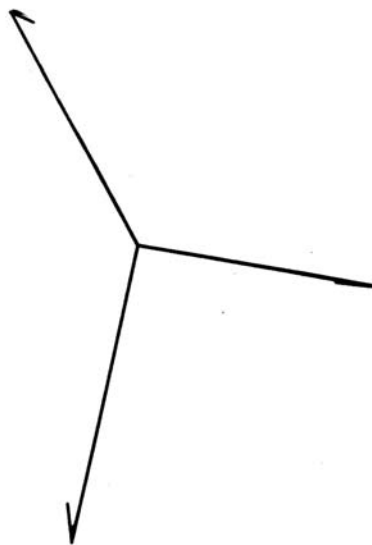
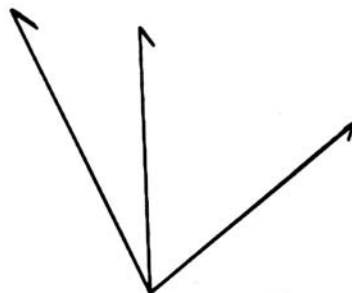
θ_{jk} is a measure of the relative information content
in $F^{(j)}(Q)$ and $F^{(k)}(Q)$

(90° is good!)

NiZr neutron + Ni/Zr EXAFS



CuZr neutron + Cu/Zr EXAFS



NiZr neutron isotopes

CuZr neutron isotopes

$$I(\mathbf{Q}, \omega) \longrightarrow S(\mathbf{Q}, \omega) = \sum S_{AB}(\mathbf{Q}, \omega) \longrightarrow G_{AB}(\mathbf{r}, t) \text{ --- } r_i(t)$$

Corrections

Separation

Transform

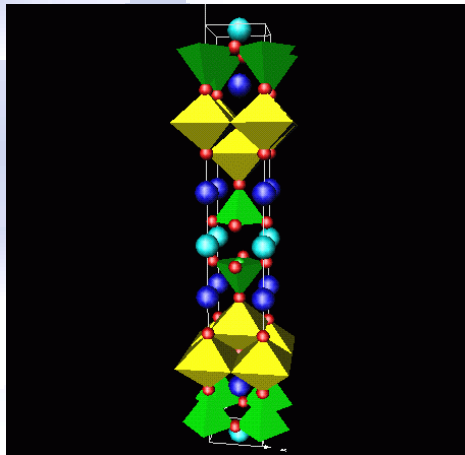
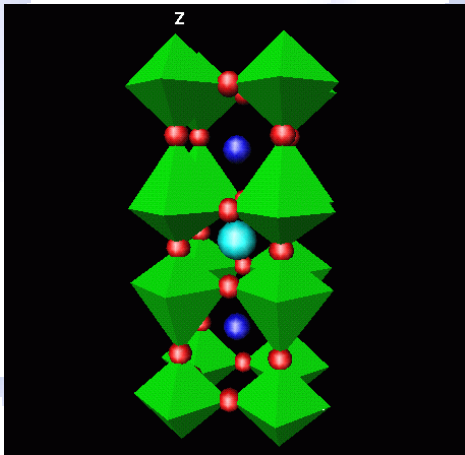
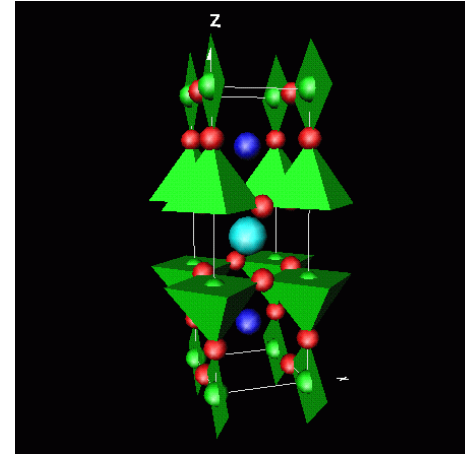
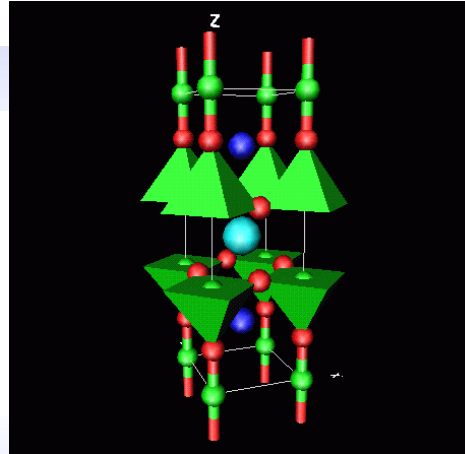
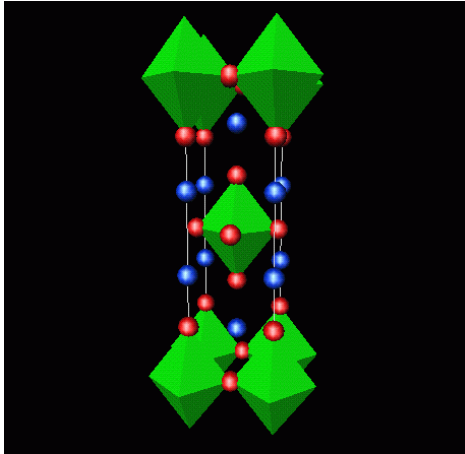
Errors

