Inverse methods of Data Analysis in Neutron Scattering

Robert McGreevy

ISIS Facility,
CCLRC Rutherford Appleton Laboratory,
Chilton, Didcot, OX11 0QX, UK.

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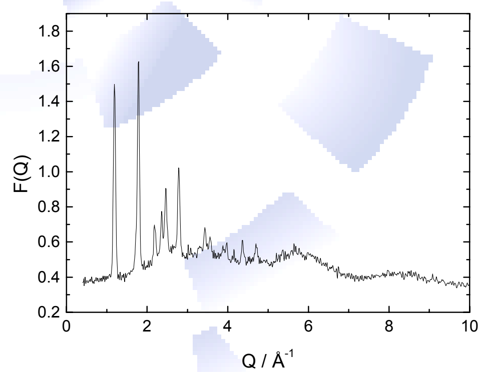
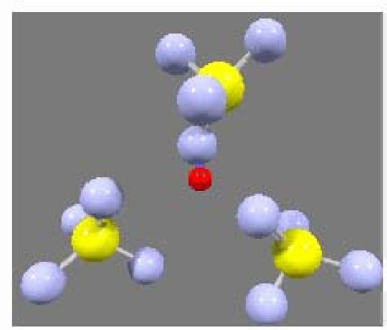
From here ……………………………………….. to there





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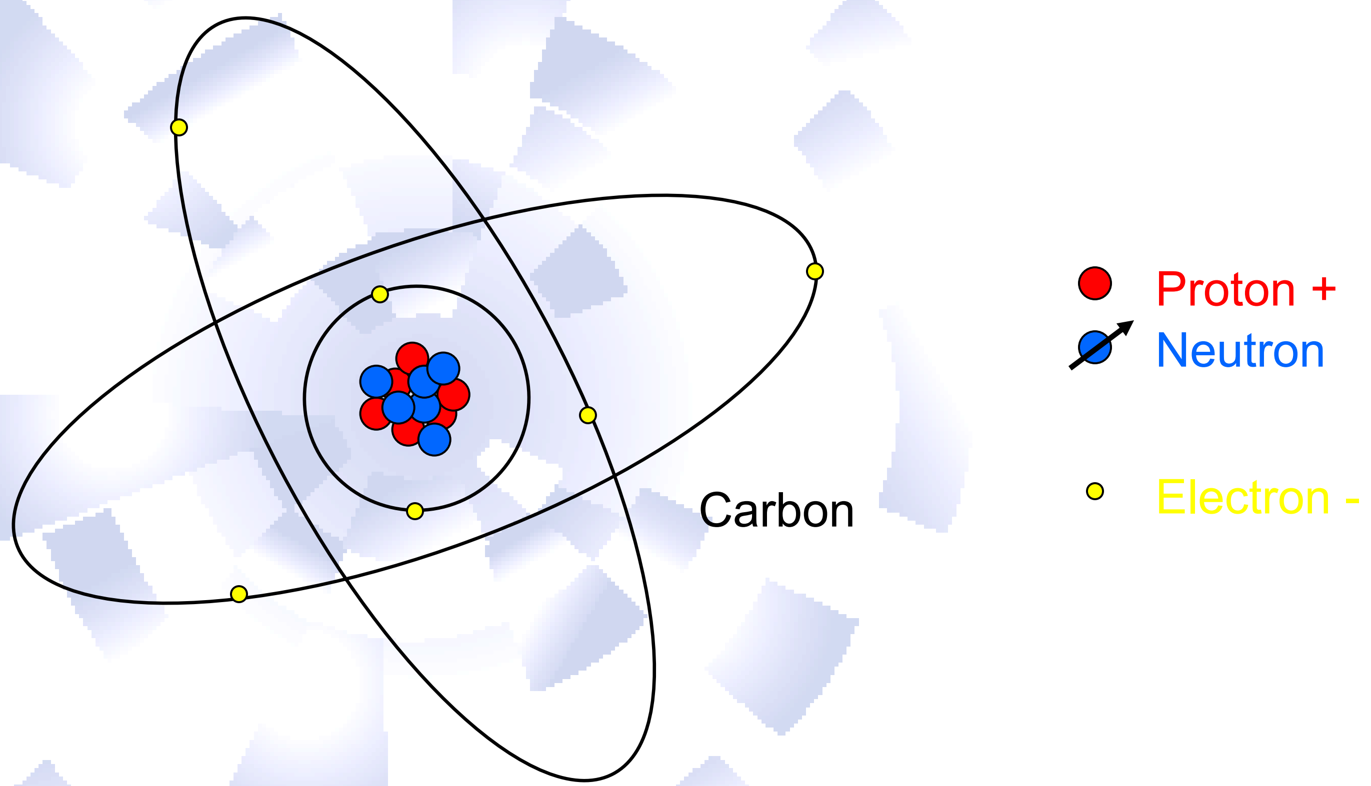
What is neutron scattering?
A short introduction



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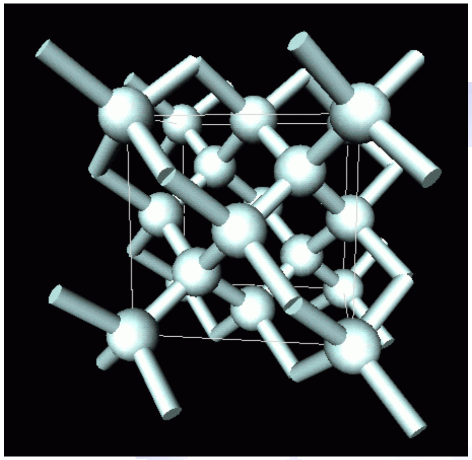
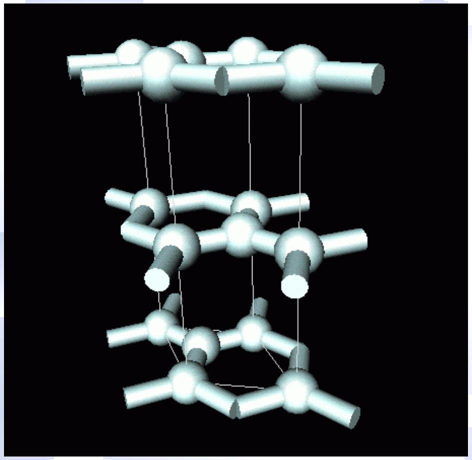
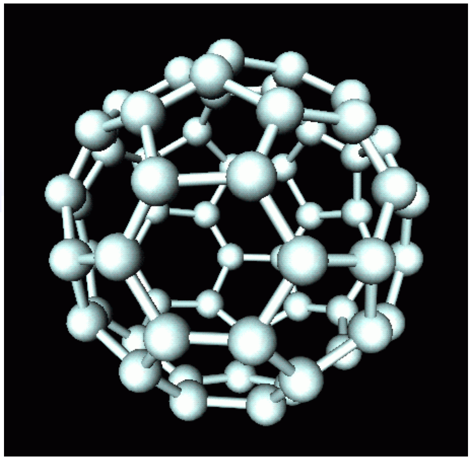