**Under defined
Poorly conditioned**

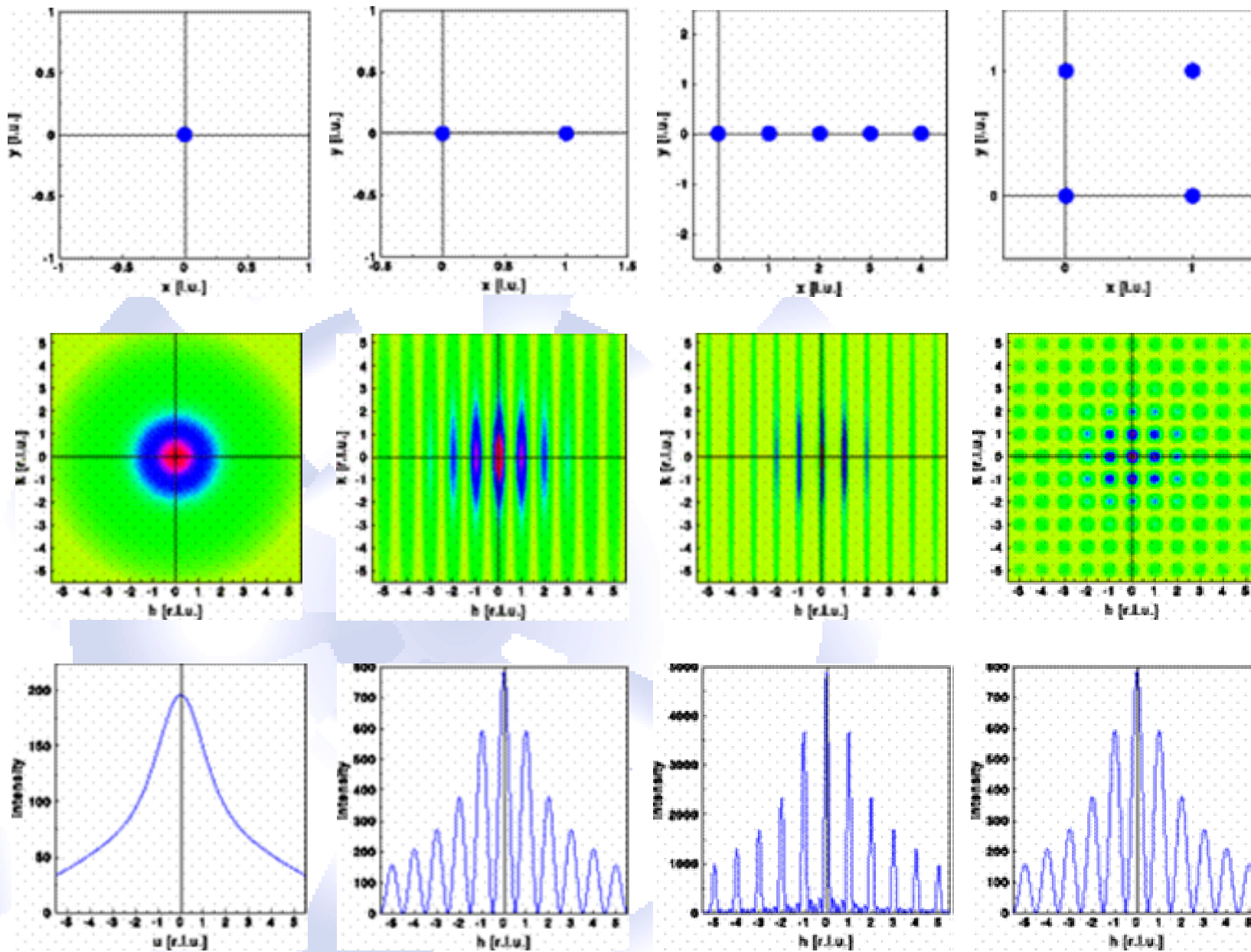
Truncation

Phase problem

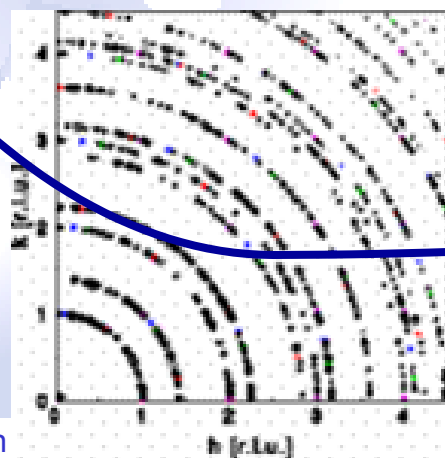
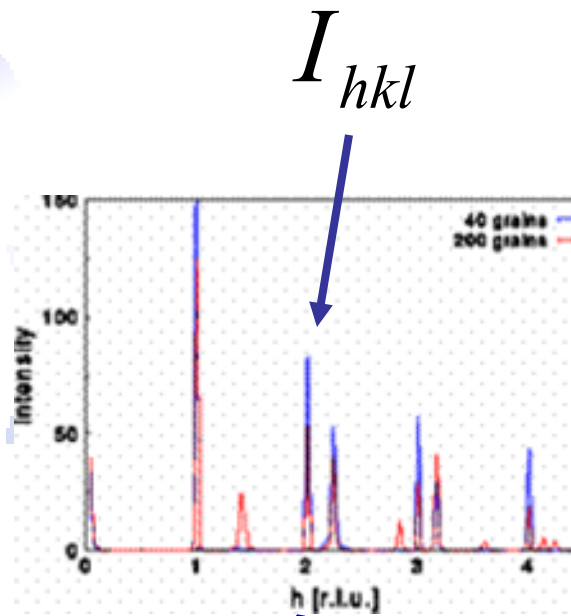
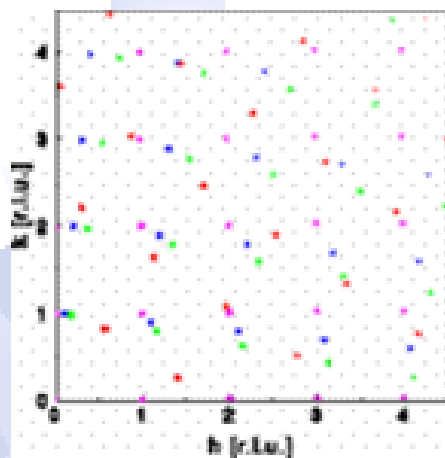
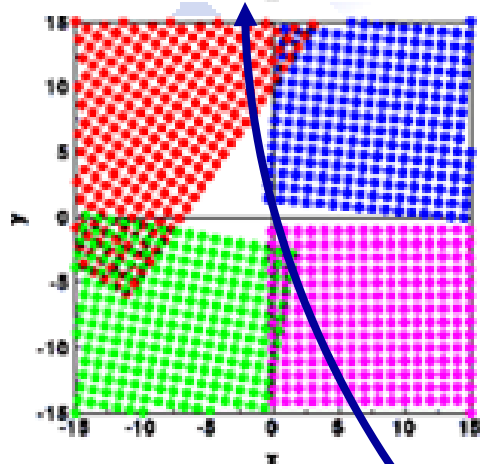
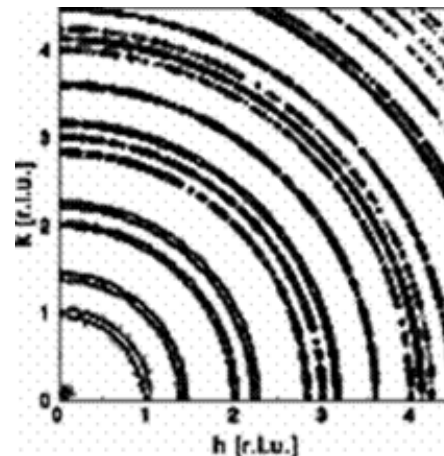
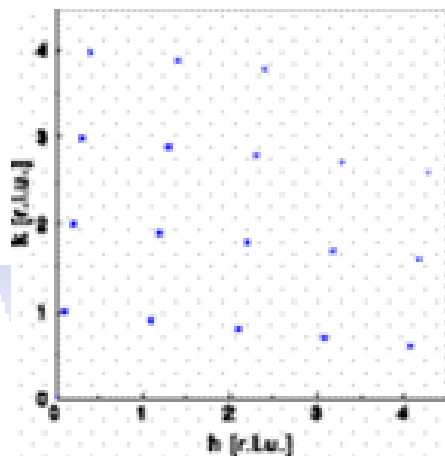
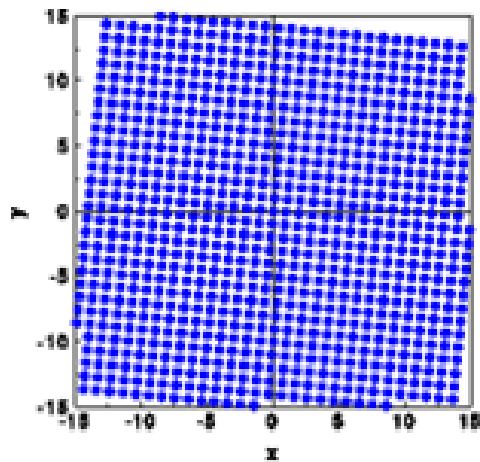
SO ...



High temperature superconductors

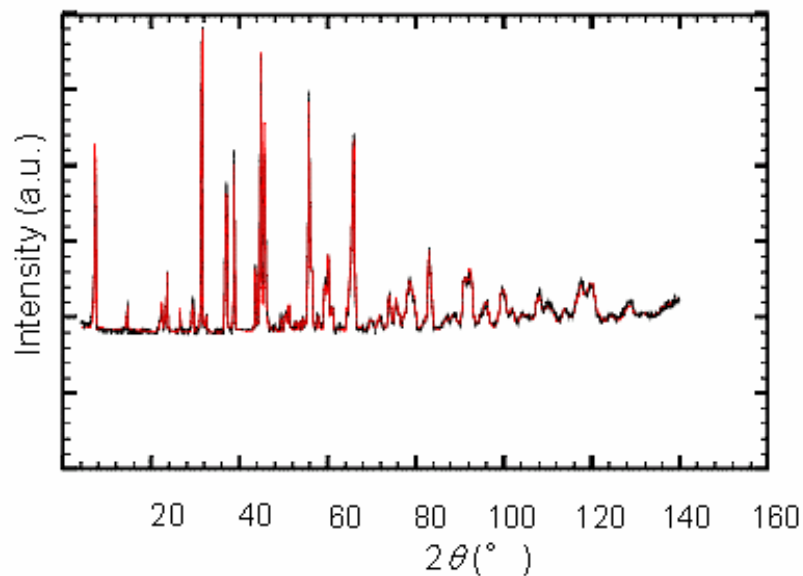


Figures courtesy of Thomas Proffen



Figures courtesy of Thomas Proffen

$$I_{hkl} \propto |F_{hkl}^2|$$



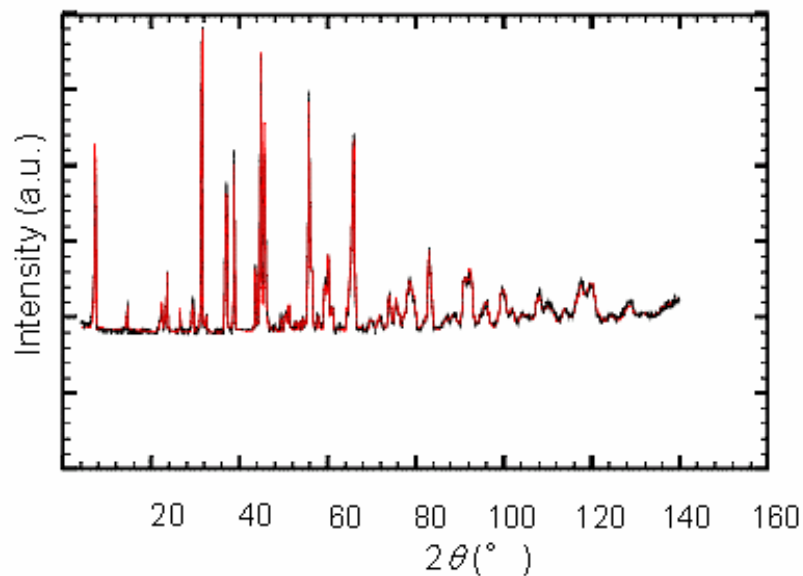
$$F_{hkl} = \sum_{j=1}^{N_j} b_j \exp(2\pi i(hx_j + ky_j + lz_j))$$

$$F_{hkl} = \sum_{j=1}^{N_j} b_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{s}_{hkl})$$

$$\mathbf{r}_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$$

$$\mathbf{s}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

Rietveld refinement (parametric modeling)



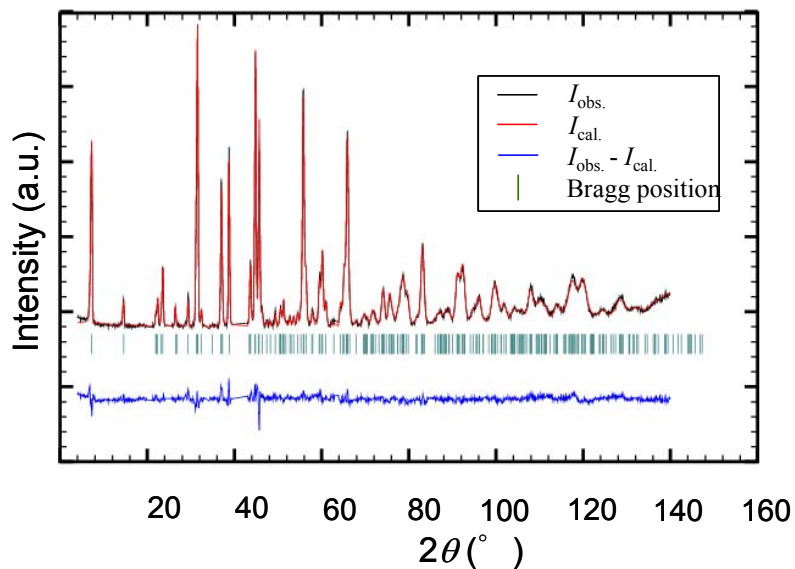
$$y_i^c = s \sum_{hkl} L_{hkl} |F_{hkl}|^2 \phi(2\theta_i - 2\theta_{hkl}) P_{hkl} A + y_i^b$$

$$s_y = \sum_i w_i (y_i - y_i^c)^2$$

Name	x	y	z	B	occ.	Mult
Yb	0.50000	0.50000	0.50000	0.244	1.000	1
Sr	0.50000	0.50000	0.18448	0.971	0.452	2
Ba	0.50000	0.50000	0.18448	0.971	0.548	2
Cu1	0.00000	0.00000	0.00000	0.335	1.000	1
Cu2	0.00000	0.00000	0.35540	0.095	1.000	2
O1	0.00000	0.50000	0.00000	0.100	0.914	1
O2	0.50000	0.00000	0.37812	0.448	1.000	2
O3	0.00000	0.50000	0.38058	0.583	1.000	2
O4	0.00000	0.00000	0.16120	0.895	1.000	2
O5	0.50000	0.00000	0.00000	0.100	0.013	1