Diamond

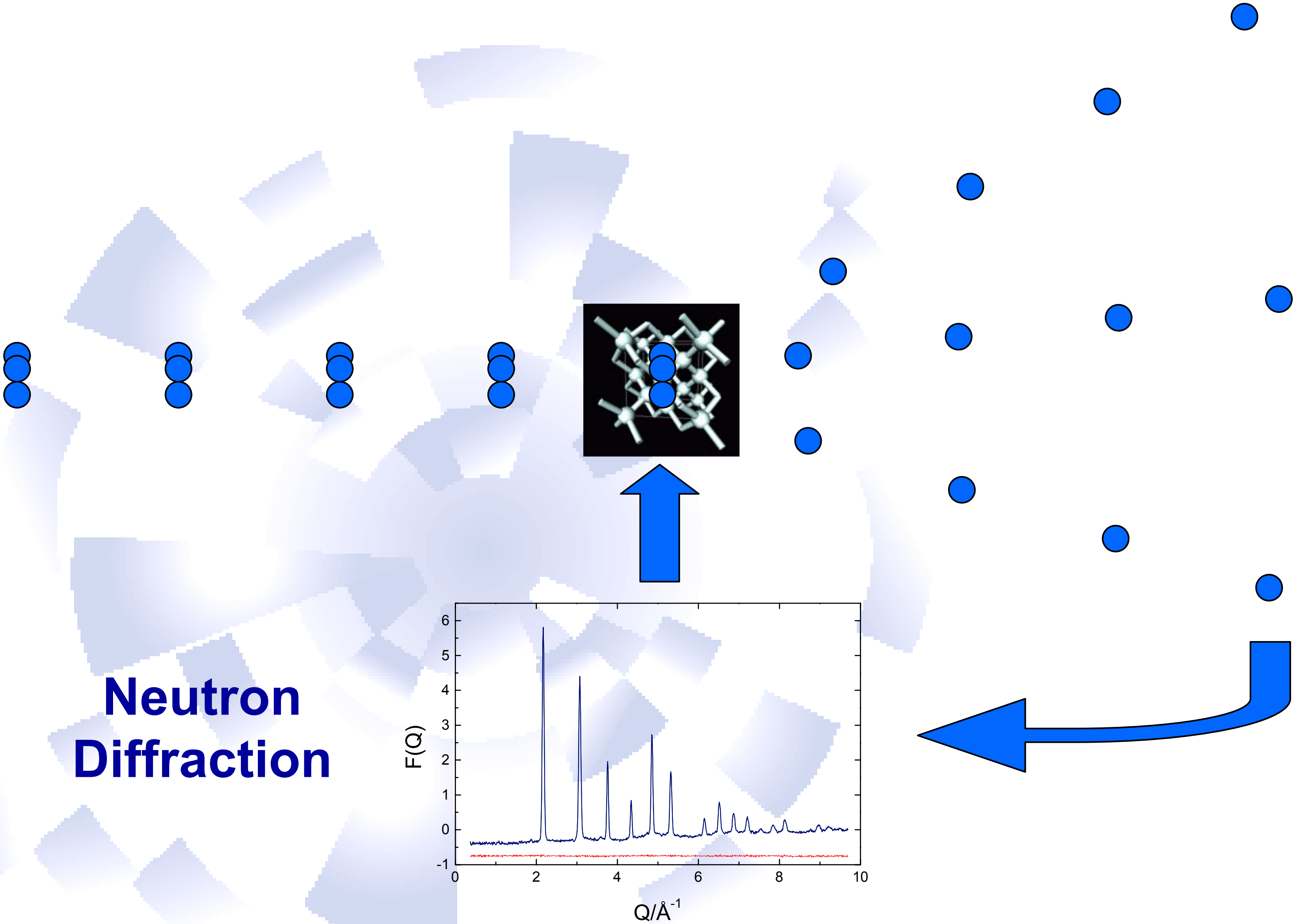


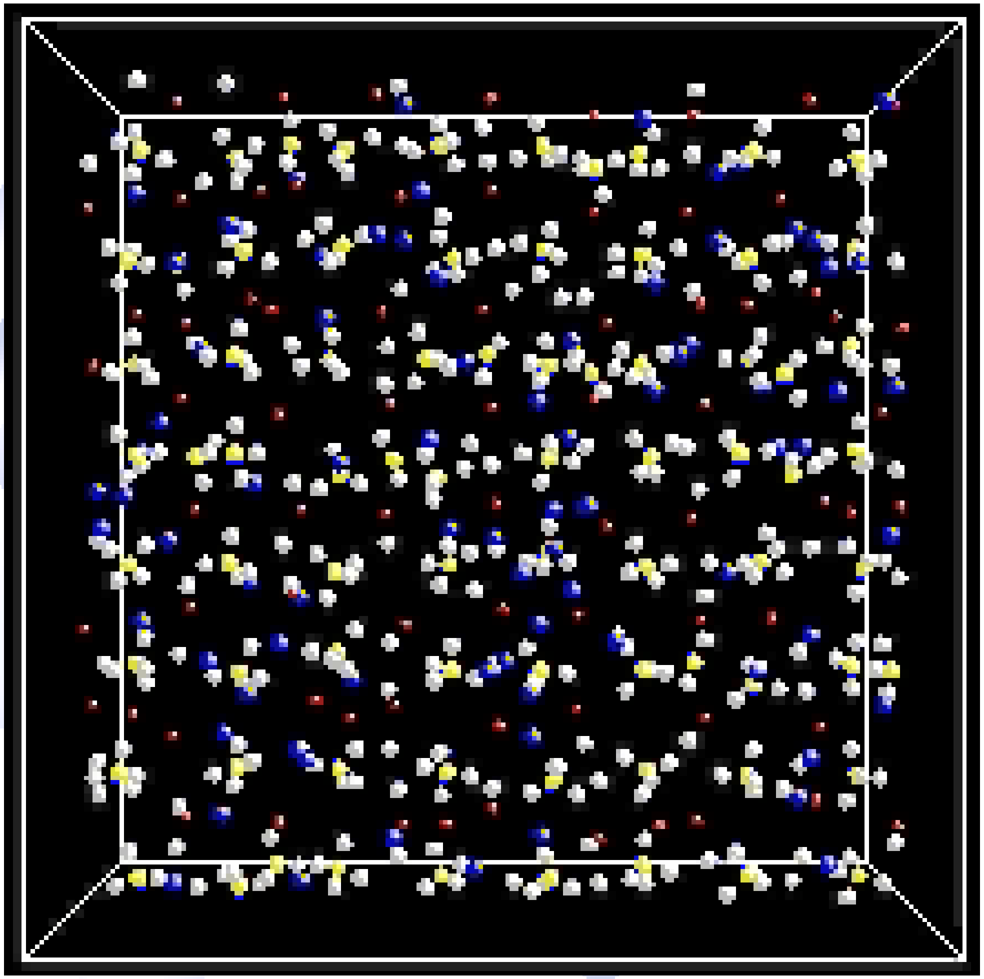
Graphite



Fullerene

Neutron Diffraction





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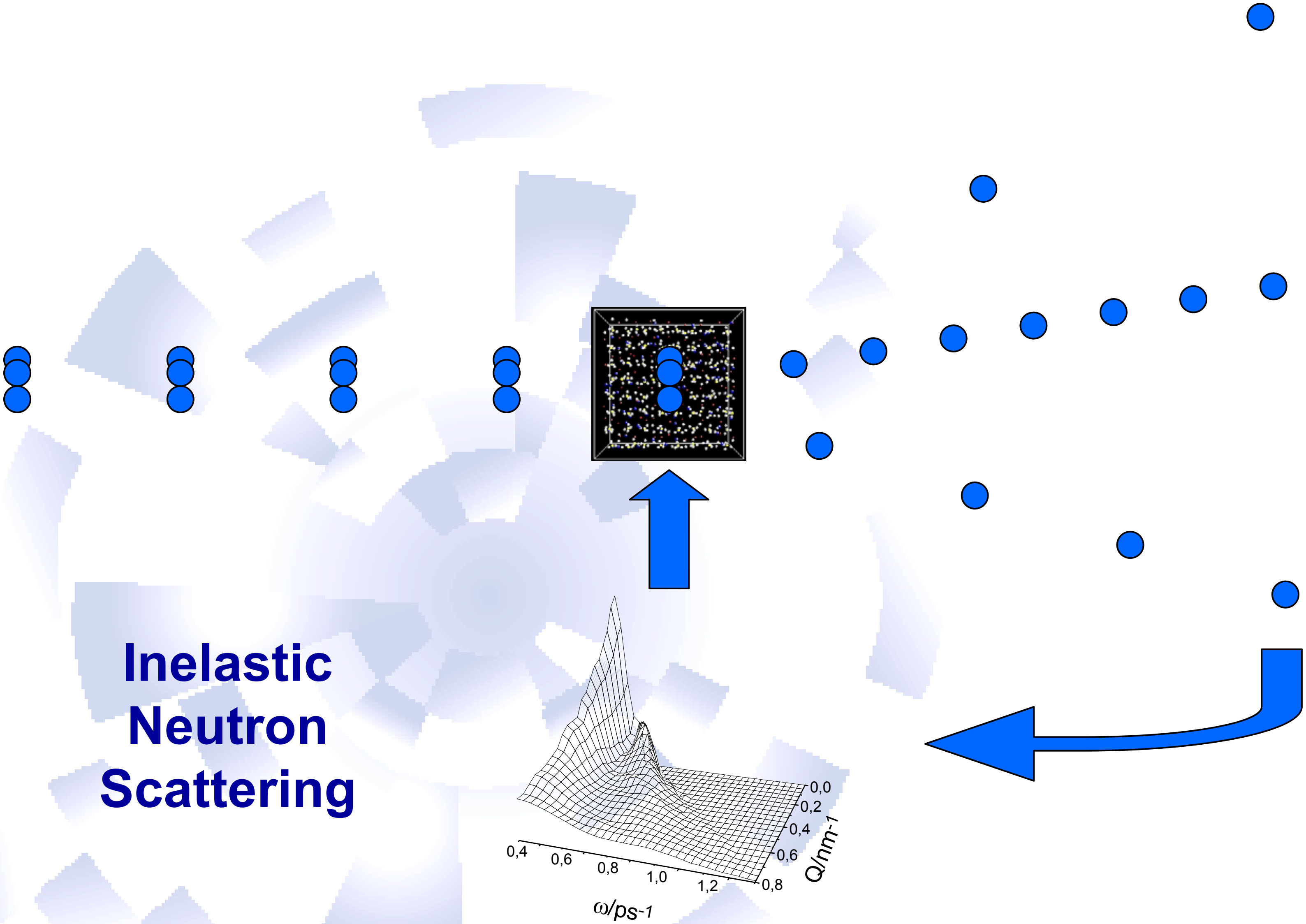
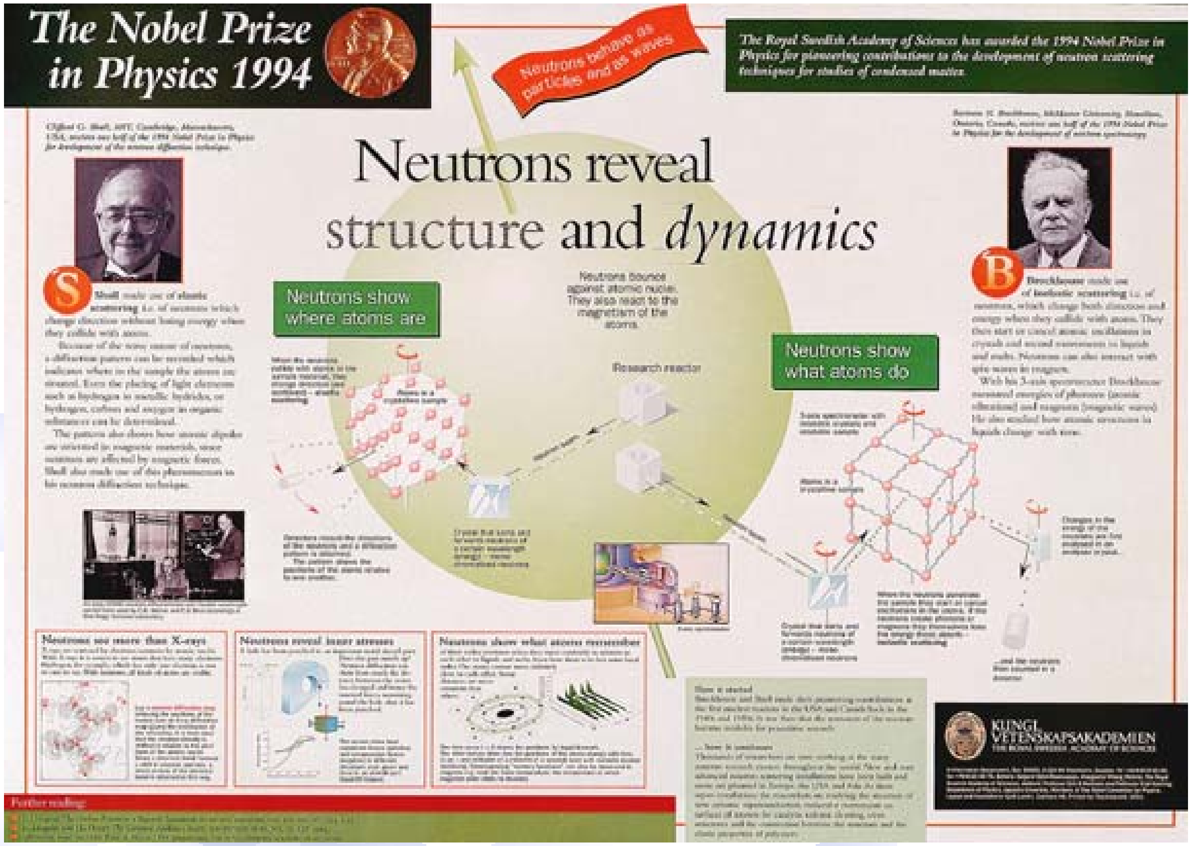
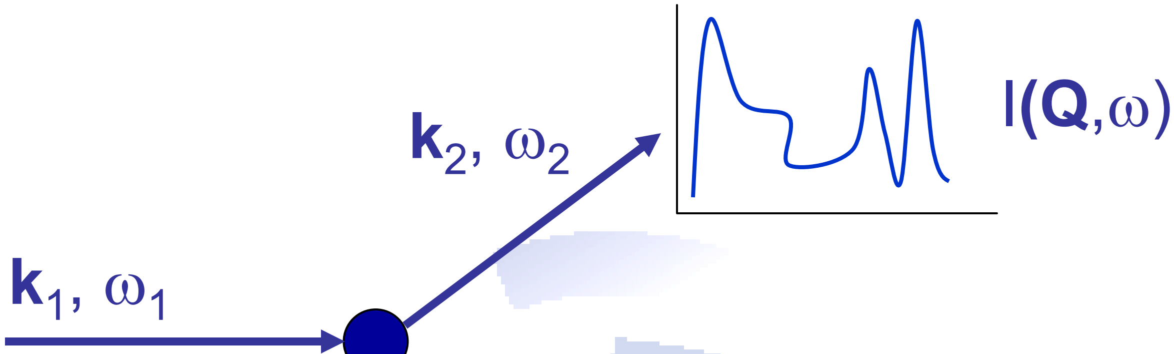
Inelastic Neutron Scattering





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

No they don’t!



$$\mathbf{Q} = \mathbf{k}_1 - \mathbf{k}_2$$
$$\omega = \omega_1 - \omega_2$$

Measurement → Understanding

$I(\mathbf{Q},\omega)$ → $S(\mathbf{Q},\omega) = \Sigma\, S_{AB}(\mathbf{Q},\omega)$ → $G_{AB}(\mathbf{r},t)$ - - - - $\mathbf{r}_i(t)$

Corrections	Separation	Transform	?
Constant b Weak probe	Isotopic substitution	Wide $(\mathbf{Q},\omega)$ range	
Errors	**Under defined** **Poorly conditioned**	**Truncation**	**Phase problem**

SO …

Neutron scattering data analysis

is an

INVERSE

problem

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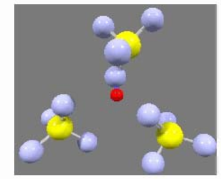
$$I(\mathbf{Q},\omega) \longrightarrow S(\mathbf{Q},\omega) = \Sigma\, S_{AB}(\mathbf{Q},\omega) \longrightarrow G_{AB}(\mathbf{r},t) \;-\,-\,-\,-\; \mathbf{r}_i(t)$$

Corrections Separation Transform

Errors **Under defined Poorly conditioned** **Truncation** **Phase problem**



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

Corrections | Separation | Transform

Errors

Under defined
Poorly conditioned

Truncation

Phase problem

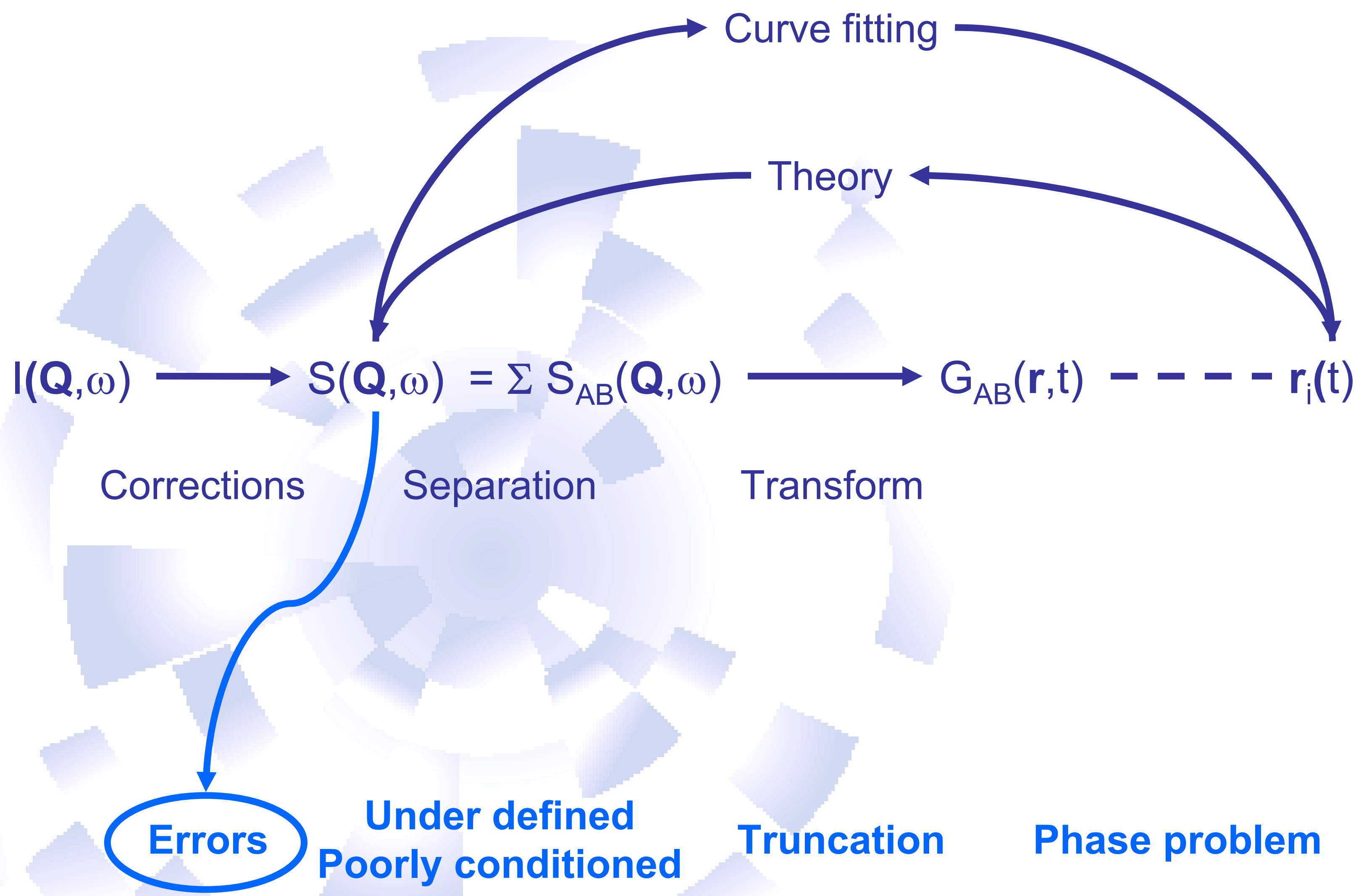
$$S(\mathbf{Q},\omega) = \frac{1}{2\pi}\int \mathrm{e}^{-i\omega t} S(\mathbf{Q},t)dt \qquad S(\mathbf{Q},t) = \int \mathrm{e}^{i\mathbf{Q}.\mathbf{r}} G(\mathbf{r},t)d\mathbf{r}$$

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

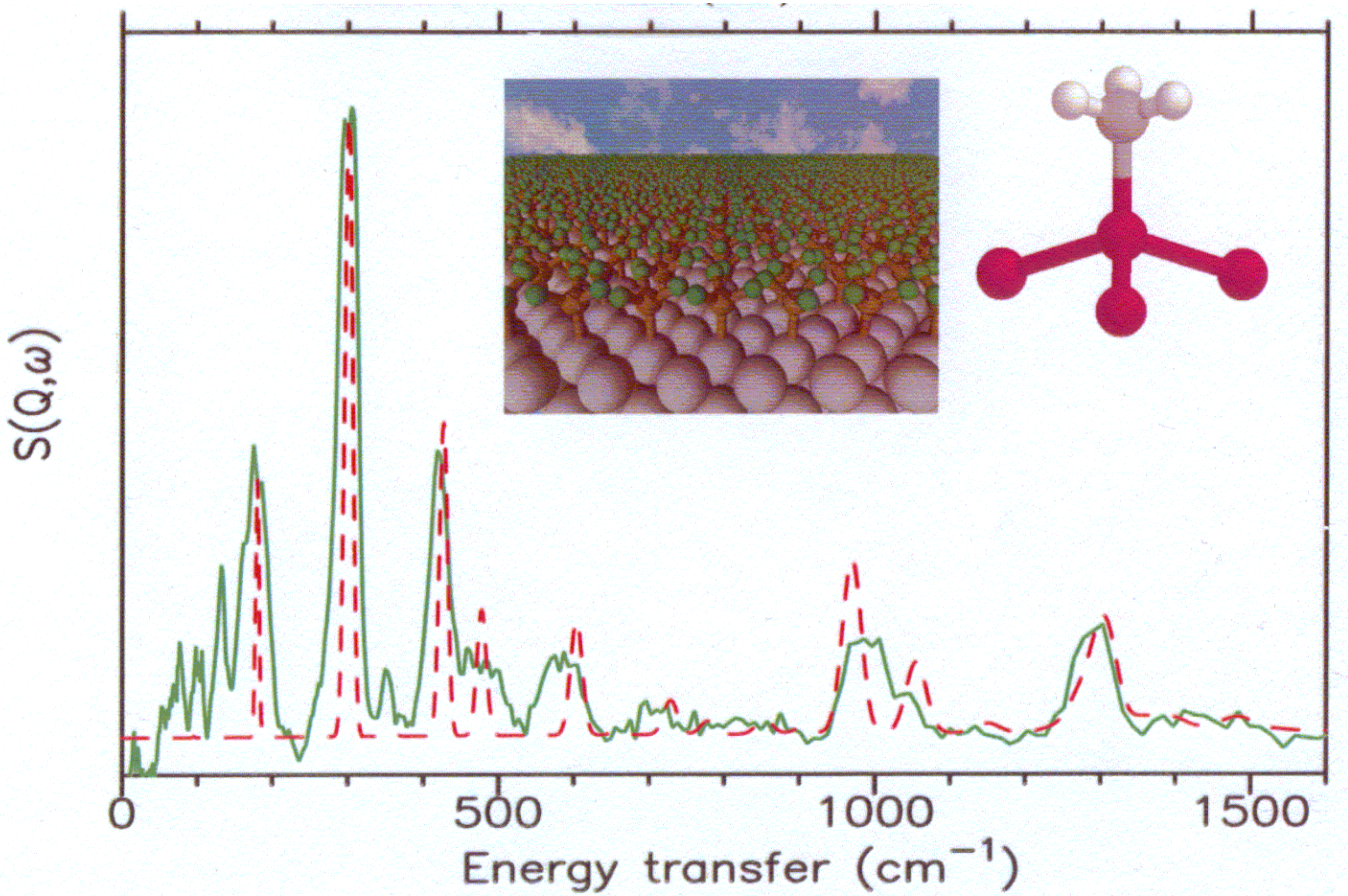
$$S(\mathbf{Q}) = \frac{1}{N_c} e^{-WQ^2} \left| \sum_k e^{-i\mathbf{Q}.<\mathbf{R}_k(t)>} \right|^2$$

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

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



Curve fitting
Theory
I(Q,ω)
S(Q,ω) = Σ S_AB(Q,ω)
G_AB(r,t)
r_i(t)
Corrections
Separation
Transform
Errors
Under defined
Poorly conditioned
Truncation
Phase problem



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

What is *N* ?

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

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Bayes theorem

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

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

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

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

If we assume no knowledge of N then

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

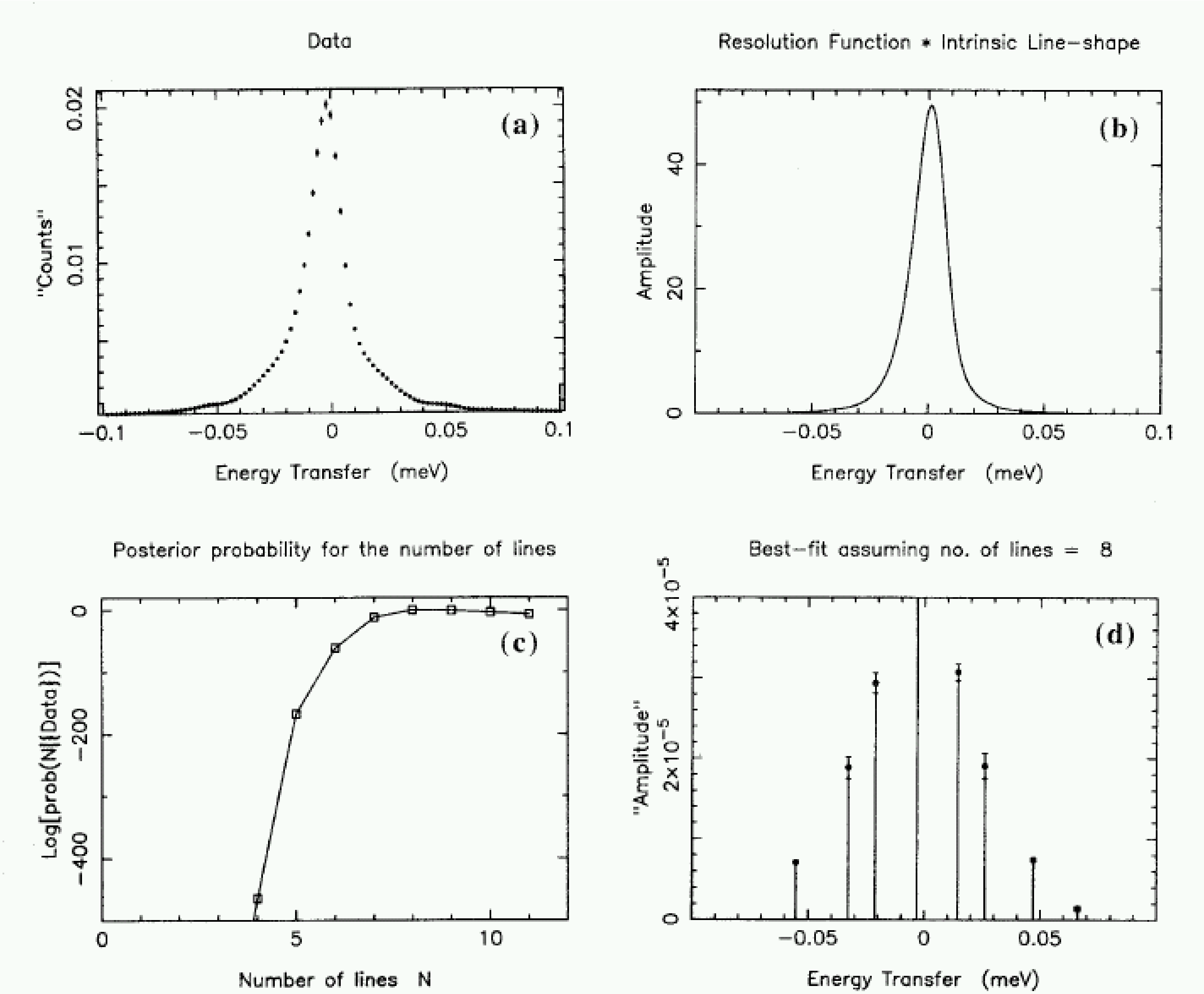
so

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

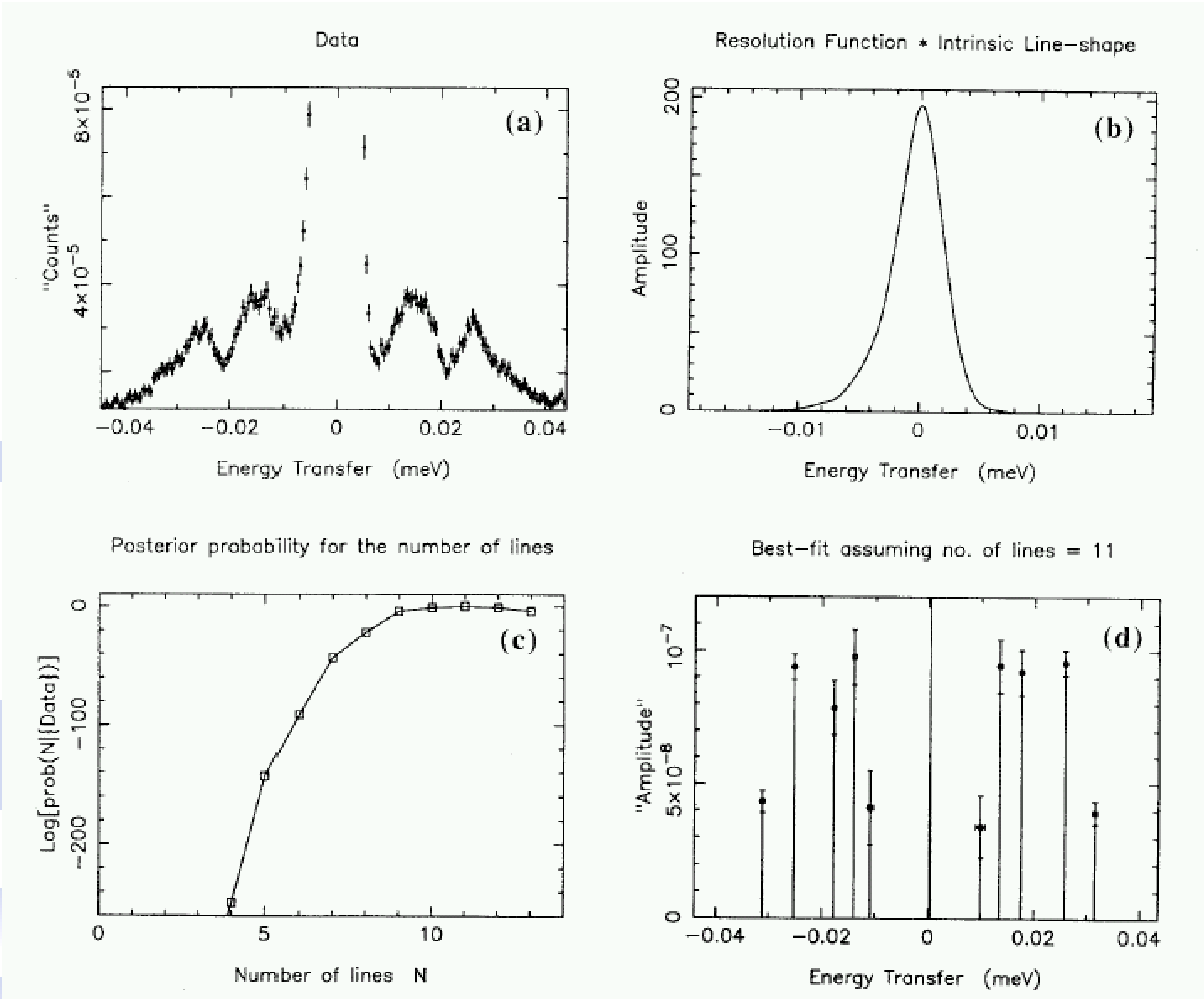
so calculate the integral above and then maximise

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

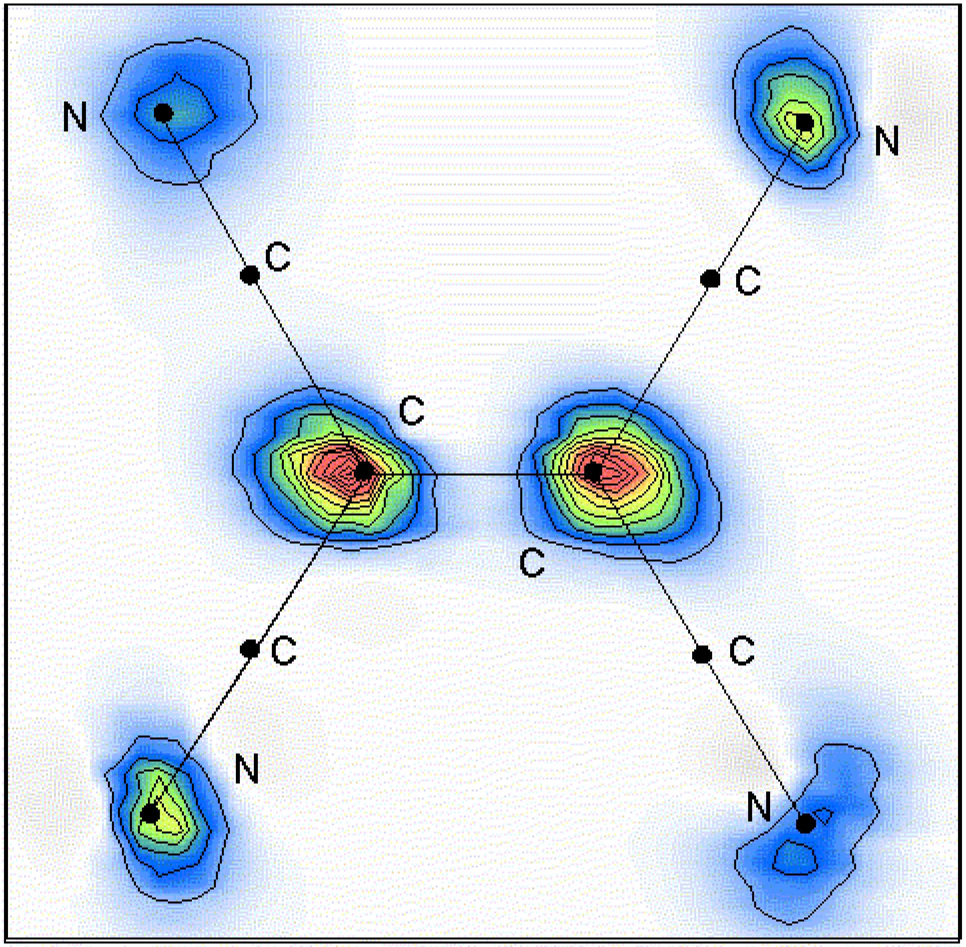
D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992



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



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

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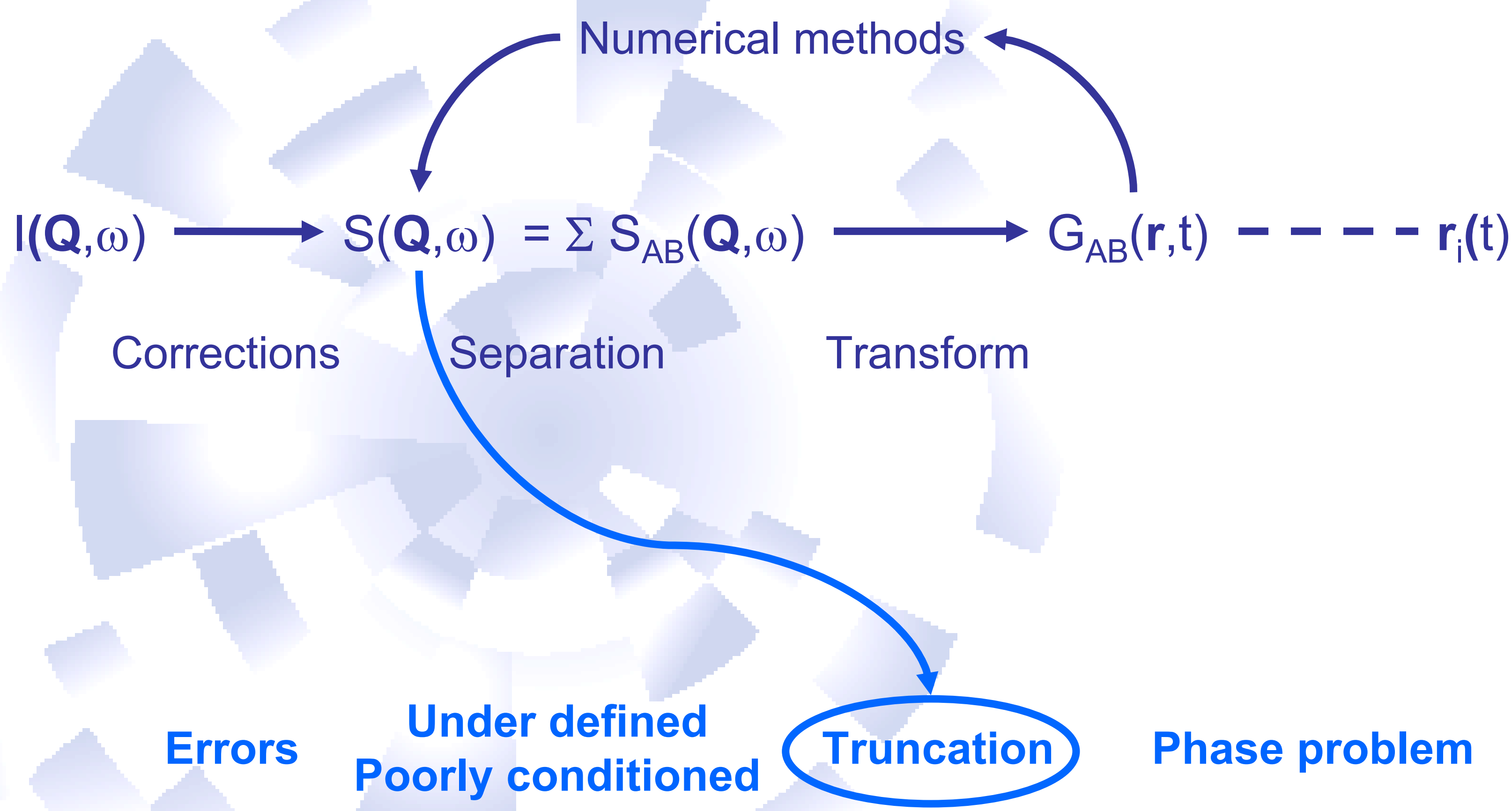
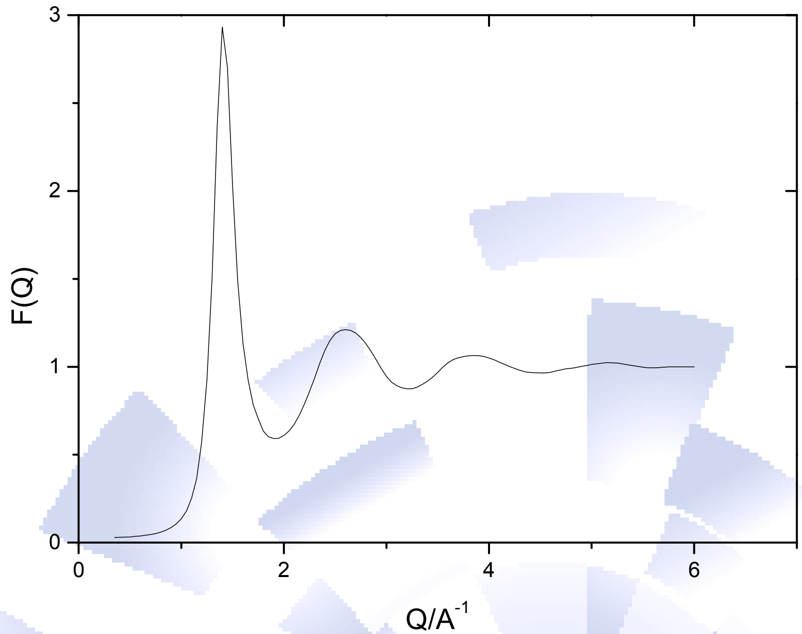
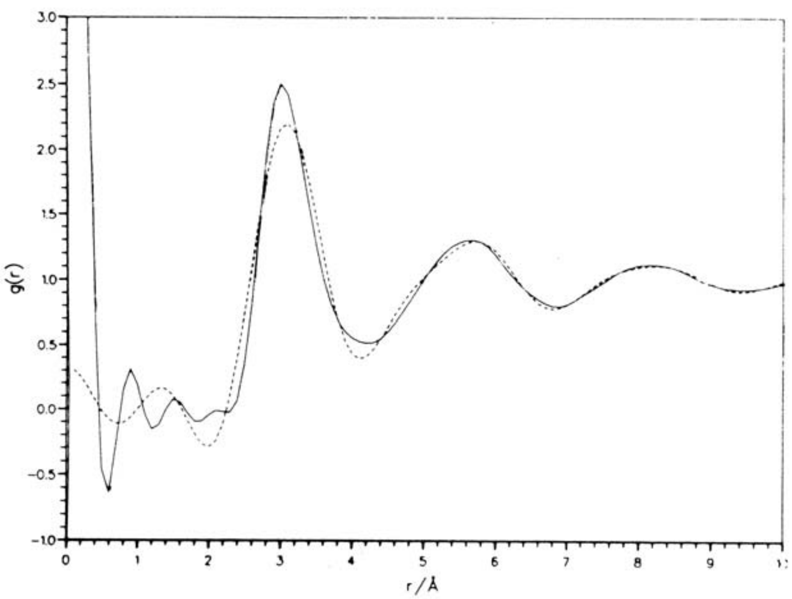

Numerical methods
I(Q,ω)
S(Q,ω) = Σ S_AB(Q,ω)
G_AB(r,t)
r_i(t)
Corrections
Separation
Transform
Errors
Under defined
Poorly conditioned
Truncation
Phase problem