Cell parameters : 3.78672 3.85536 11.58989
 90.00000 90.00000 90.00000
 Overall scale factor : 5.364356990 0.041989010
 Eta(p-v) or m(p-vii) : 0.32626 0.01554
 Overall tem. factor : 0.00000 0.00000
 Halfwidth parameters : 1.64226 -0.93251 0.22901
 Asymmetry parameters : 0.08420 0.02110

GLOBAL PARAMETERS
 Zero-point: -0.0016 0.0028
 Background Polynomial Parameters
 757.356 -10.6976 0.243093 -0.211296E-02 0.664176E-05

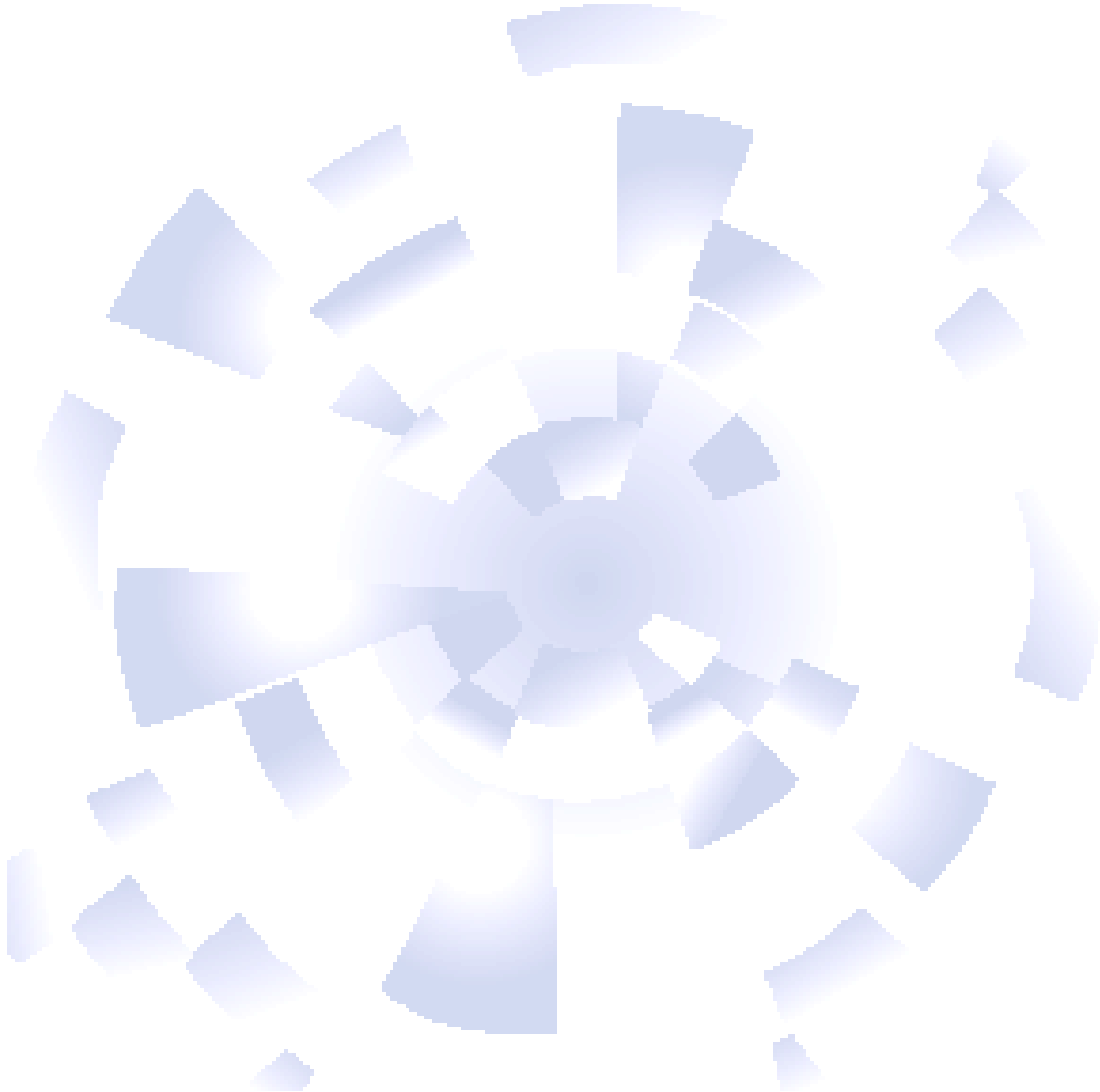


$$R_p = 4.17, R_{wp} = 5.47, \chi^2 = 3.68$$

Constrained Rietveld refinement

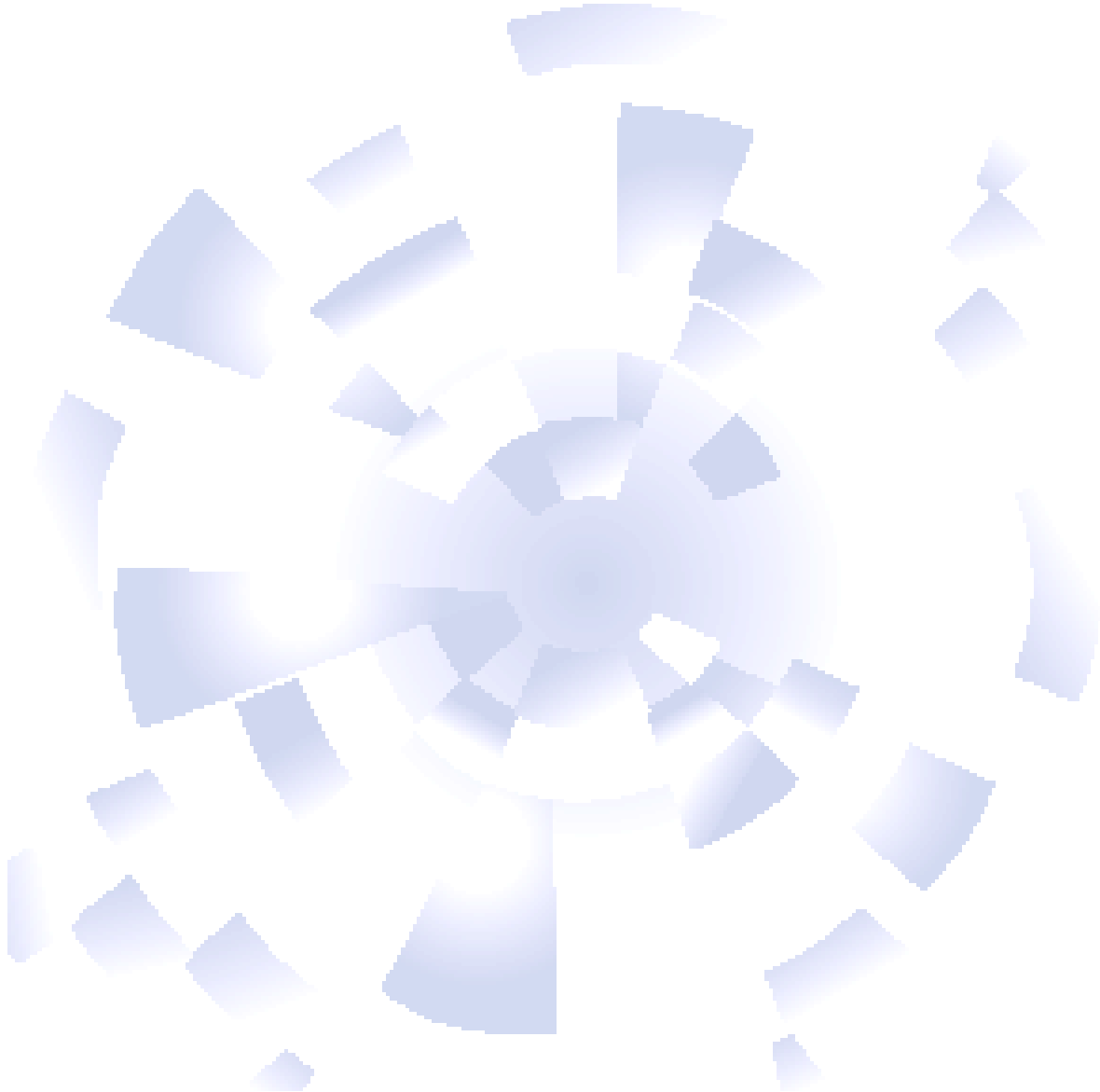
Simulated annealing (Monte Carlo)