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’

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

Corrections   Separation   Transform

Errors   **Under defined**
Poorly conditioned   **Truncation**   **Phase problem**

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

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

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

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 $\mathbf{C}$

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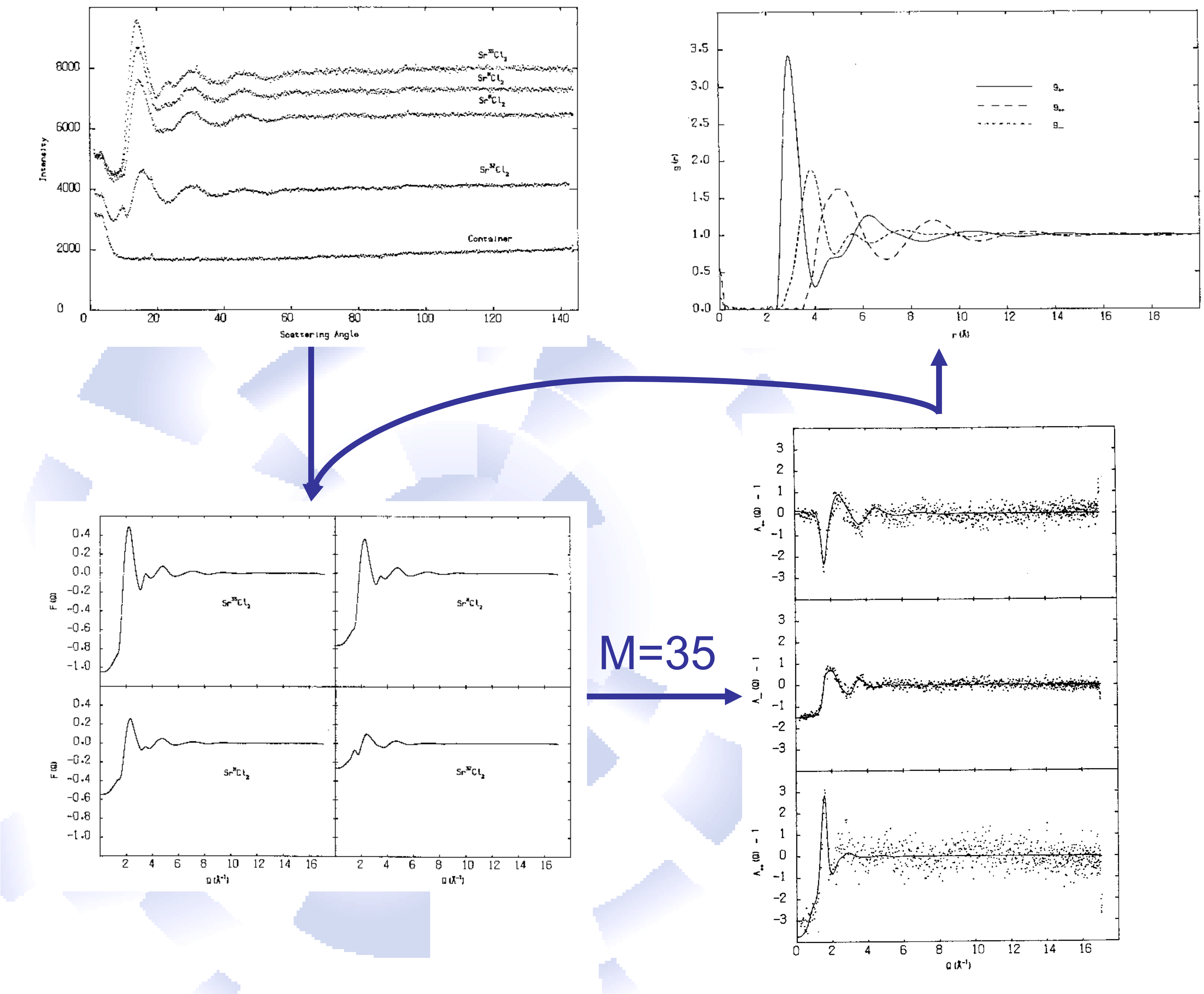
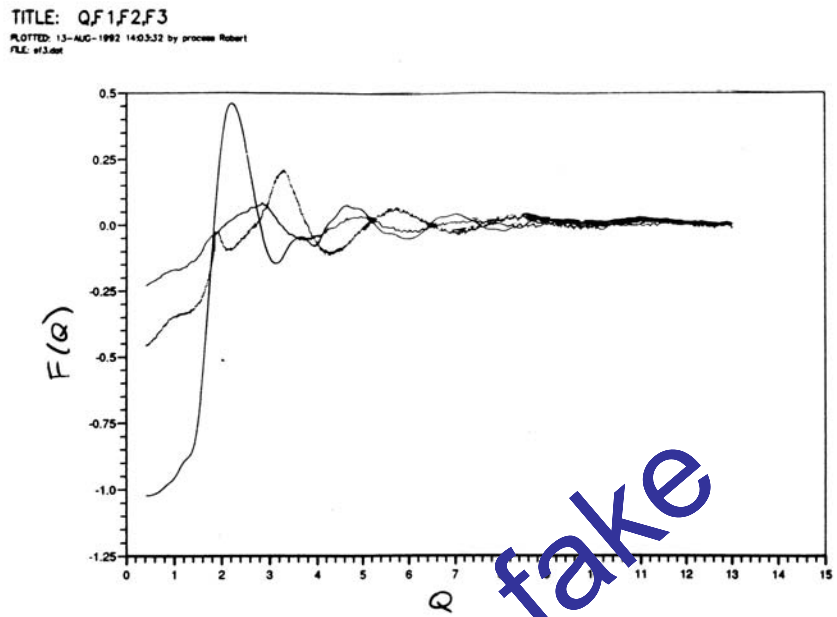

Intensity
Scattering Angle
Container
g(r)
r (Å)
F(Q)
Q (Å⁻¹)
M=35

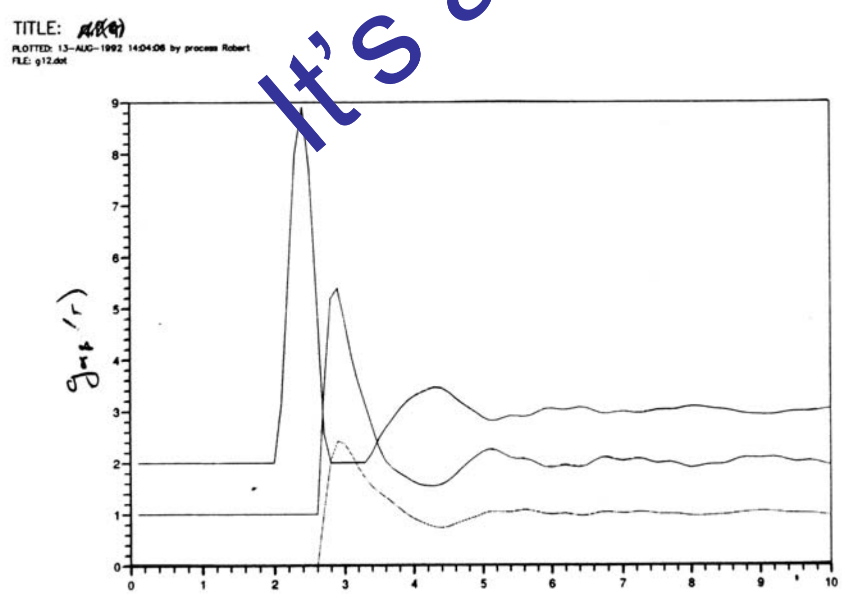
0.136538	0.200896	0.168601
0.754507	0.657018	0.704565
0.641932	0.726614	0.68932

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

841.7145



It's a fake



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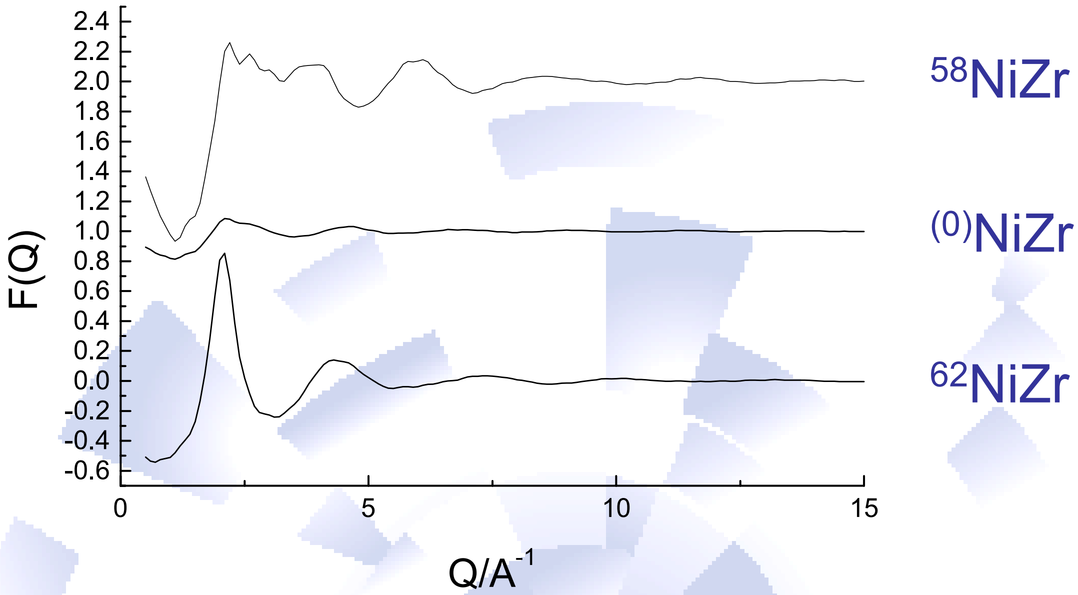
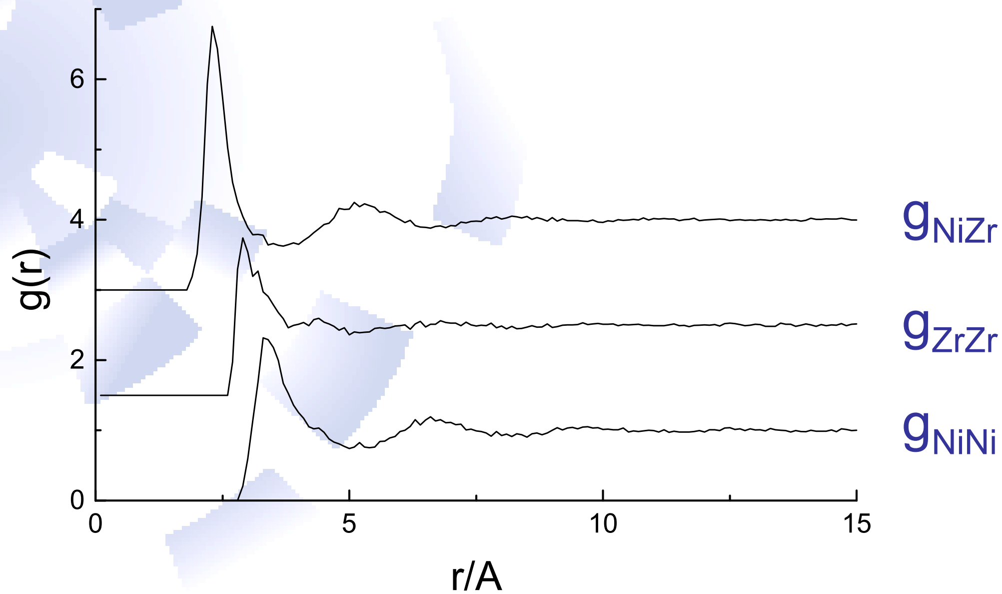
Metallic glass: NiZr



M=11



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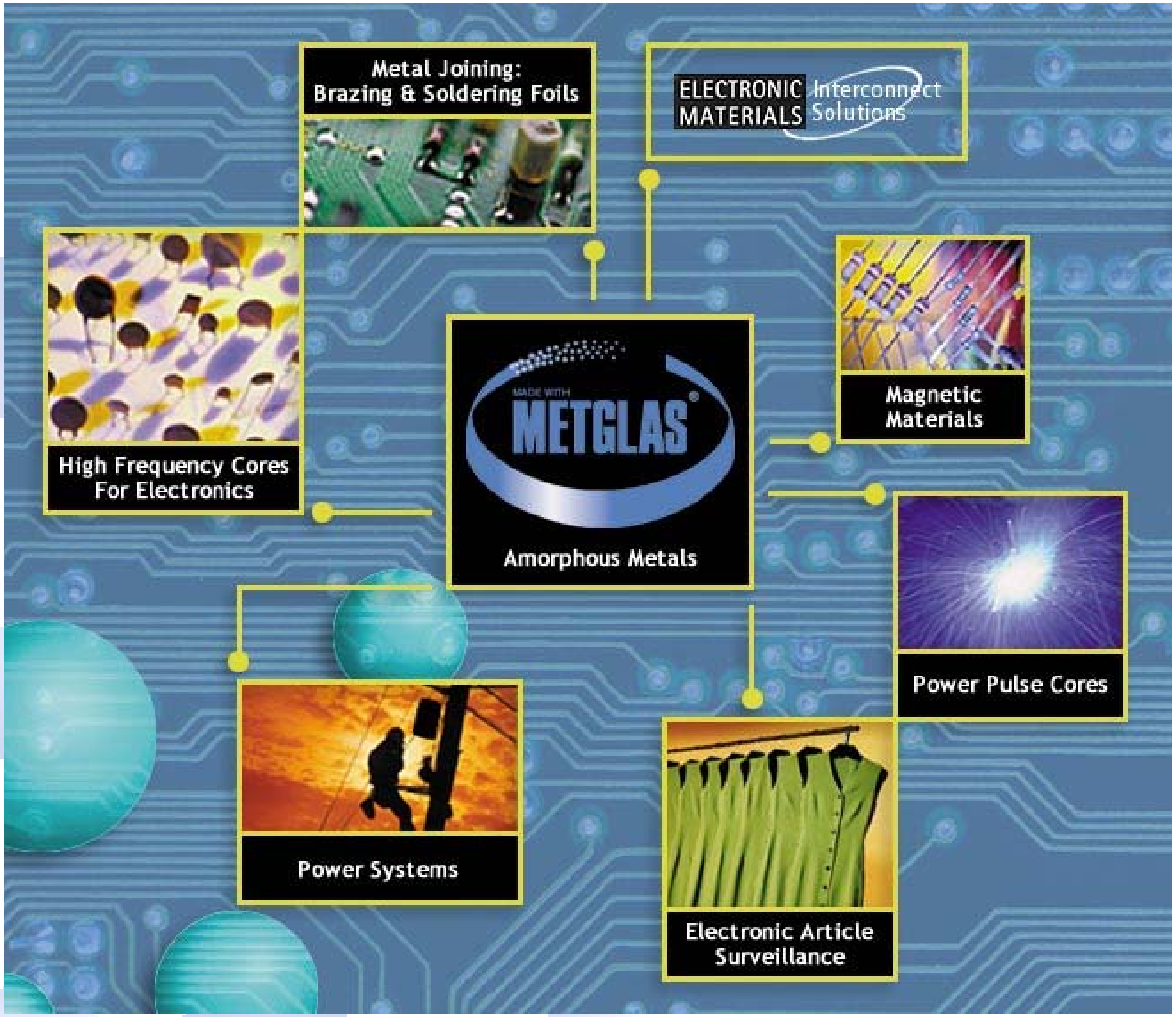
Metallic glasses



Metallic glasses

ISBN 0-9658970-0-1 $14.95
9 780965 897006 51495>

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Metallic glass: CuZr

^{63}CuZr

$^{(63+65)/2}$CuZr M=286

^{65}CuZr

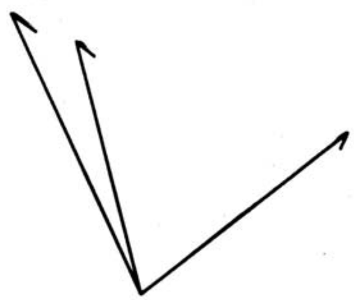
$$c^{(k)} = \begin{pmatrix} c_{11} \\ c_{12} \\ . \\ . \\ c_{nn} \end{pmatrix} \qquad \hat{c}^{(k)} = c^{(k)} / \sum c_{\alpha\beta}^2$$

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

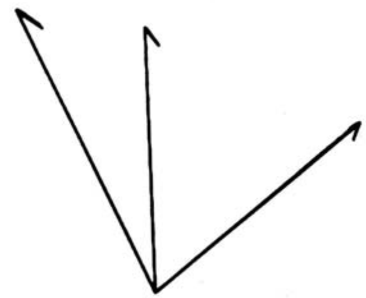
θ_{jk} is a measure of the relative information content in $F^{(j)}(Q)$ and $F^{(k)}(Q)$

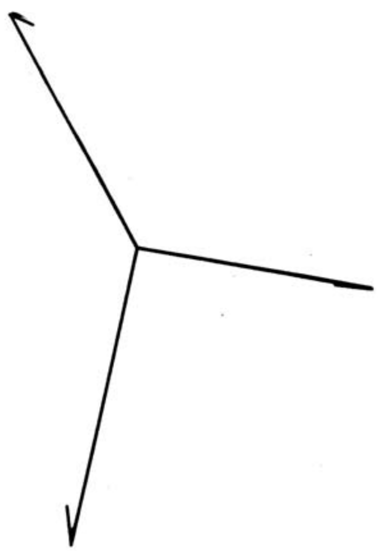
(90° is good!)

NiZr neutron + Ni/Zr EXAFS



CuZr neutron + Cu/Zr EXAFS





NiZr neutron isotopes

CuZr neutron isotopes

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

Corrections | Separation | Transform

Errors | **Under defined Poorly conditioned** | **Truncation** | **Phase problem**

so …

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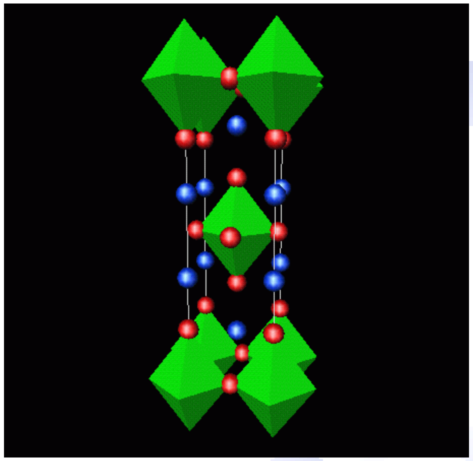
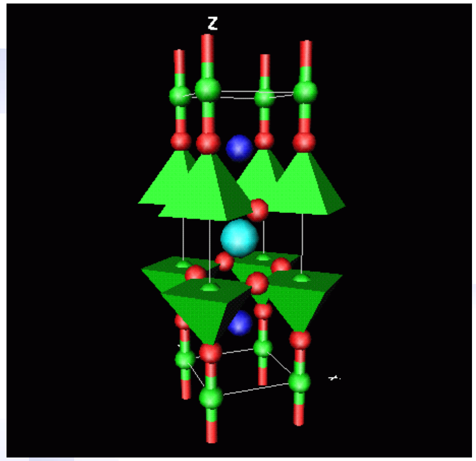
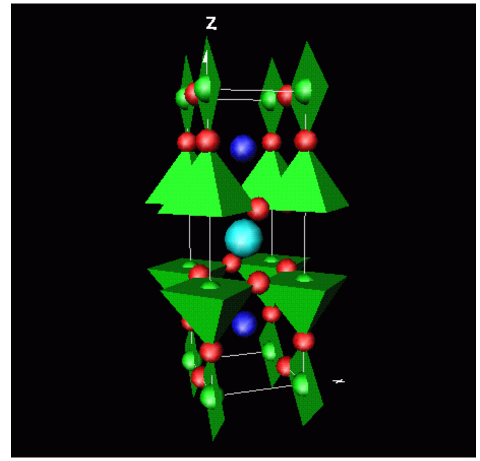
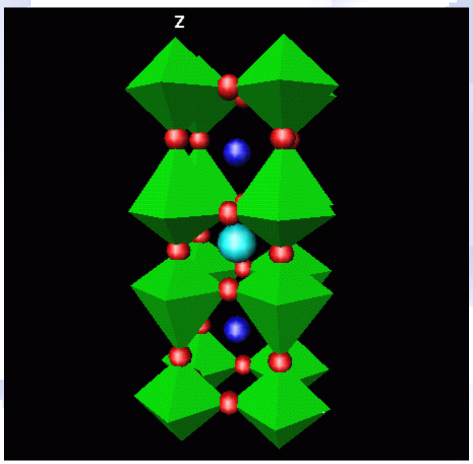
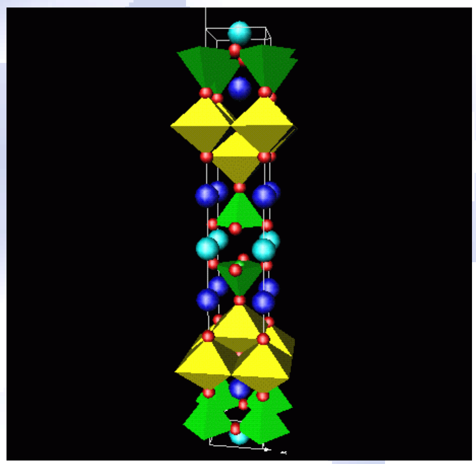


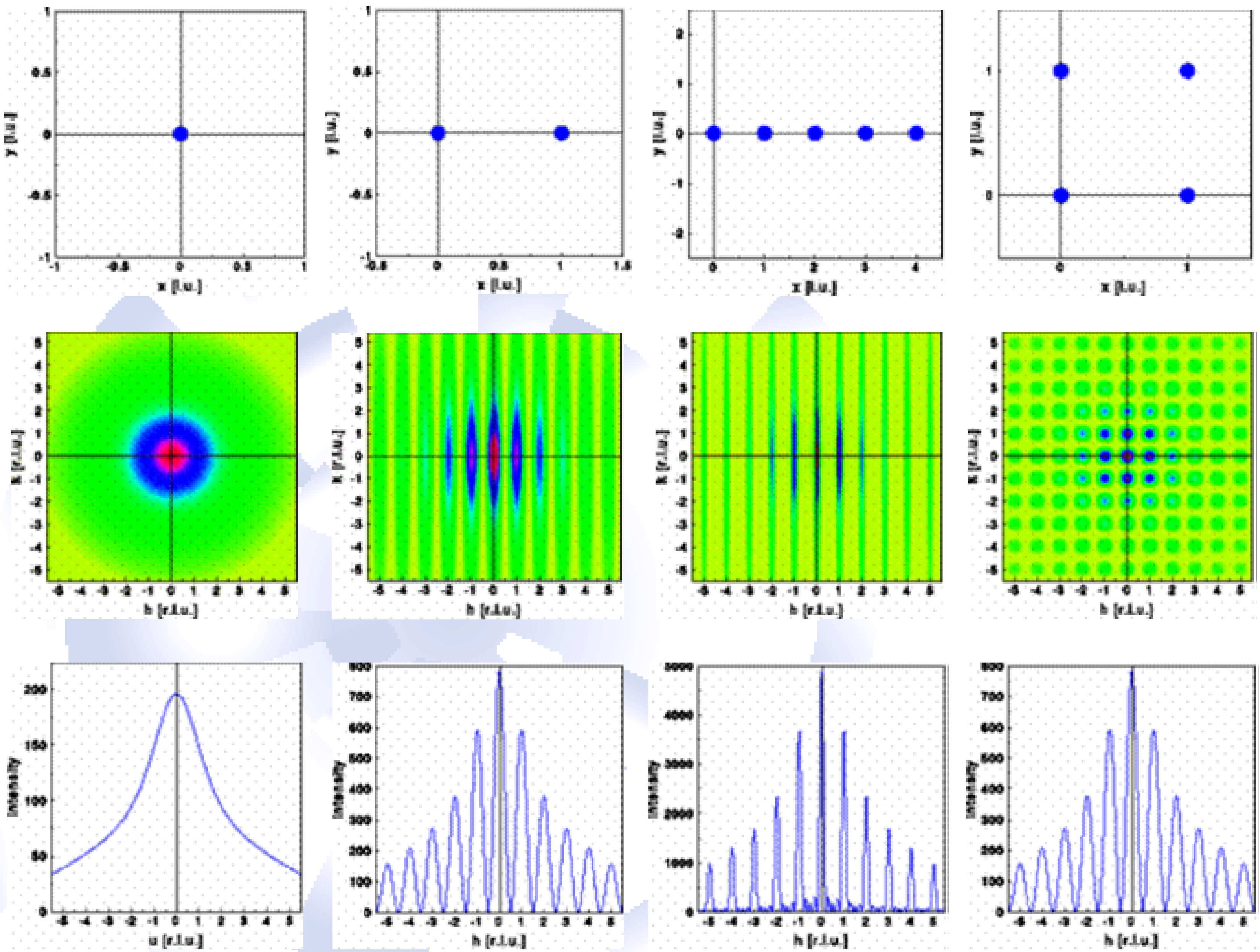




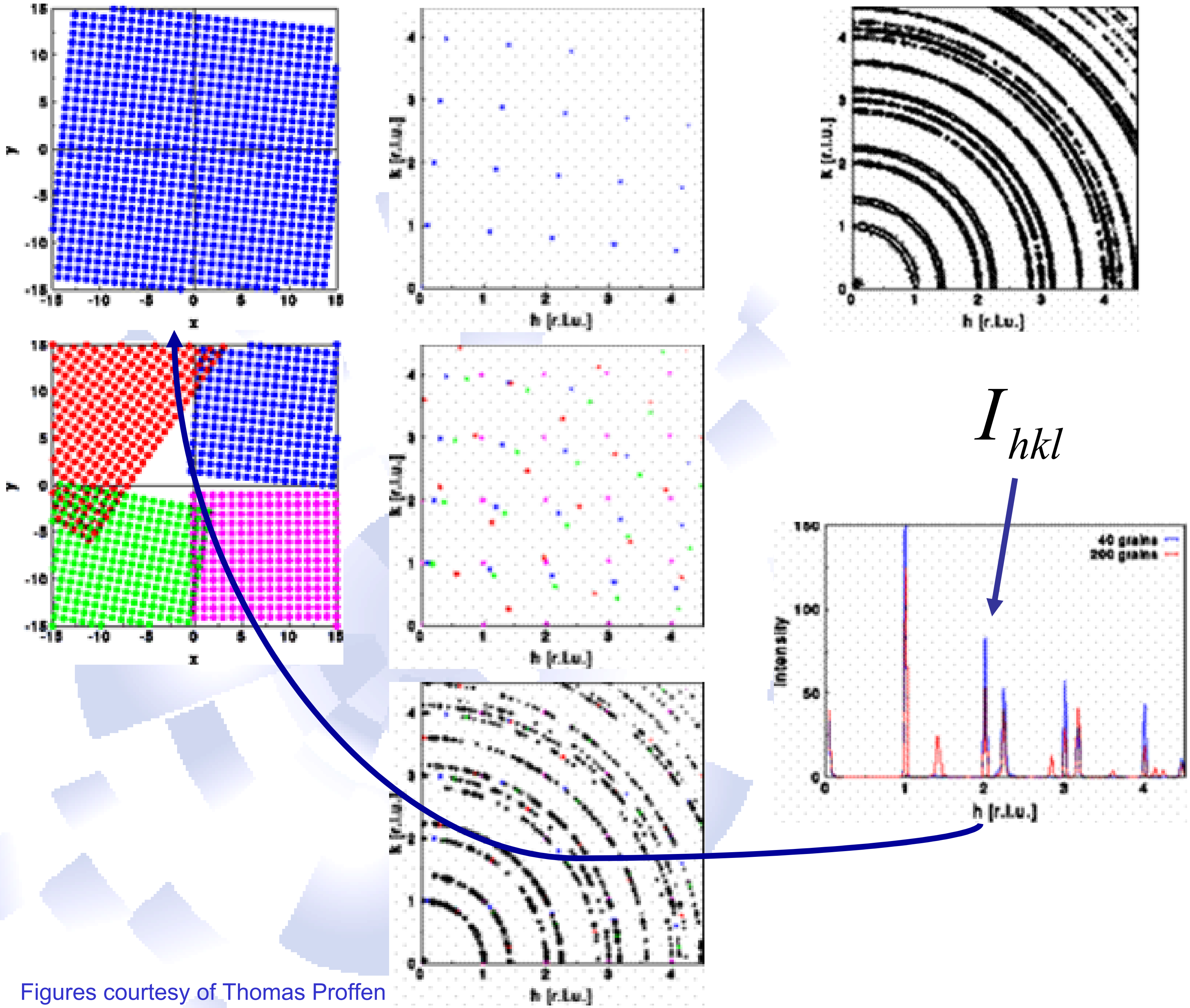




High temperature superconductors

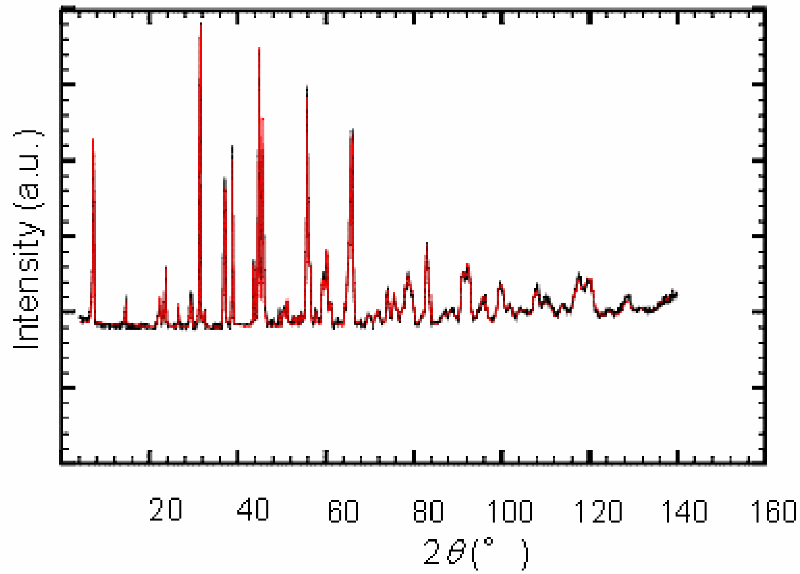


Figures courtesy of Thomas Proffen



Figures courtesy of Thomas Proffen

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



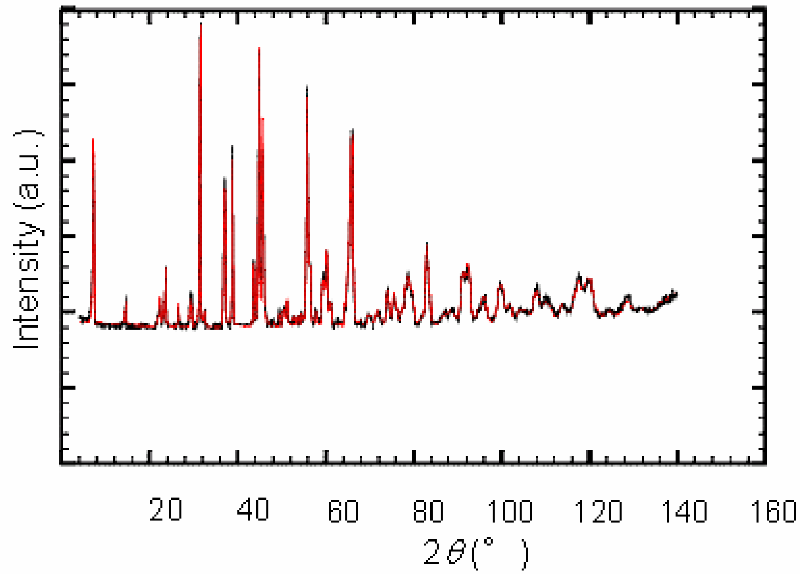
$$F_{hkl} = \sum_{j=1}^{N_j} b_j \exp\left(2\pi i(hx_j + ky_j + lz_j)\right)$$

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

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

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

Rietveld refinement (parametric modeling)



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

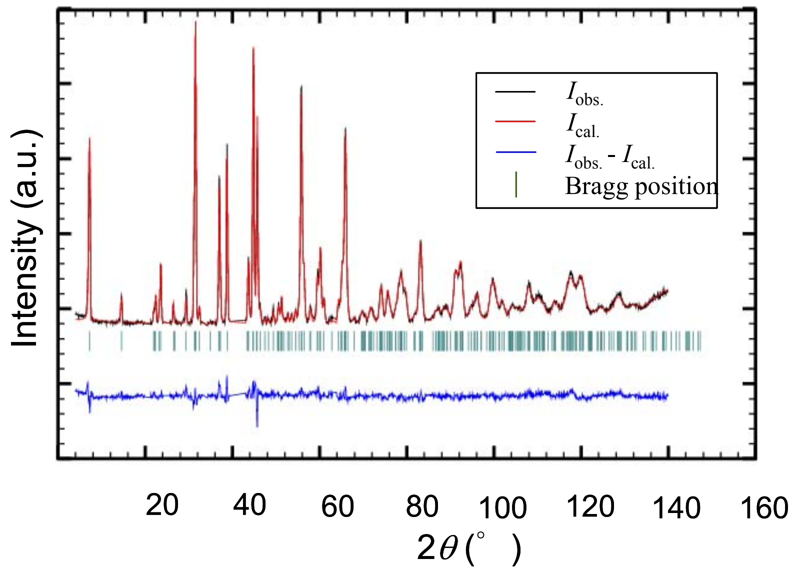
$$s_y = \sum_i w_i(y_i - y_i^c)^2$$

Constrained Rietveld refinement

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



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

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)