$$\sum_i w_i (y_i - y_i^c)^2$$



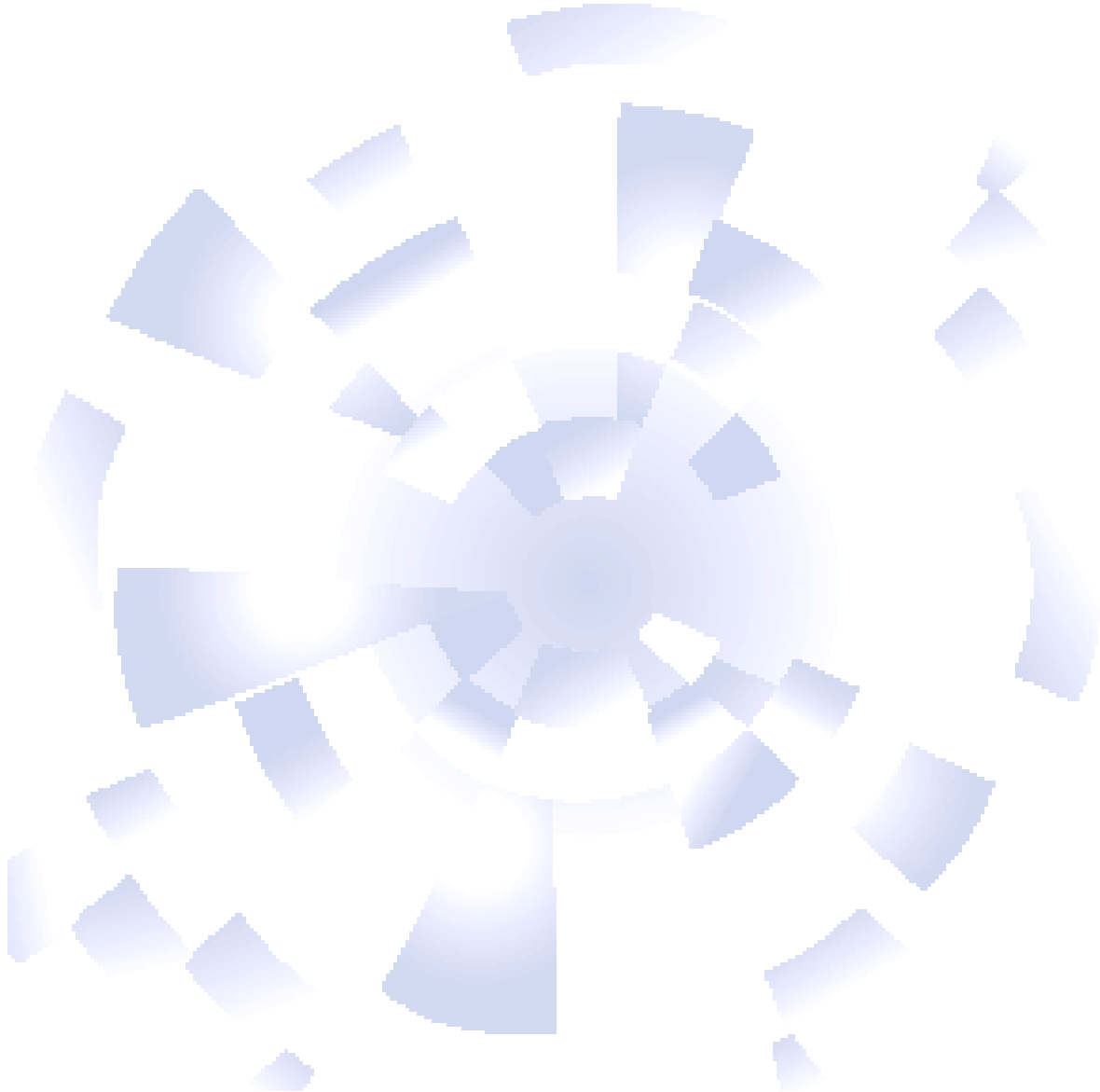
Simulated annealing (Monte Carlo)

$$\exp\left(-\sum_i w_i (y_i - y_i^c)^2\right)$$



Simulated annealing (Monte Carlo)

$$\exp\left(-\sum_i (y_i - y_i^c)^2 / T\right)$$



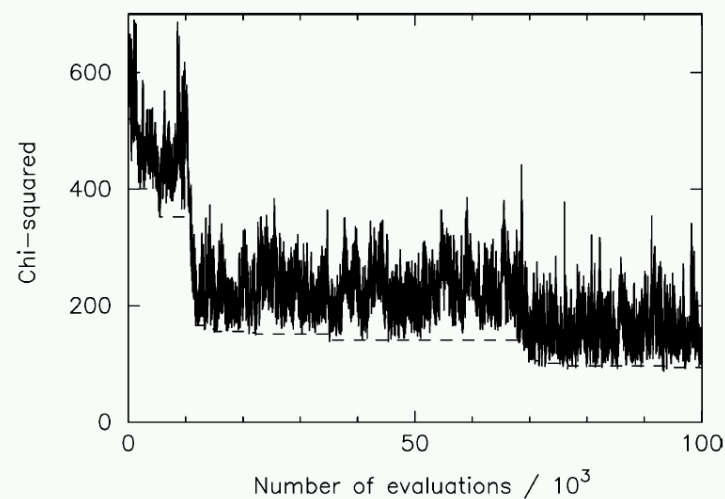
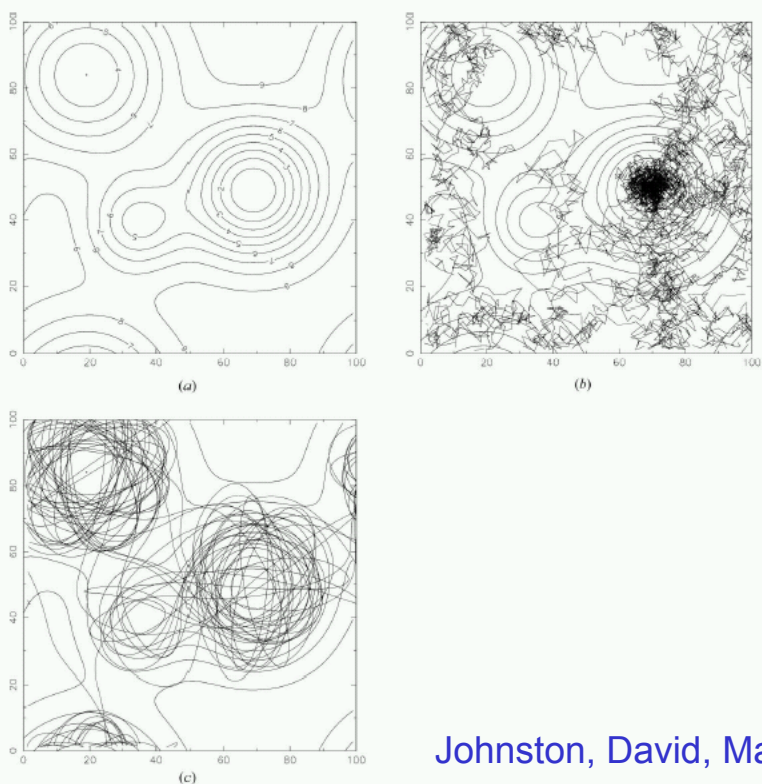
Simulated annealing (Monte Carlo)

Hybrid Monte Carlo (molecular dynamics)

$$\exp\left(-\sum_i (y_i - y_i^c)^2 / T\right)$$

$$H(t) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2(t) + \chi^2(\mathbf{r}(t))$$

$$\exp(-(E_m - E_0) / T)$$



Johnston, David, Markvardsen, Shankland. *Acta Cryst A* **58** 441 2002

α -AgI

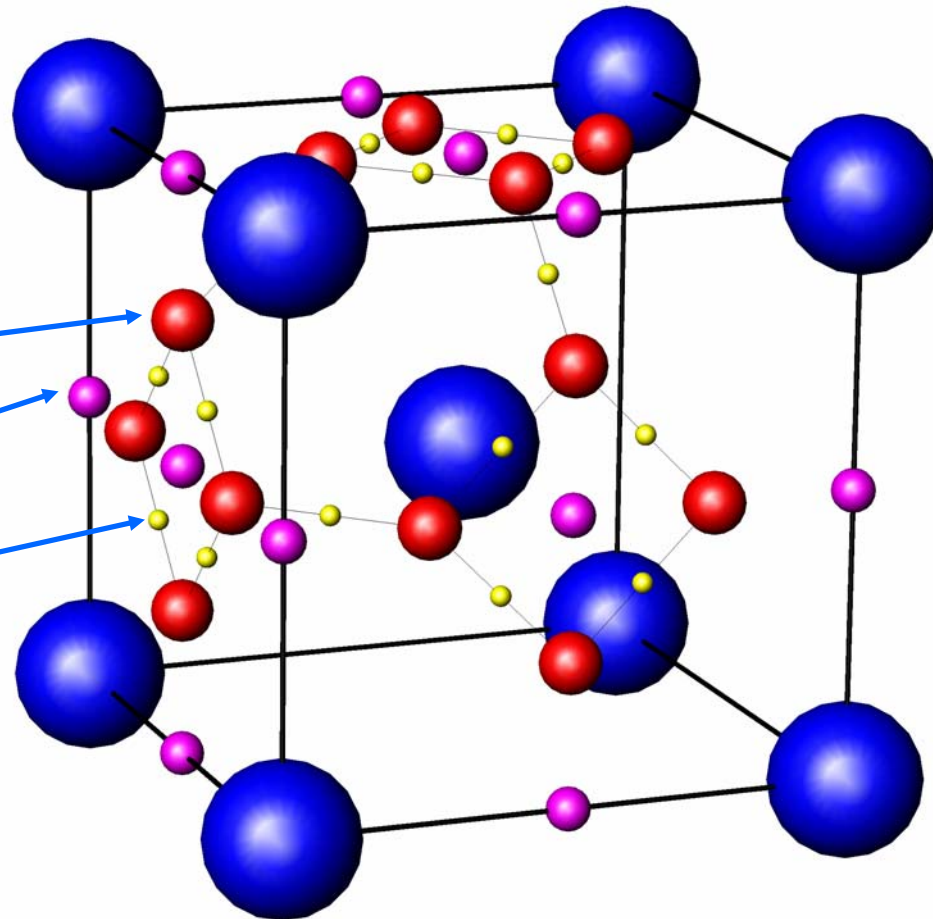
b.c.c. I⁻

Ag⁺ sites.....