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

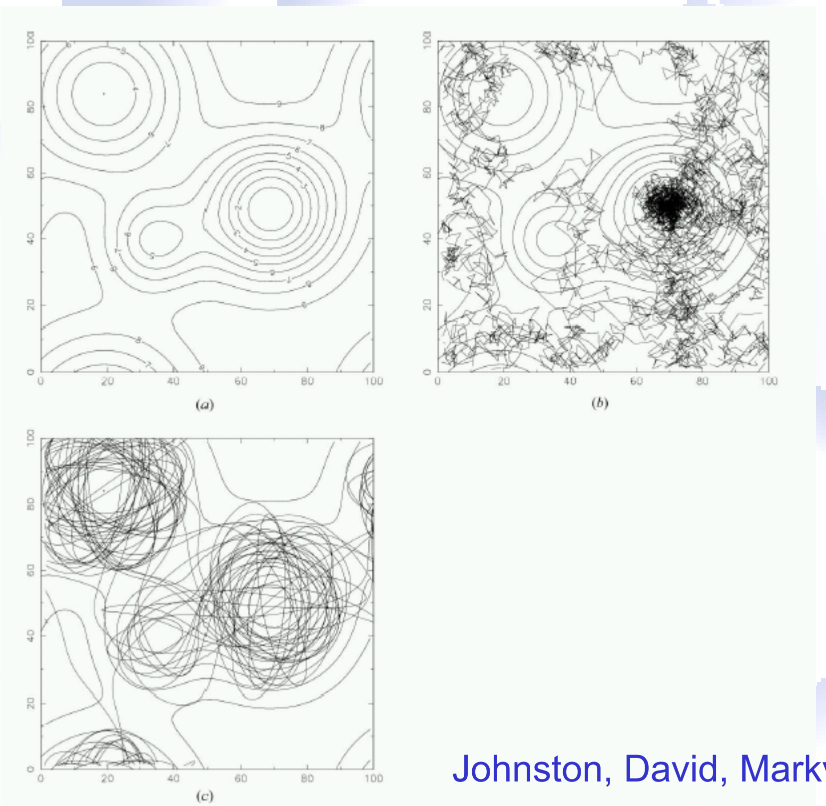
Simulated annealing
(Monte Carlo)

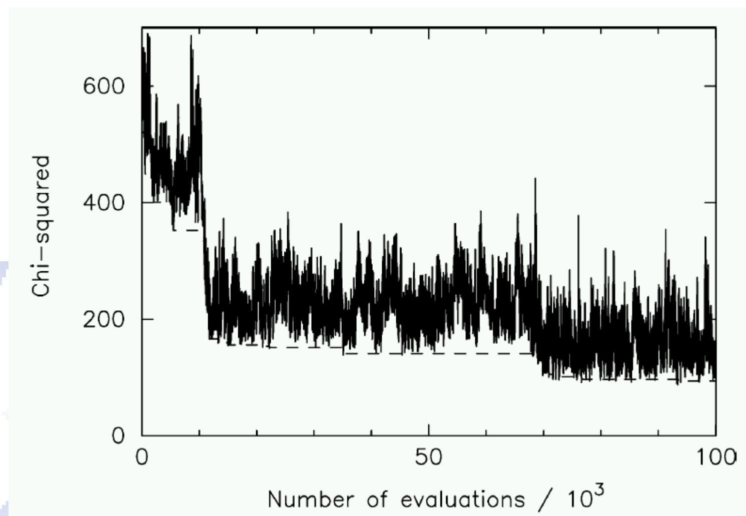
$$\exp\left(-\sum_i (y_i - y_i^c)^2 / T\right)$$

Hybrid Monte Carlo
(molecular dynamics)

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

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





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

α-AgI

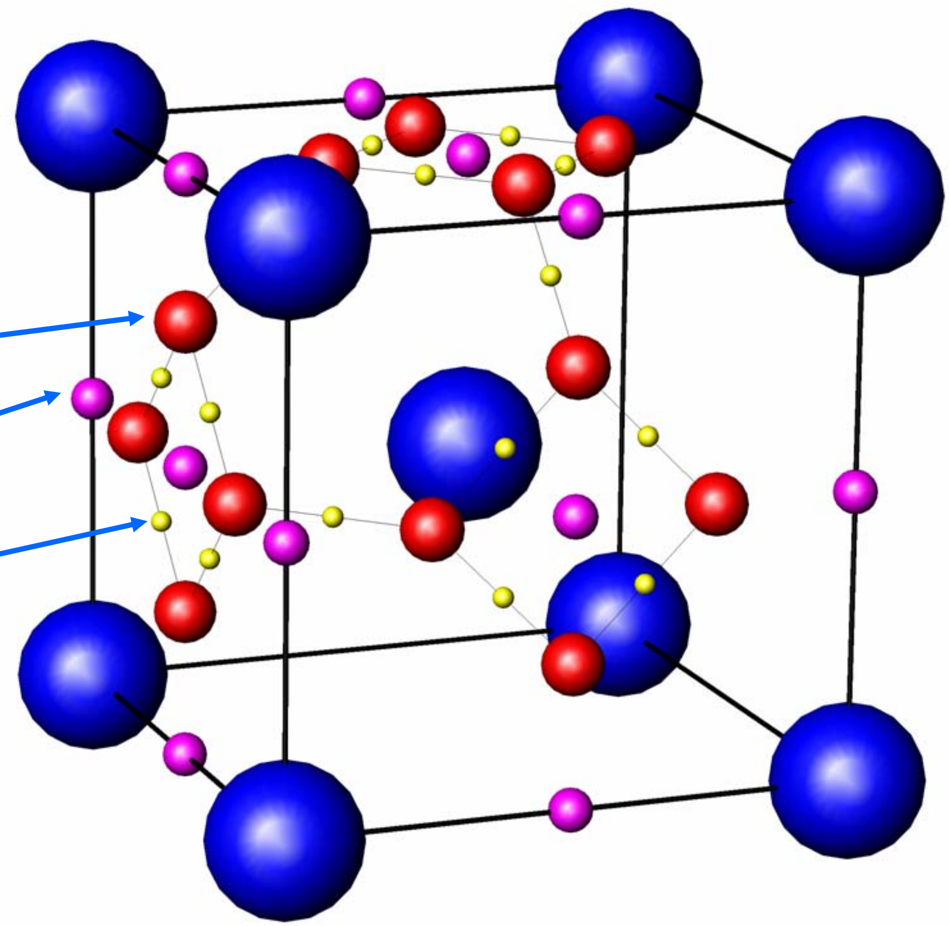
b.c.c. I^-

Ag$^+$ sites.....

12 × tetrahedral

6 × octahedral

24 × trigonal



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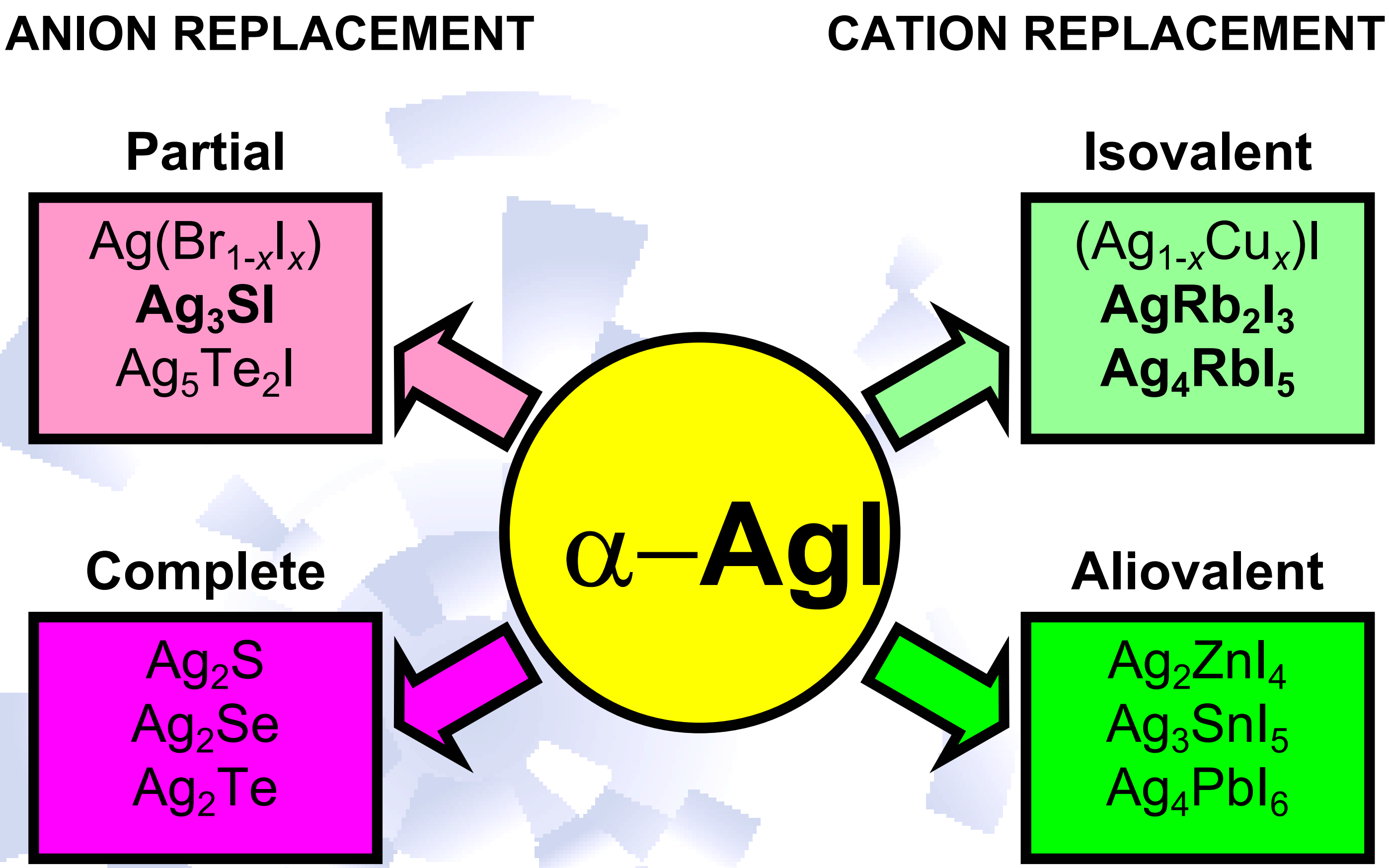
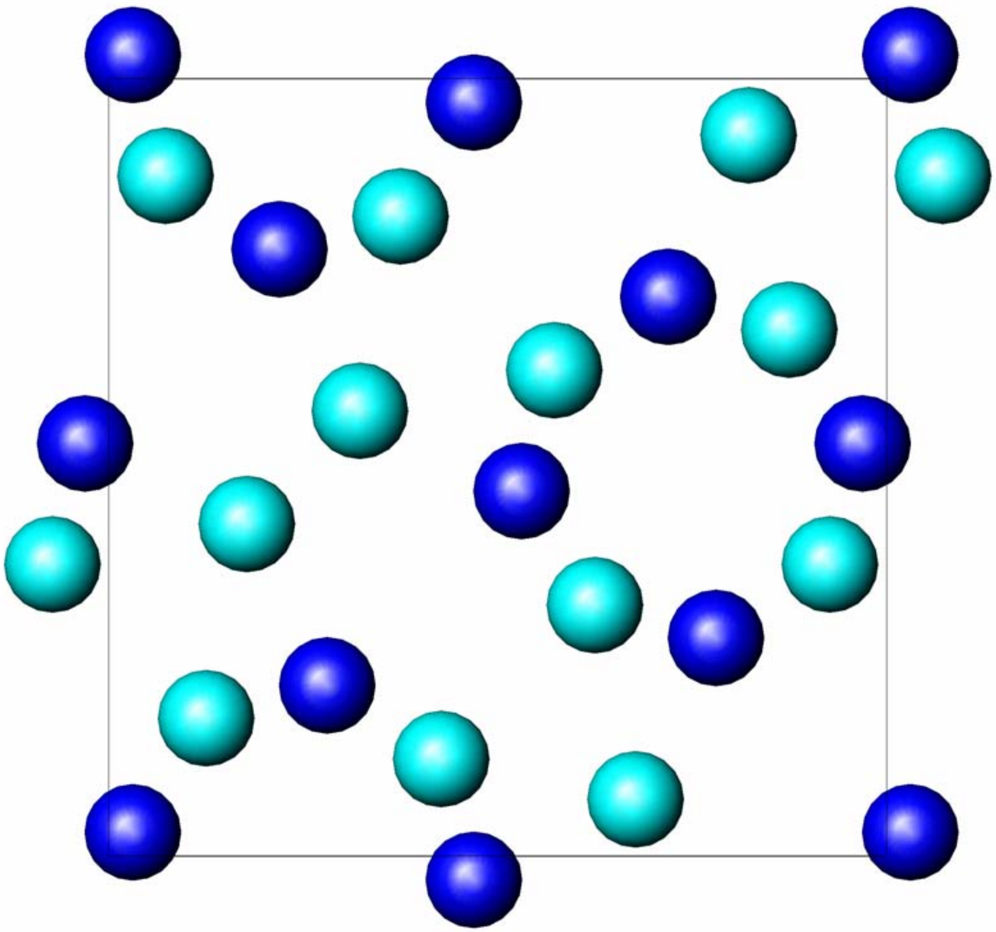


AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag_4RbI_5 : IODINE SUBSTRUCTURE