12 × tetrahedral

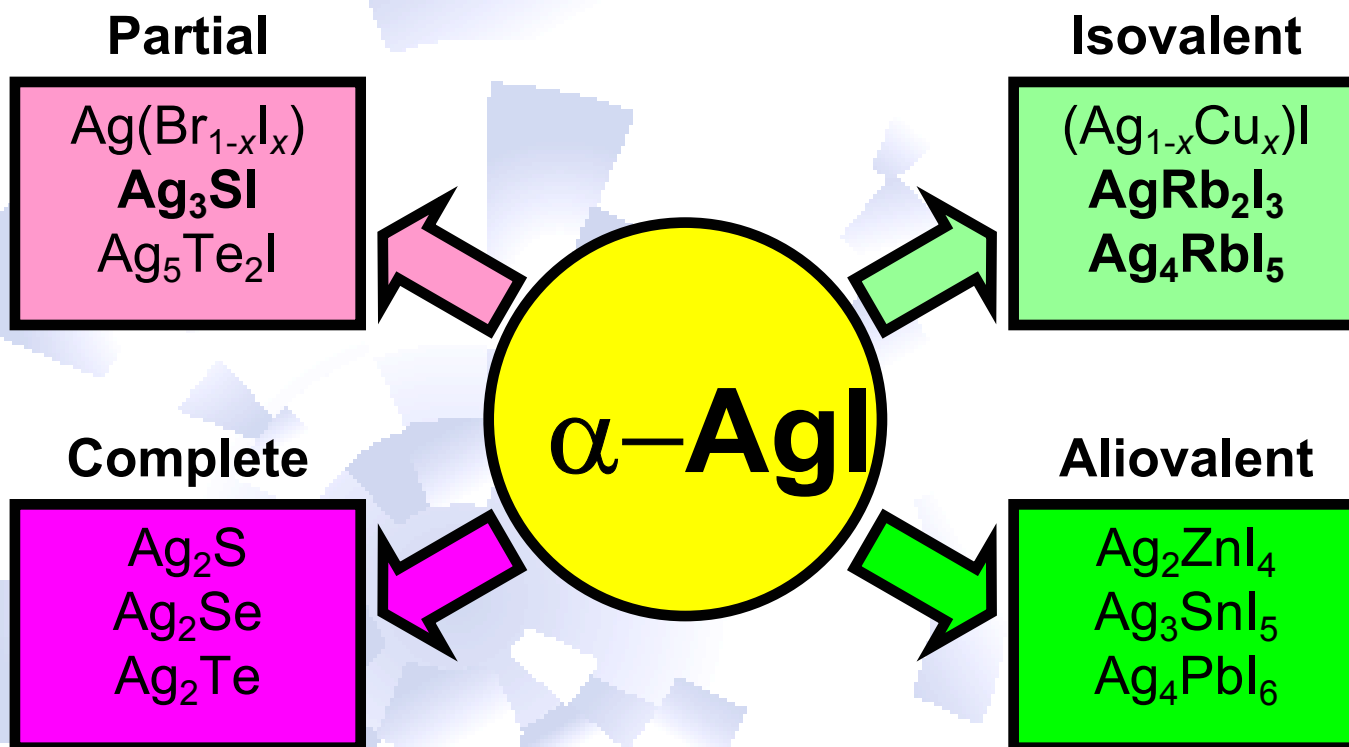
6 × octahedral

24 × trigonal



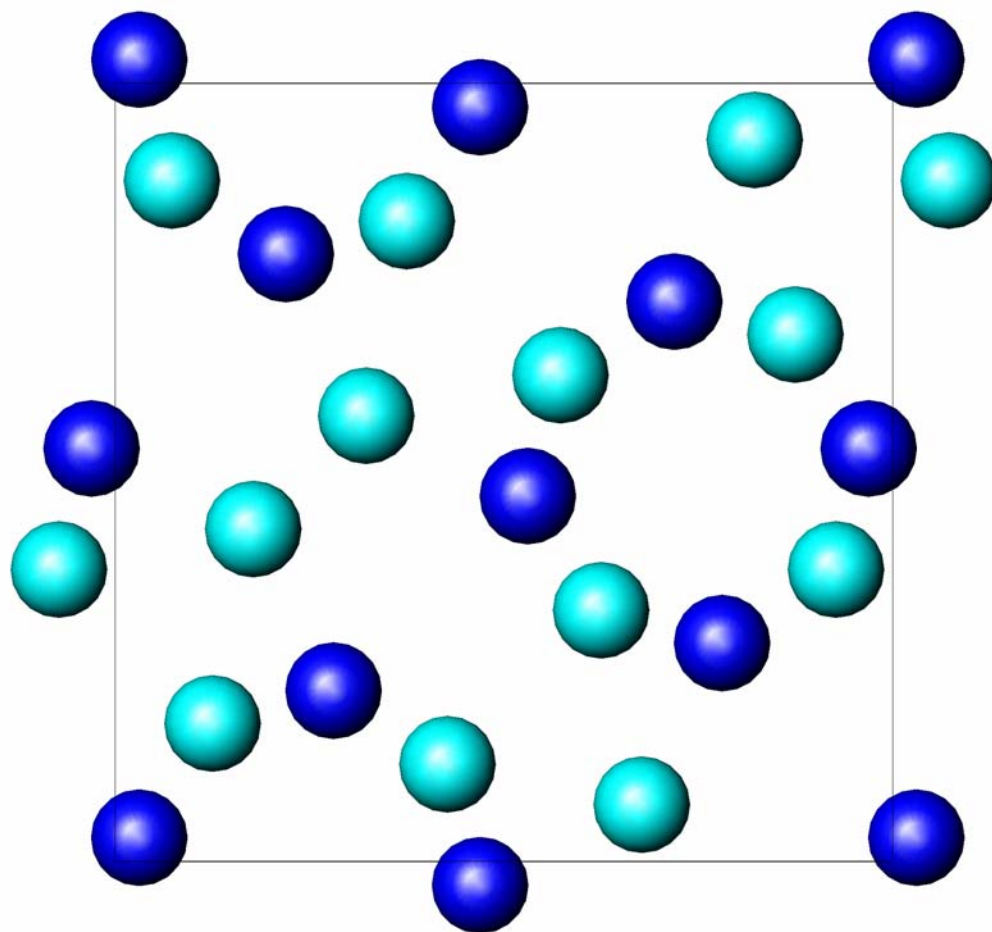
ANION REPLACEMENT

CATION REPLACEMENT



AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : IODINE SUBSTRUCTURE



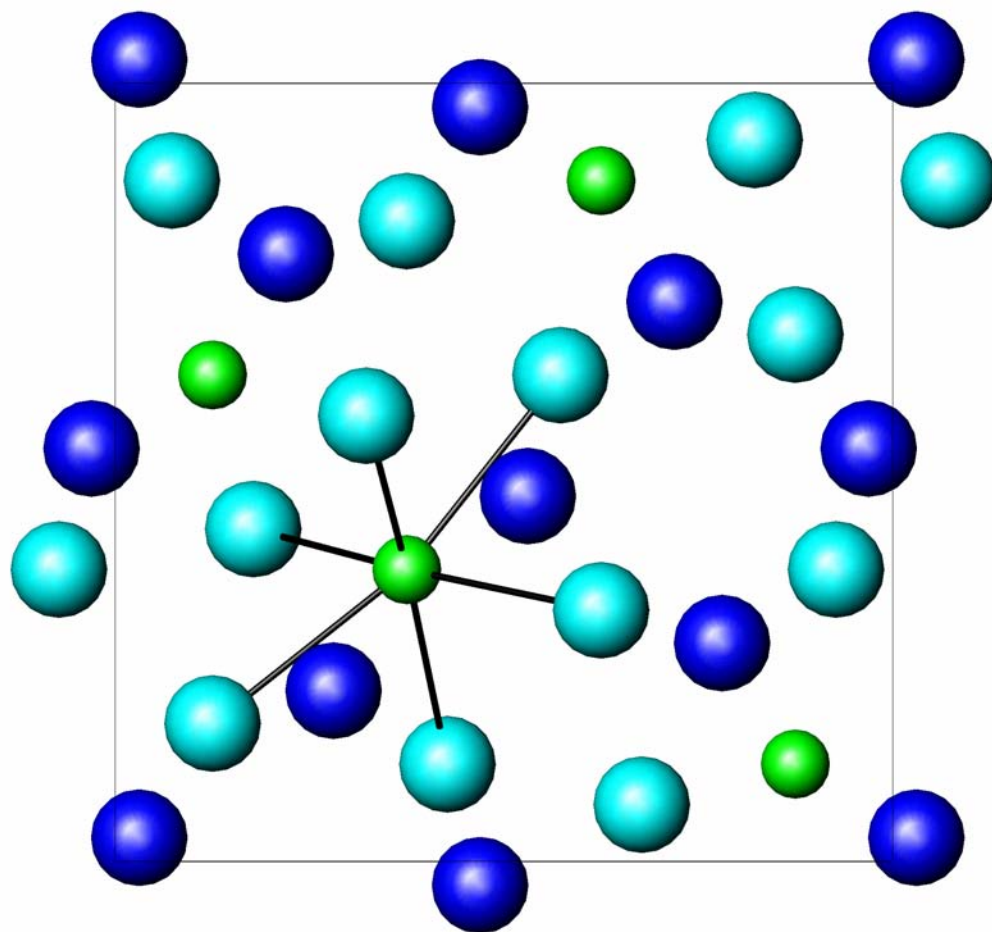
P 4₁32
a ~11.24Å

I1 in 8(c)
x,x,x
x~0.031

I2 in 12(d)
 $\frac{1}{8}, y, \frac{1}{4} + y$
y~0.177

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Rb POSITIONS

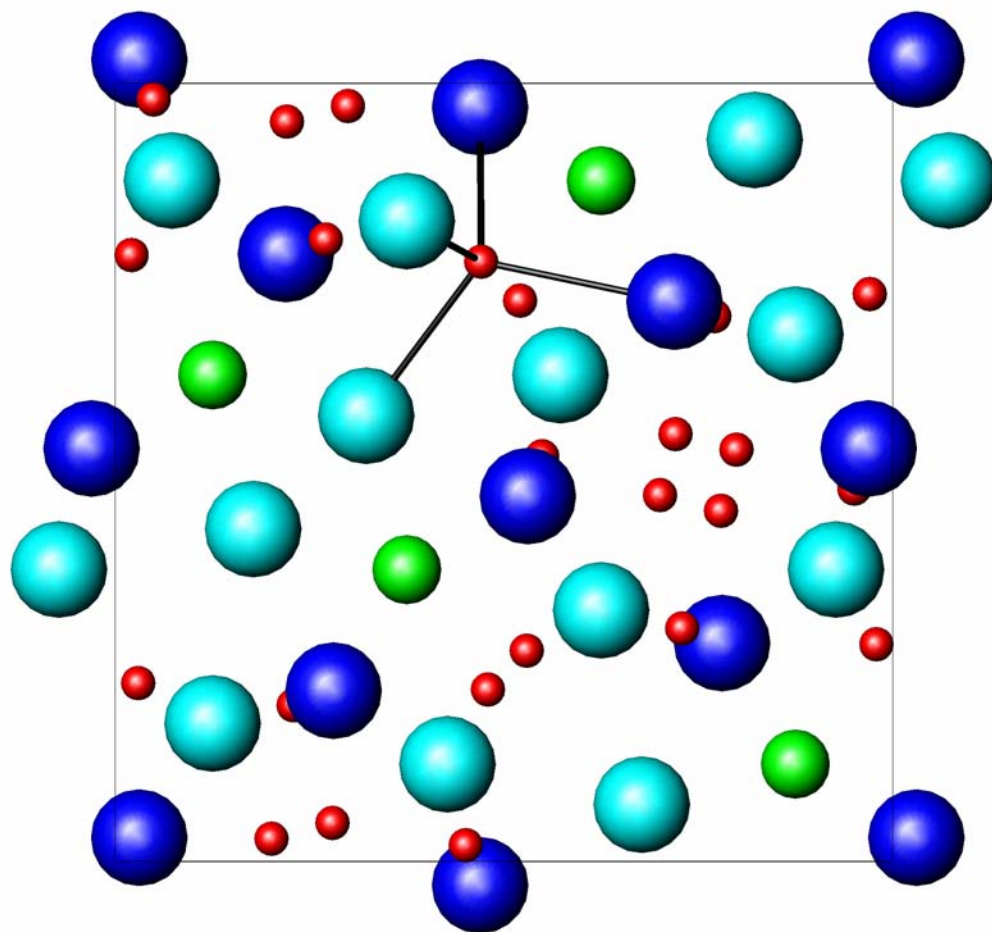


P 4₁32
a ~11.24Å

Rb in 4(a)
 $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag1 SITES



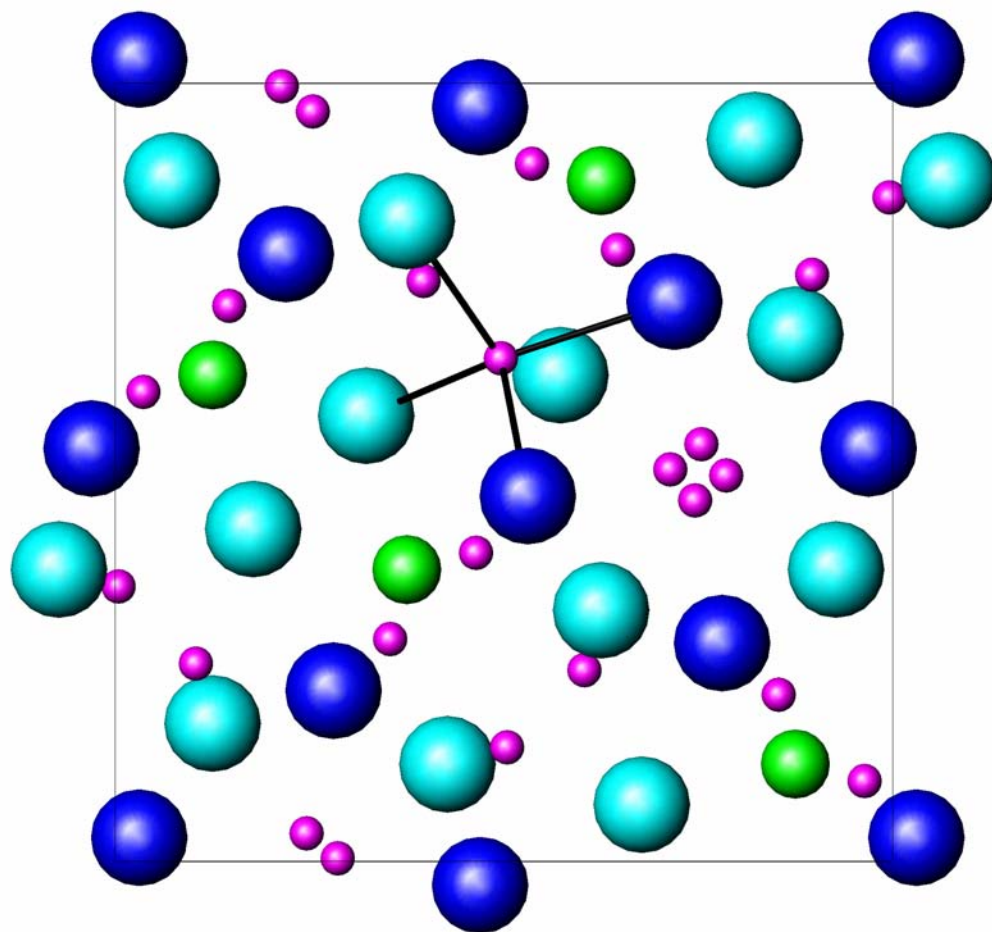
P 4₁32
a ~11.24Å

Ag1 in 24(e)

x,y,z
x~0.531
y~0.272
z~0.806

Ag1 : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag₂ SITES



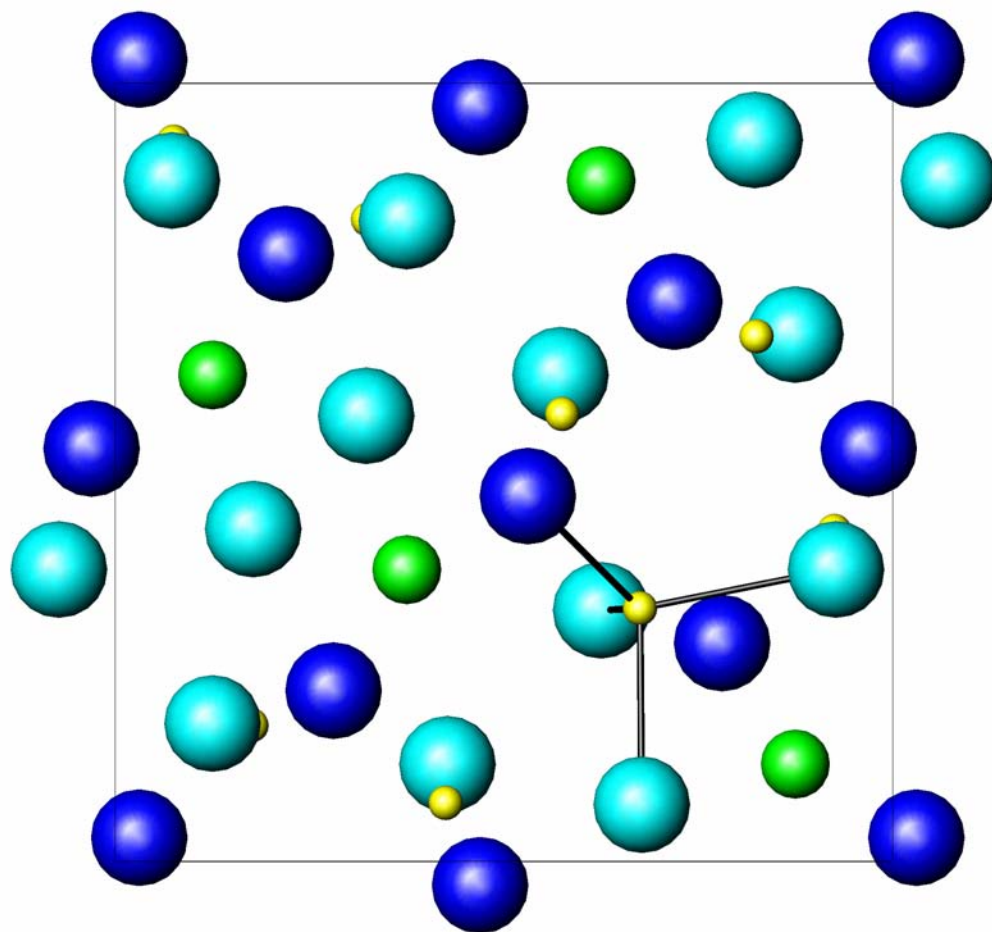
P 4₁32
a ~11.24Å

Ag₂ in 24(e)