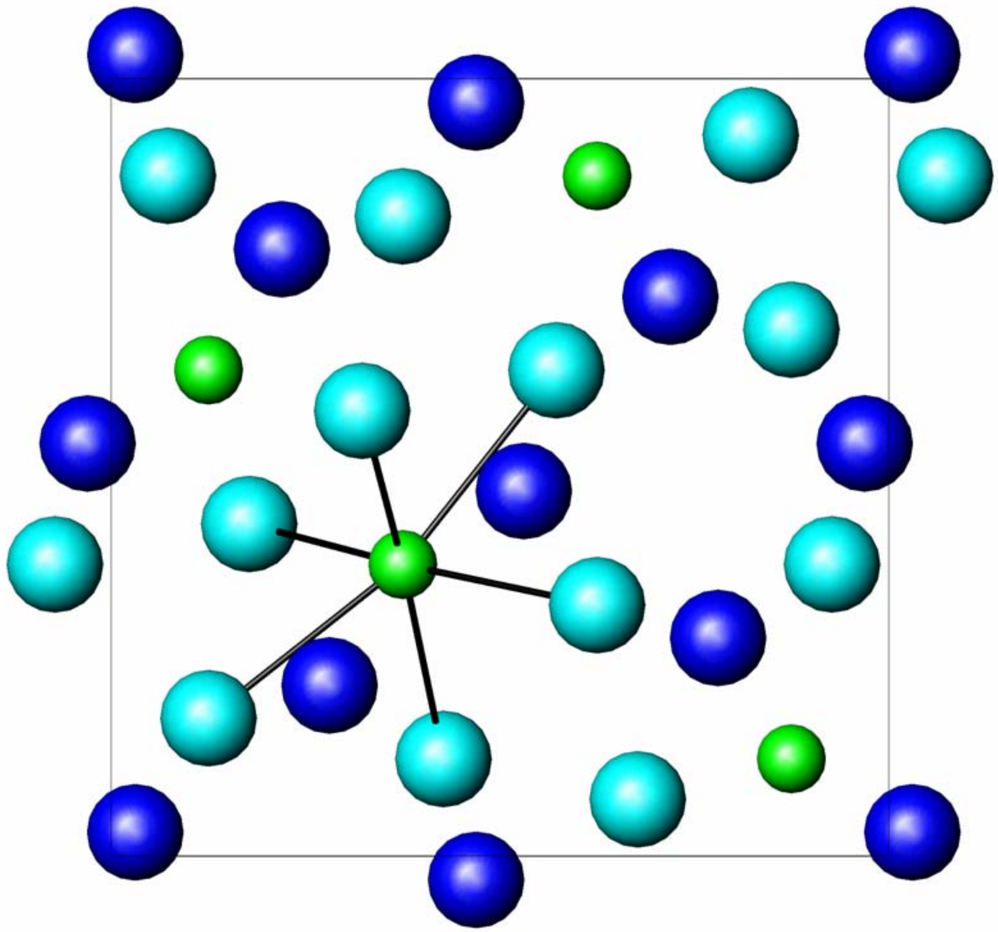
P 4_132
a ~11.24Å

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

I2 in 12(*d*)
$^1/_8$,*y*,$^1/_4$+*y*
***y*~0.177**

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

Ag_4RbI_5 : Rb POSITIONS

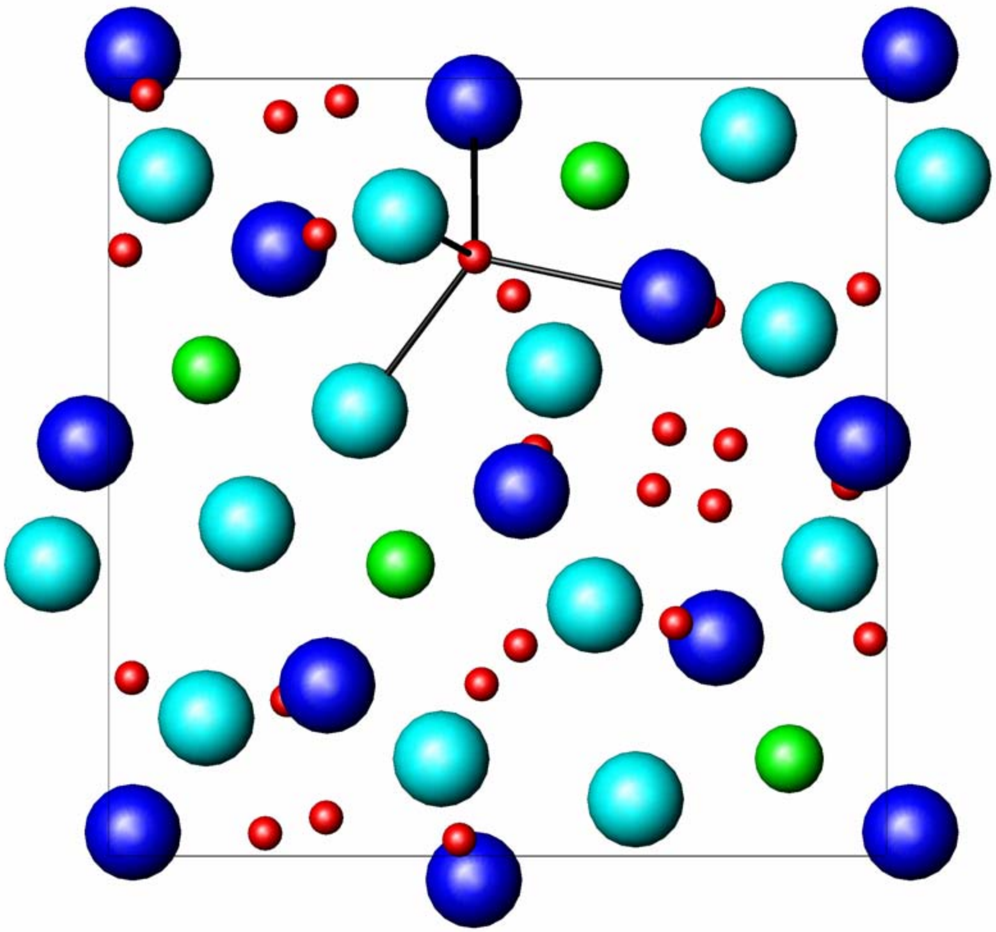


P $4_1$32
a ~11.24Å

Rb in 4(*a*)
$^3/_8, ^3/_8, ^3/_8$

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

Ag_4RbI_5 : Ag1 SITES



P 4_132
a ~11.24Å

Ag1 in 24(*e*)
x,y,z
***x*~0.531**
***y*~0.272**
***z*~0.806**

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

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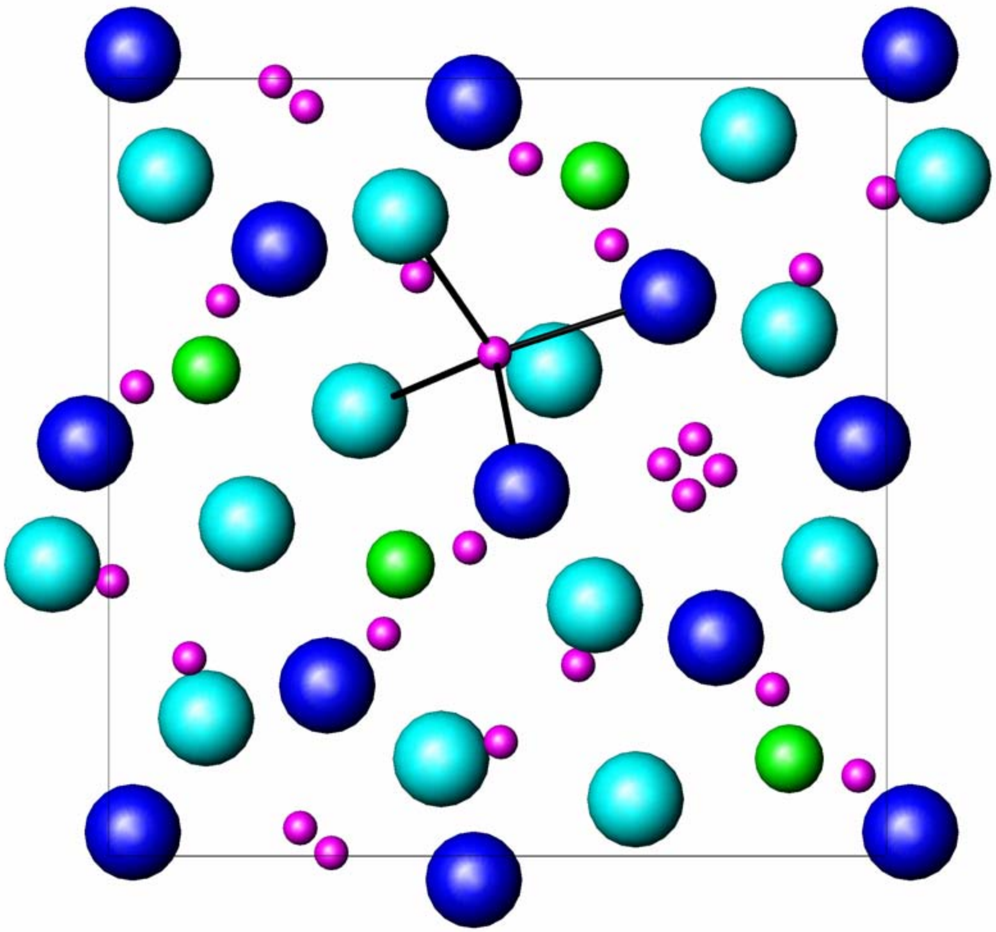
Ag_4RbI_5 : Ag2 SITES