x,y,z
x~0.993
y~0.855
z~0.206

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag₃ SITES

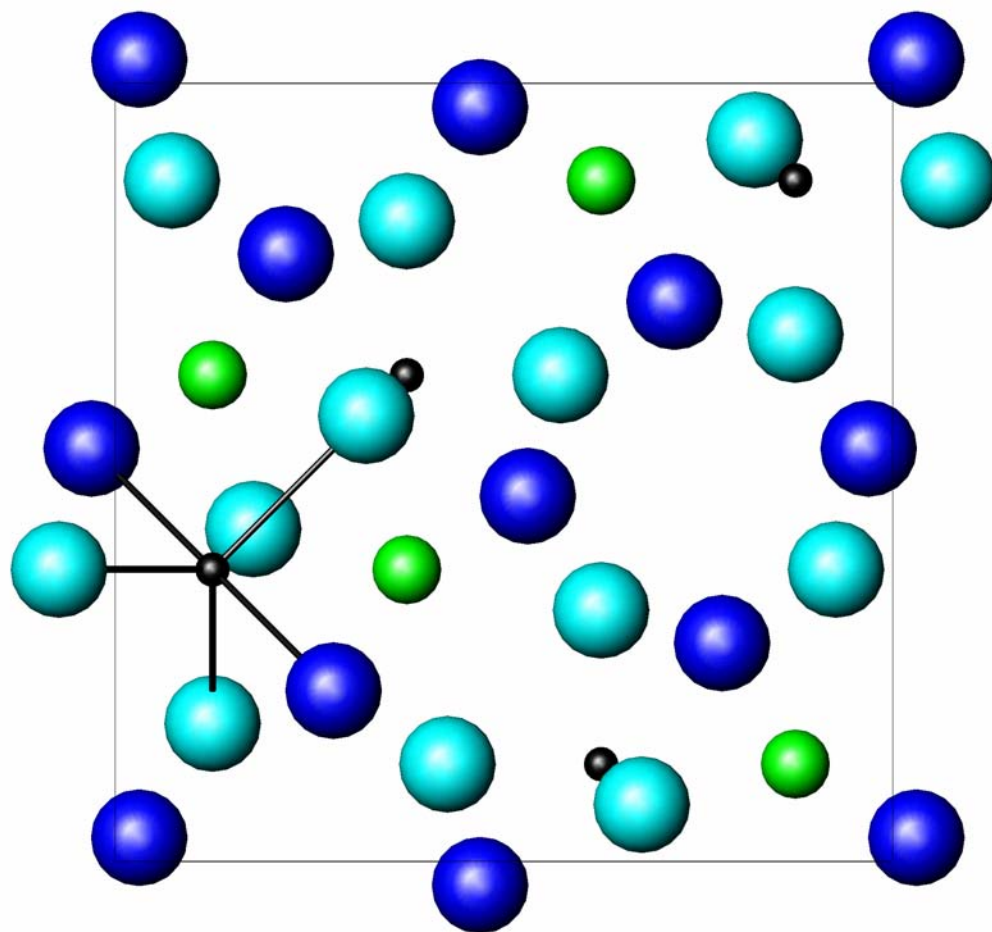


P 4₁32
a ~11.24Å

Ag₃ in 8(c)
X,X,X
x~0.177

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag₄ SITES

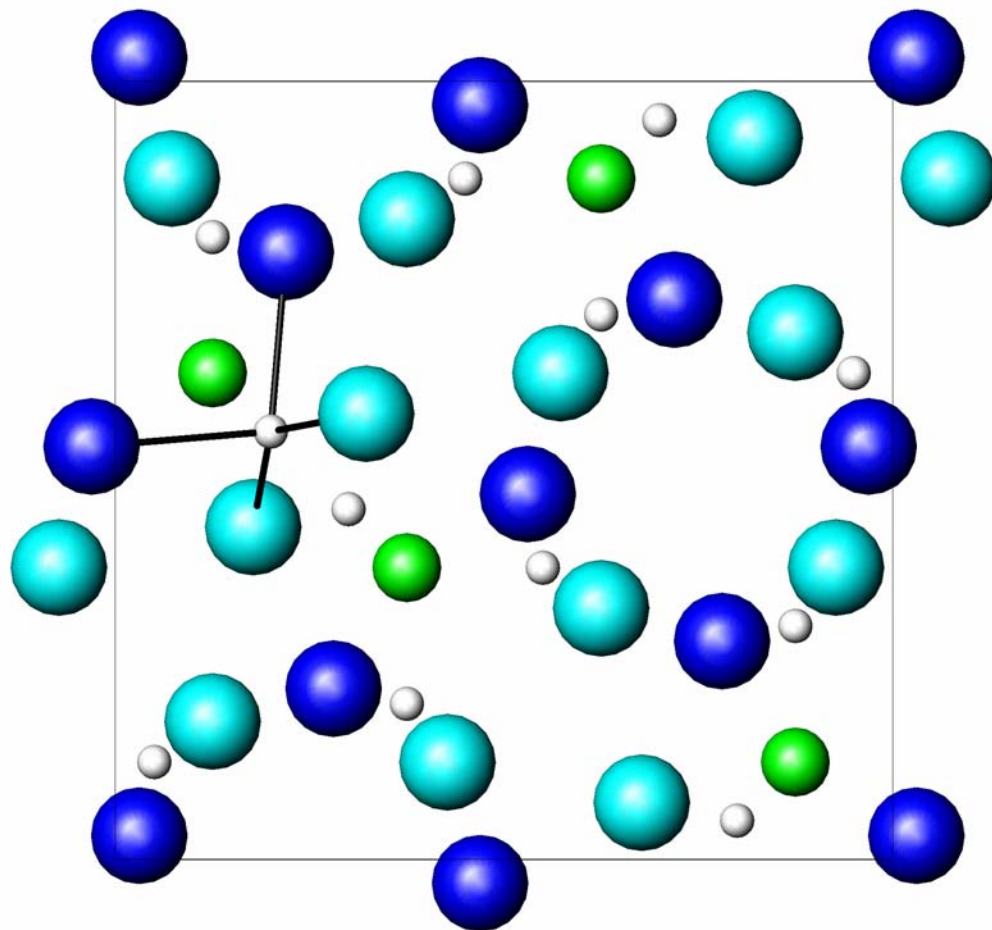


P 4₁32
a ~11.24Å

Ag₄ in 4(b)
 $\frac{7}{8}, \frac{7}{8}, \frac{7}{8}$

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag5 SITES

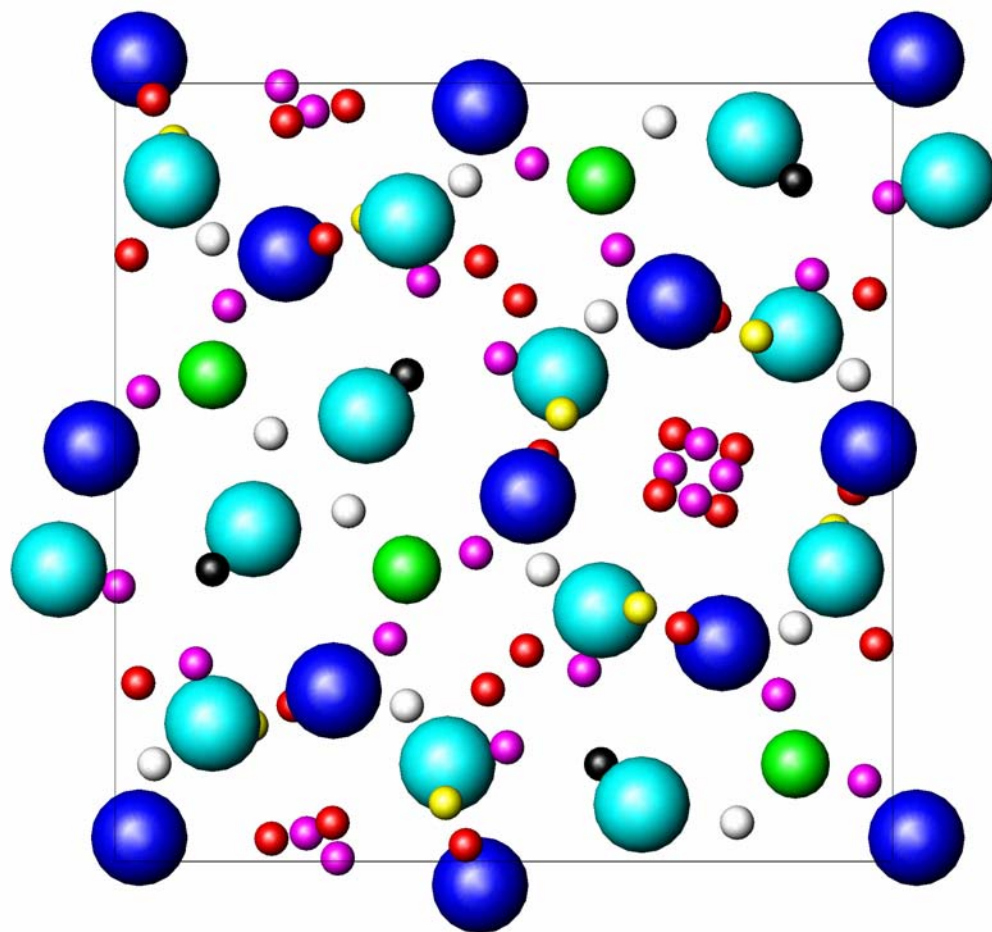


P 4₁32
a ~11.24Å

Ag5 in 12(d)
 $\frac{1}{8}, y, \frac{1}{4} + y$
y ~ 0.764

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : Ag SITES



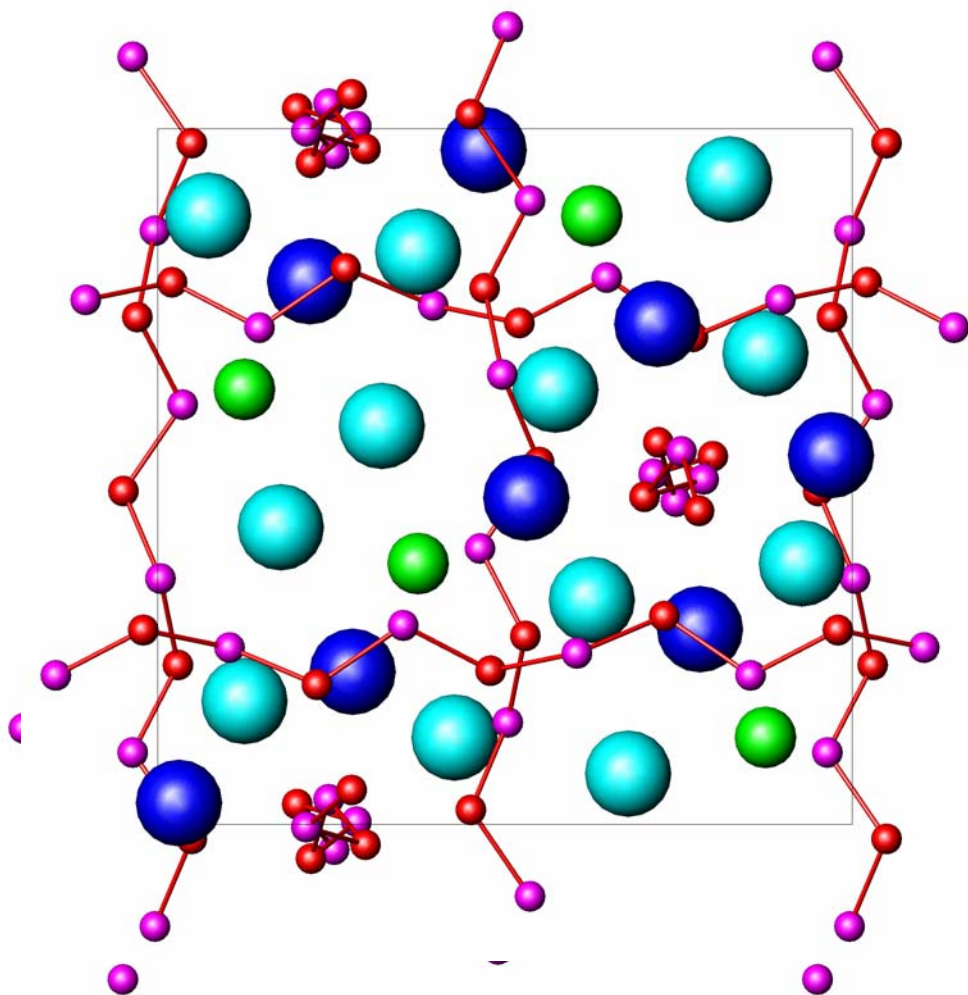
P 4₁32
a ~11.24Å

20 × Ag⁺
per unit cell

How are they
distributed
over the 72
sites?

AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : CONDUCTION PATHWAYS



Find a preferential occupancy of the **Ag1** and **Ag2** sites.

- Ag⁺ hop between pairs of these sites in <001> directions.
- conduction of Ag⁺ occurs along one-dimensional channels.

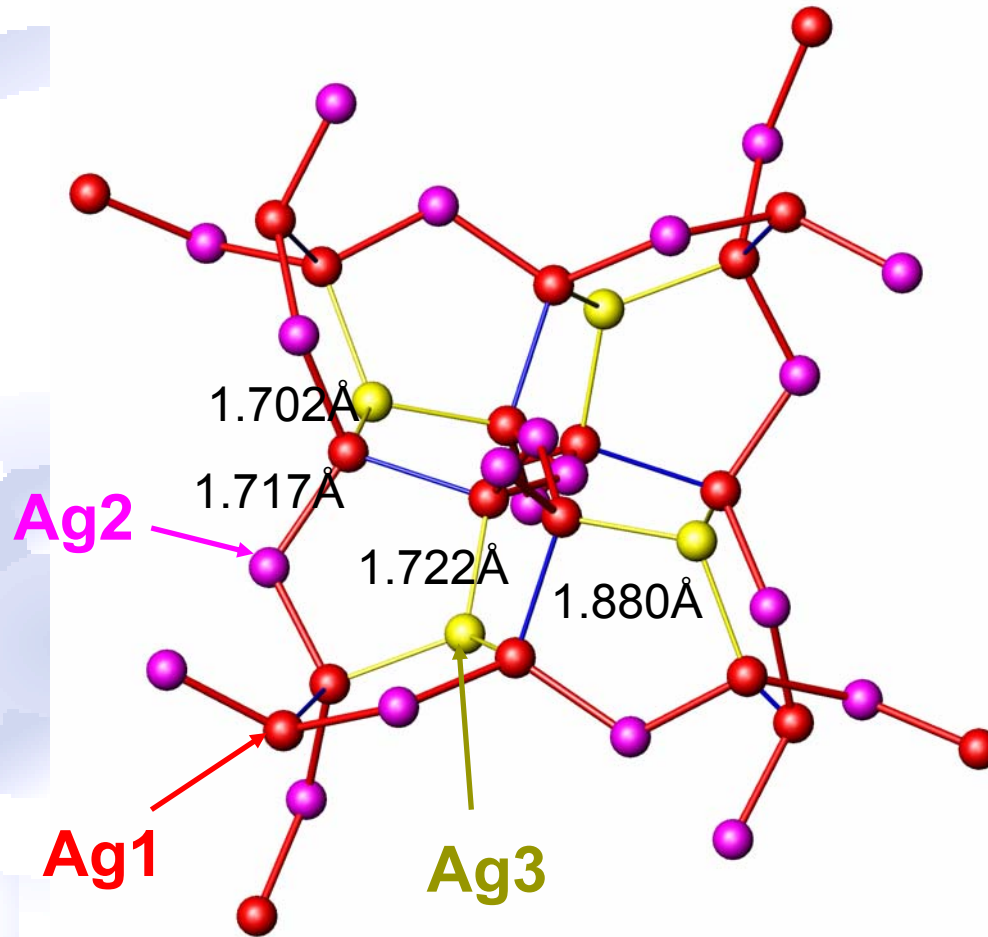
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : DIFFUSION BETWEEN CHANNELS

There are two plausible routes for Ag⁺ to hop between channels.

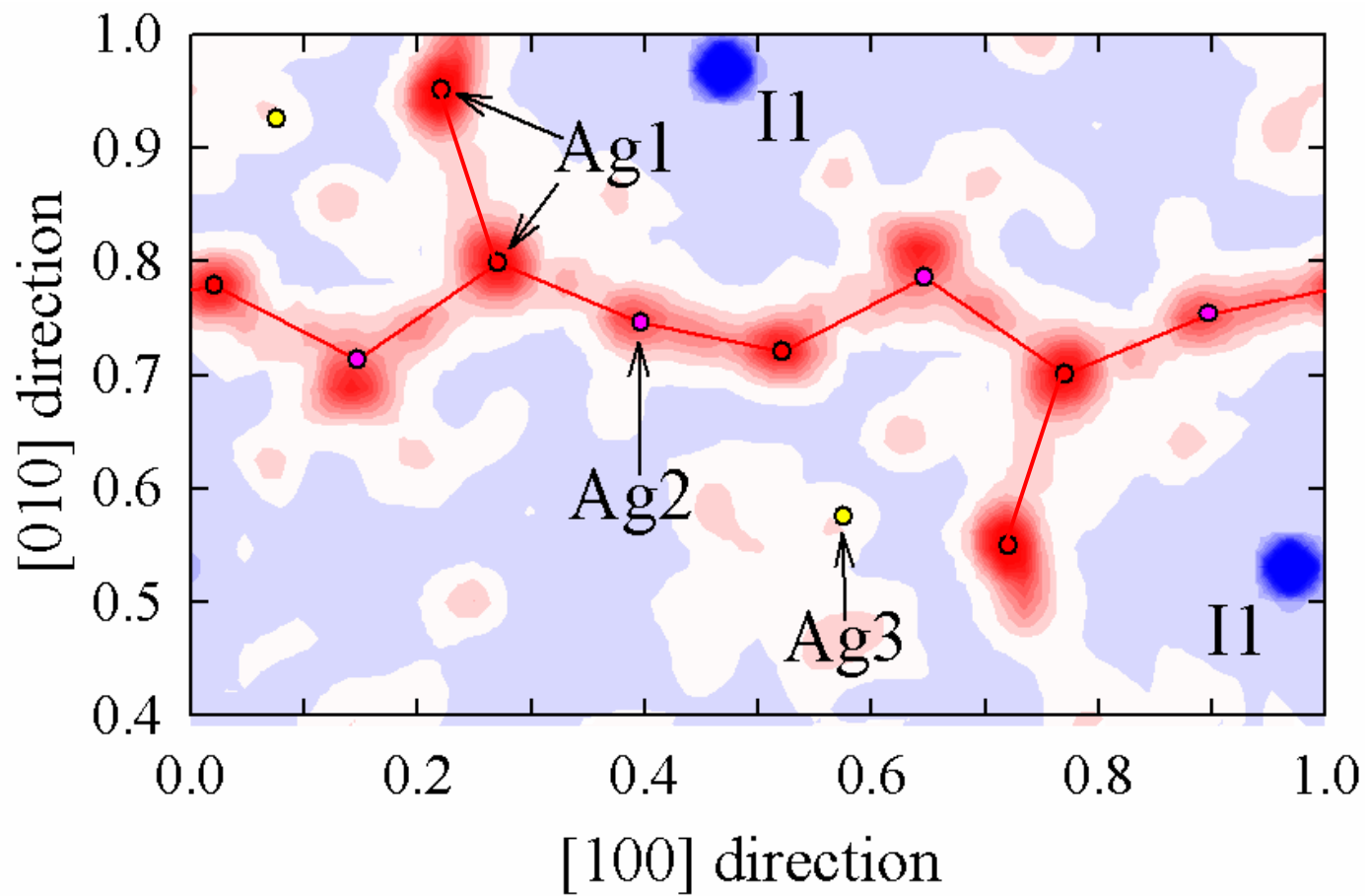
- Direct hop :
Ag1 → Ag1

- Indirect hop :
Ag1 → Ag3 → Ag1



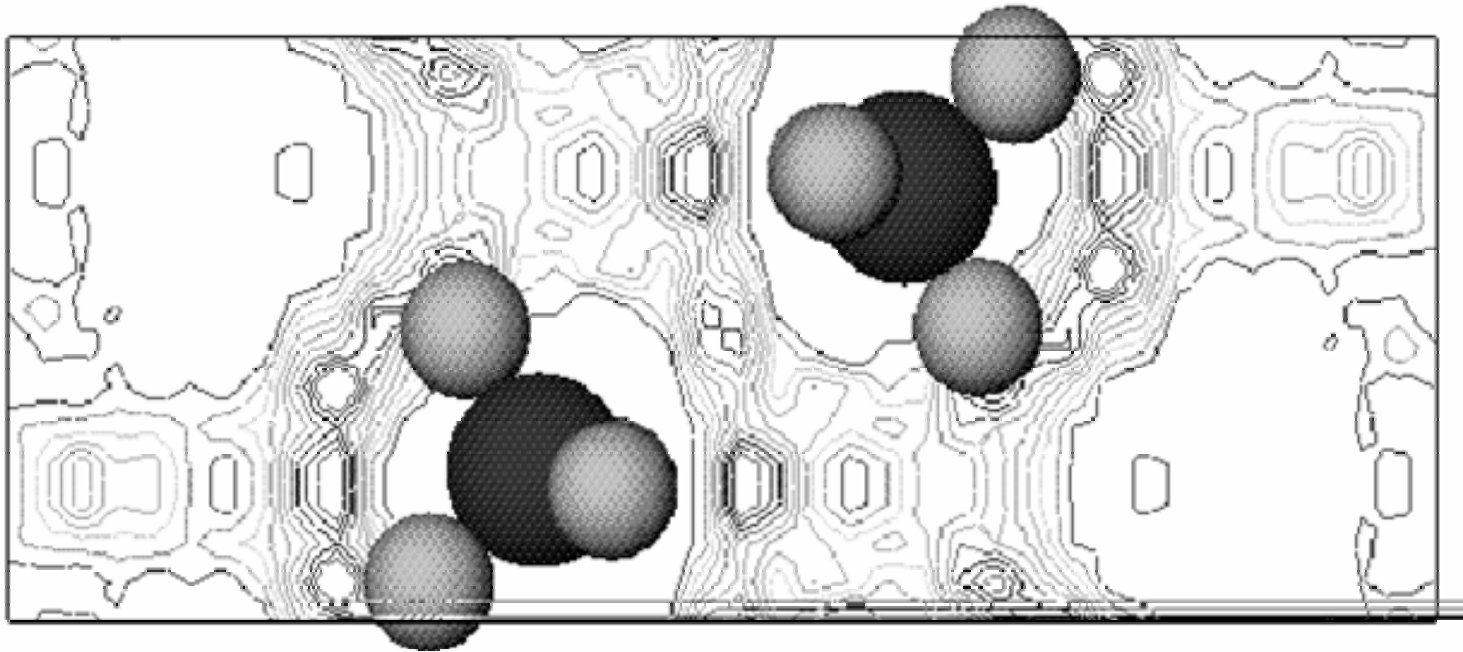
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag₄RbI₅ : MAXIMUM ENTROPY FOURIER MAP



Ag1 : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Atomic (structural) modeling



All inverse problems have solutions

Some inverse solutions have problems