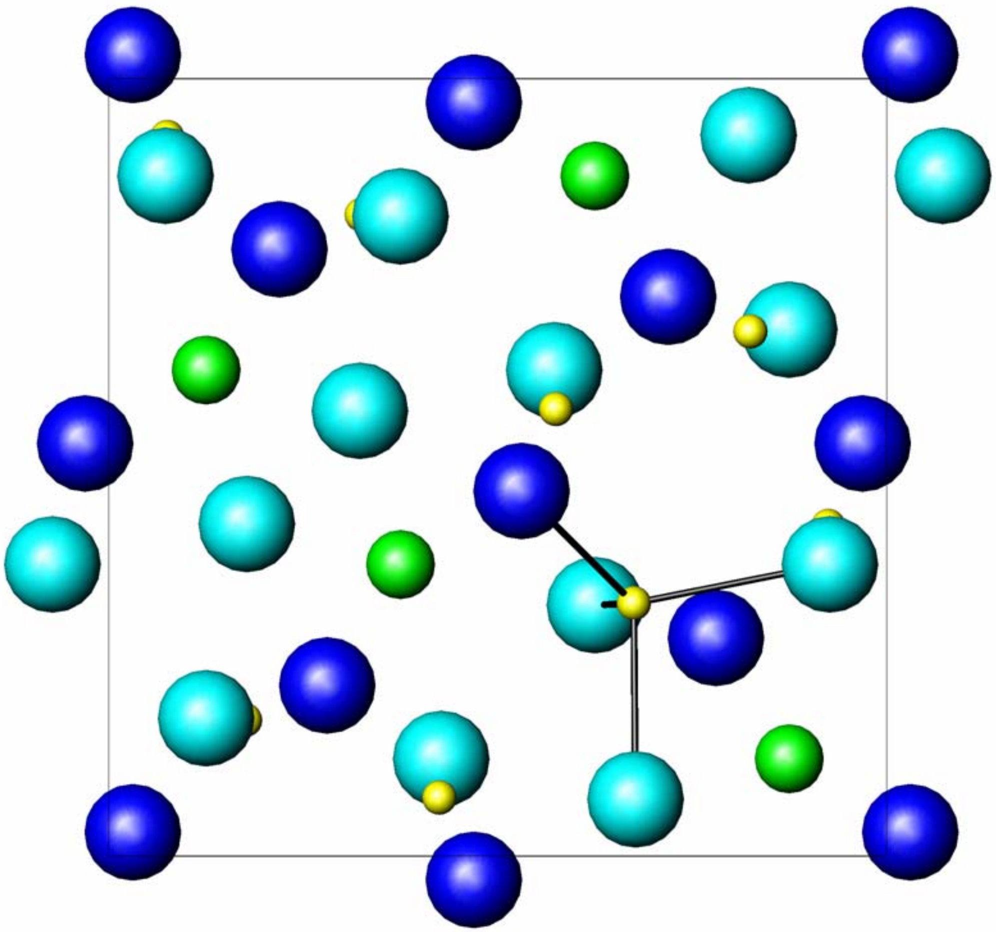


P $4_1$32
a ~11.24Å

Ag2 in 24(*e*)
x,y,z
***x*~0.993**
***y*~0.855**
***z*~0.206**

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

Ag_4RbI_5 : Ag3 SITES

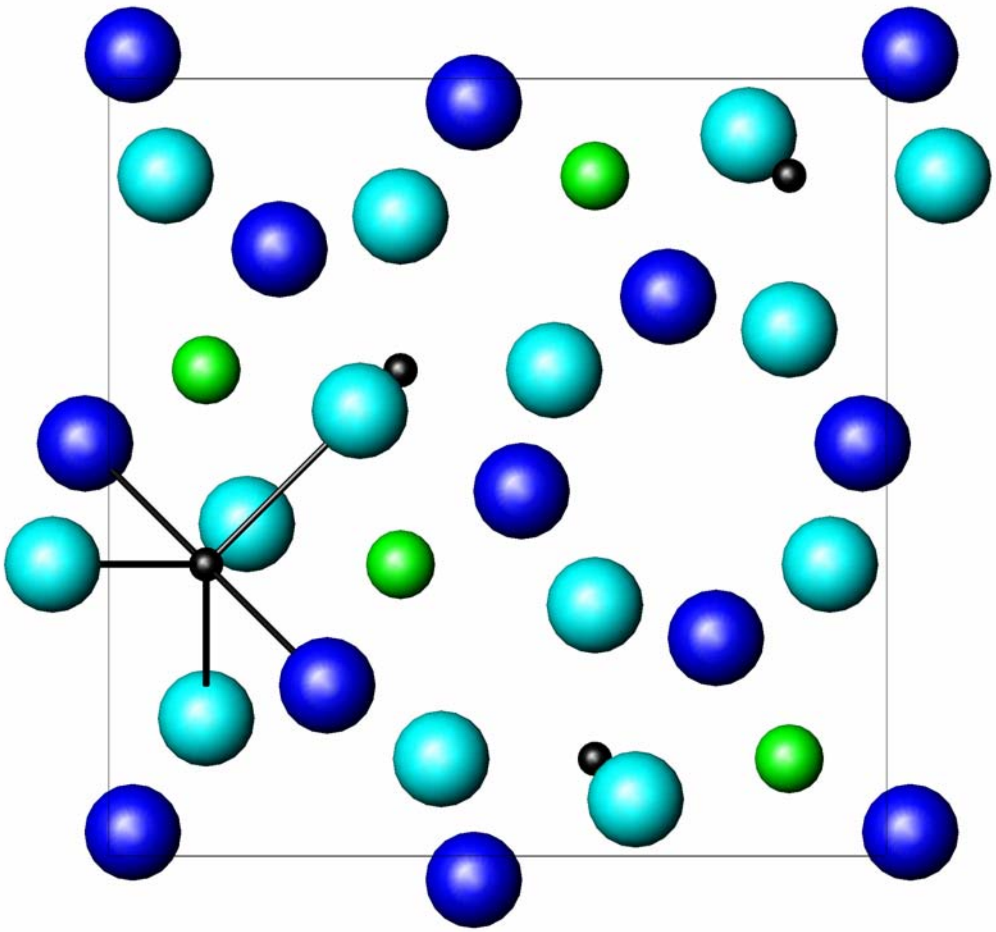


P 4_132
a ~11.24Å

Ag3 in 8(*c*)
x,x,x
***x*~0.177**

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

Ag_4RbI_5 : Ag4 SITES



P 4_132
a ~11.24Å

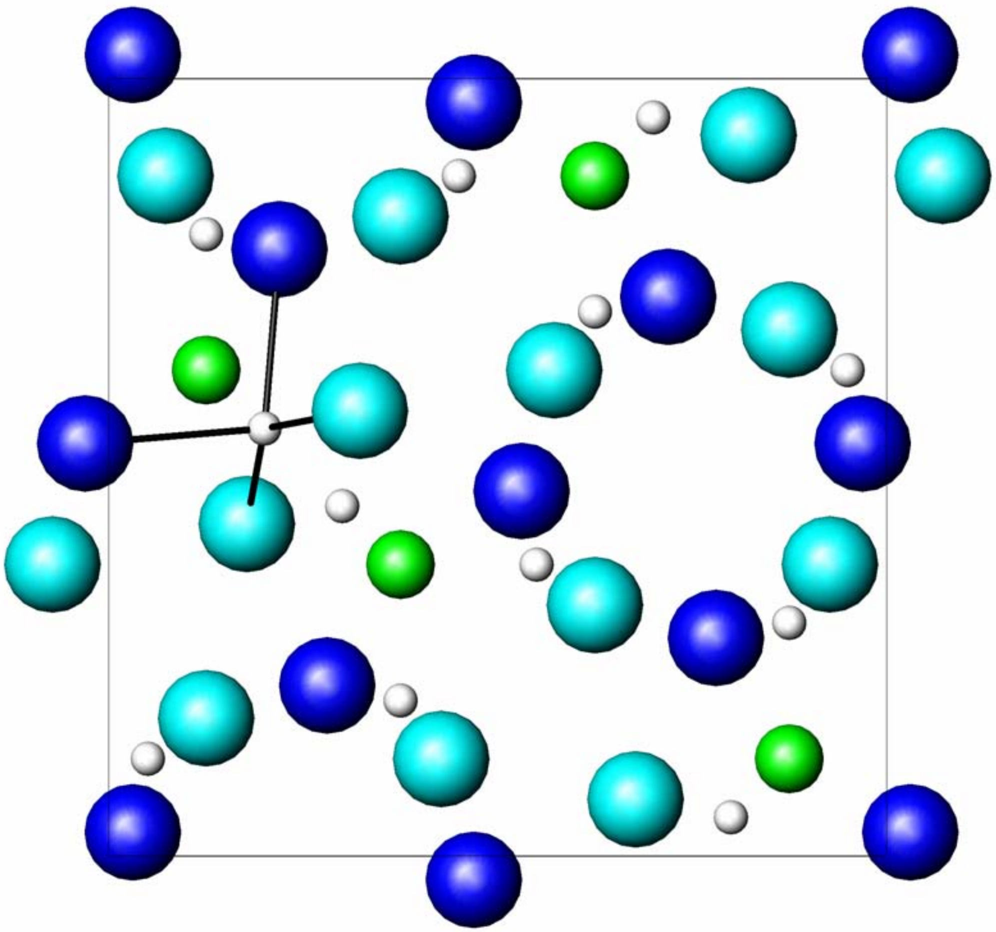
Ag4 in 4(*b*)
$^7/_8,^7/_8,^7/_8$

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

ISIS

CCLRC

Ag_4RbI_5 : Ag5 SITES

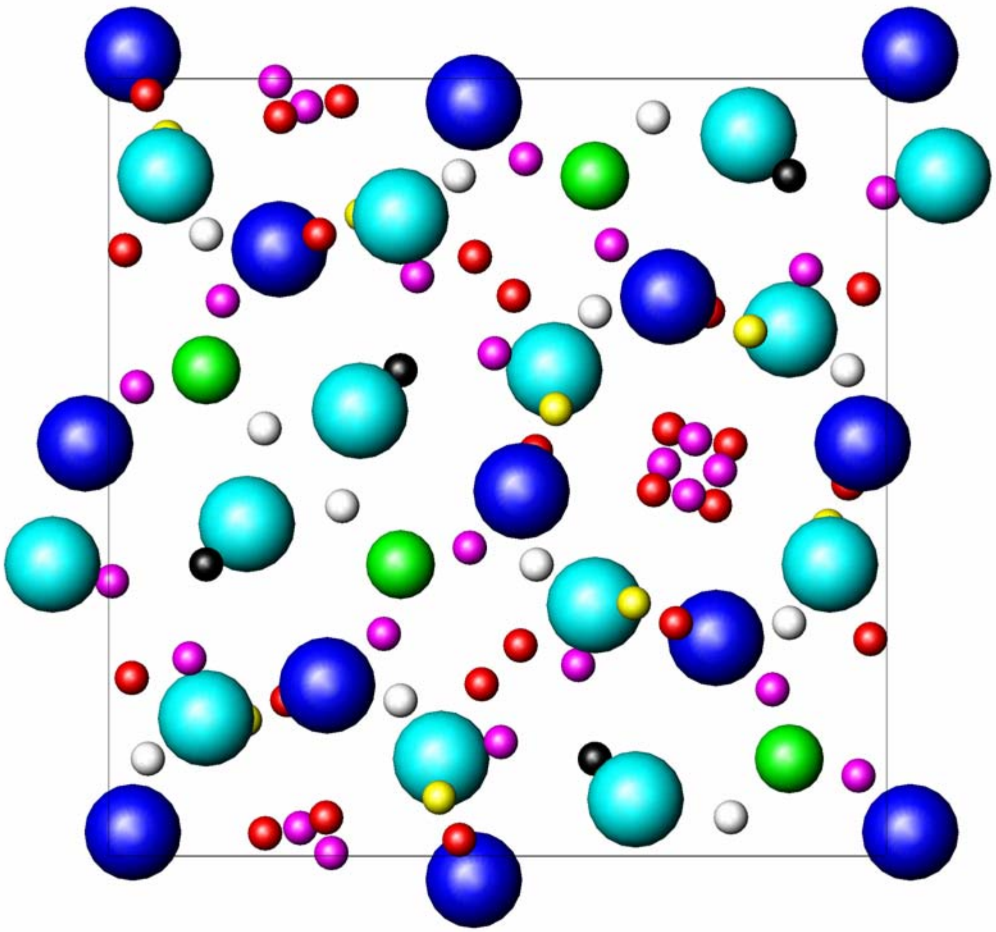


P $4_1$32
a ~11.24Å

Ag5 in 12(*d*)
$^1/_8$,*y*,$^1/_4$+*y*
***y*~0.764**

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

Ag_4RbI_5 : Ag SITES



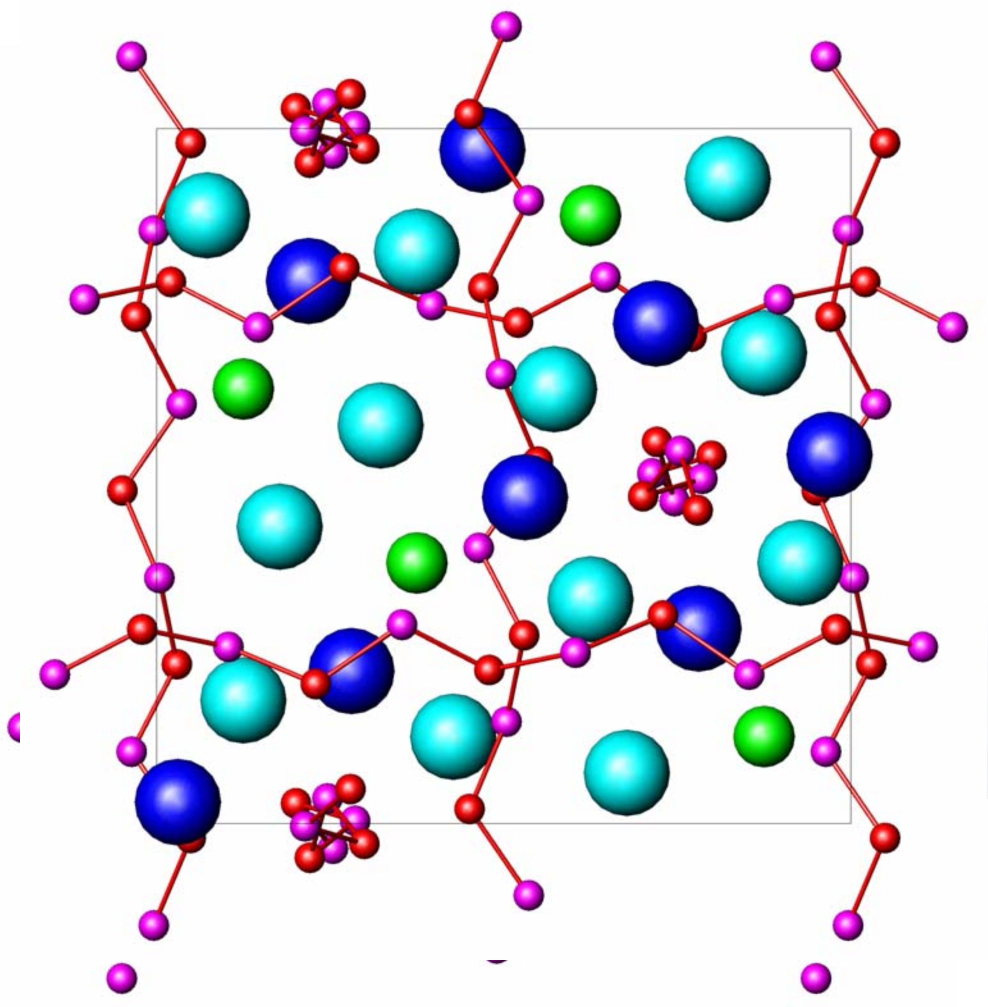
P 4_132
a ~11.24Å

20 × Ag^+ per unit cell

How are they distributed over the 72 sites?

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

Ag_4RbI_5 : CONDUCTION PATHWAYS



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

- Ag^+ hop between pairs of these sites in <001> directions.

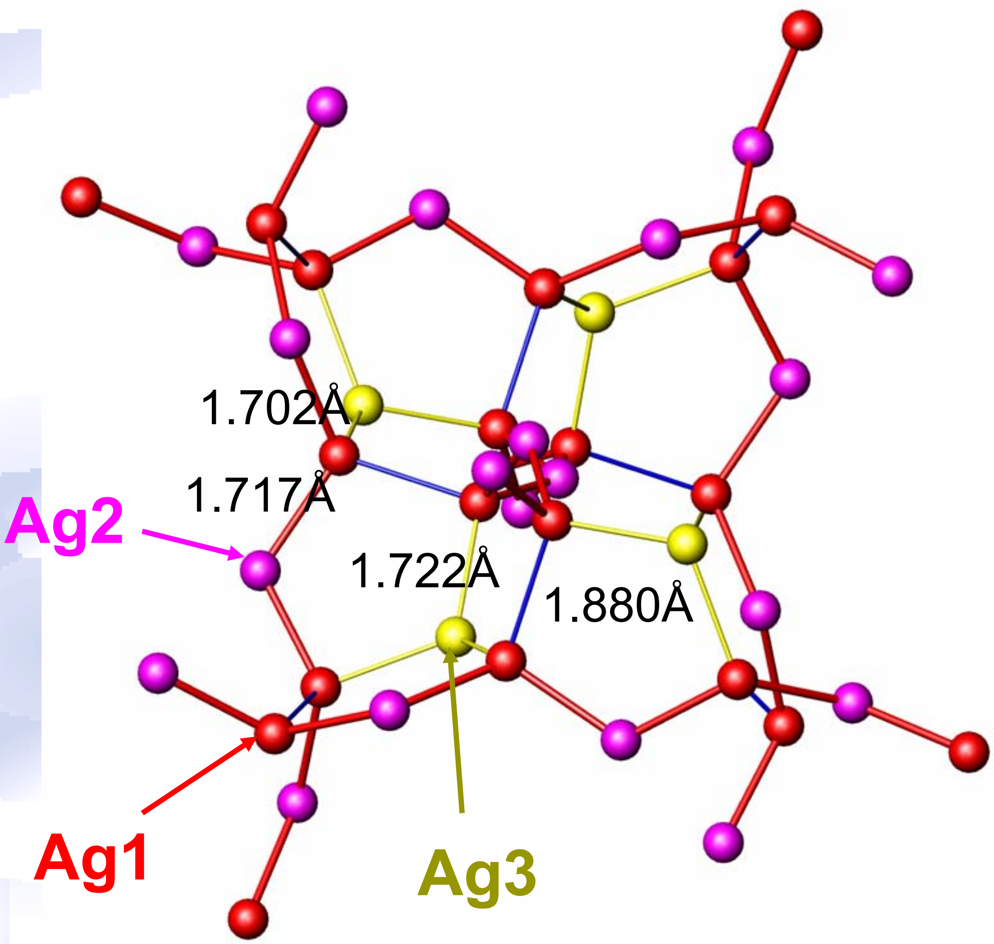
- conduction of Ag^+ occurs along one-dimensional channels.

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

Ag_4RbI_5 : DIFFUSION BETWEEN CHANNELS

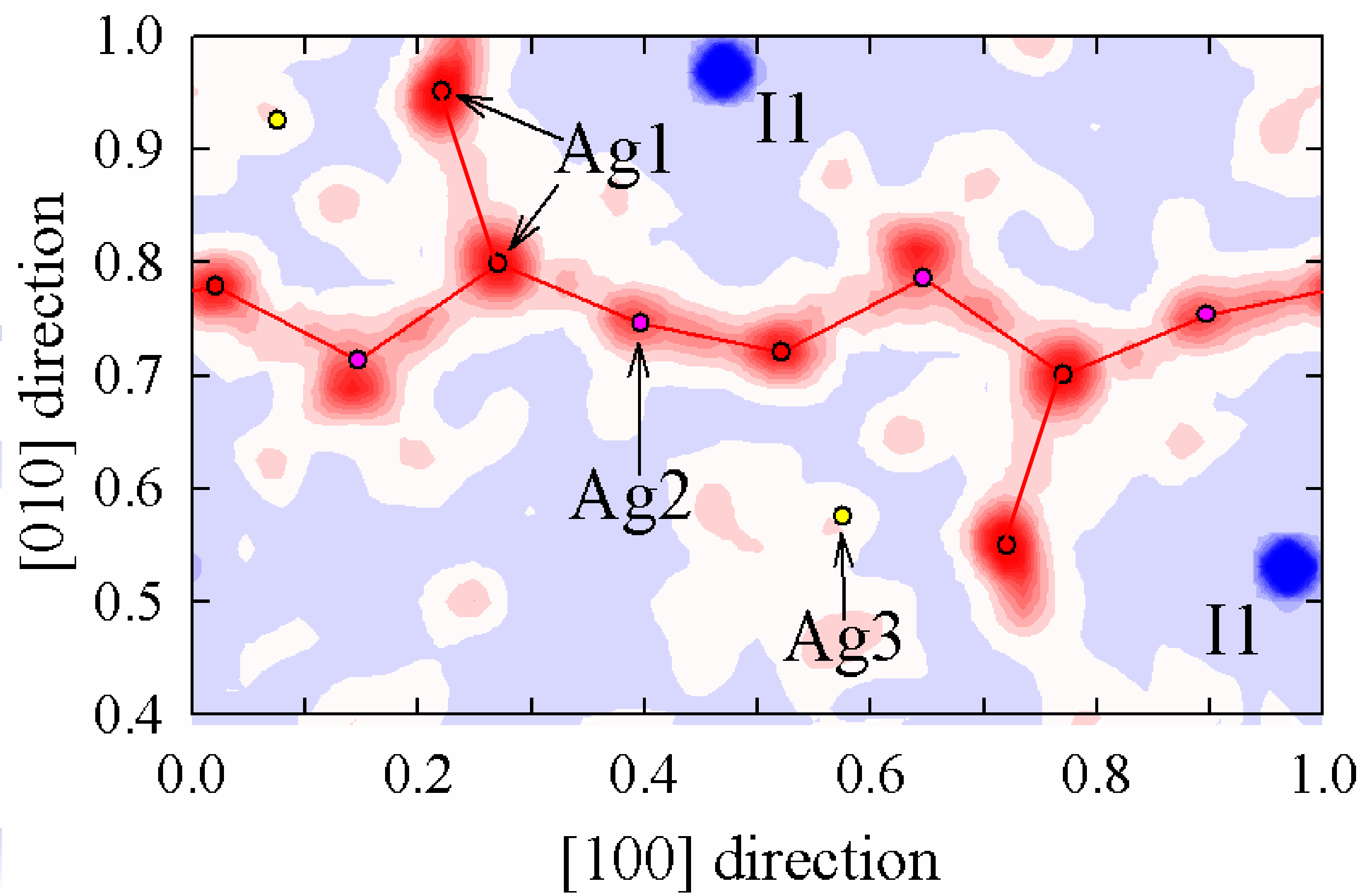
There are two plausible routes for Ag^+ to hop between channels.

- Direct hop :
  Ag1 → Ag1
- Indirect hop :
  Ag1 → Ag3 → Ag1



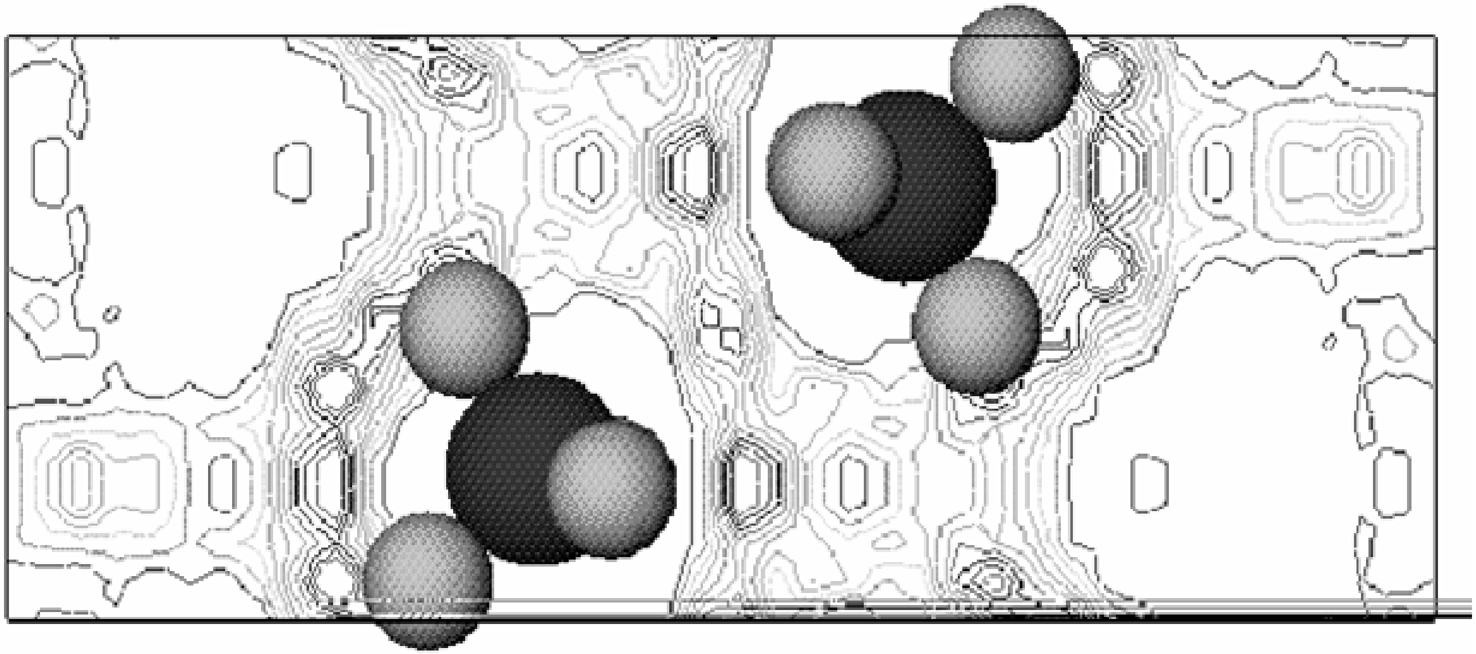
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag_4RbI_5 : MAXIMUM ENTROPY FOURIER MAP



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

Atomic (structural) modeling



All inverse problems have solutions

Some inverse solutions have problems