Neutron Scattering Data Analysis

Robert McGreevy

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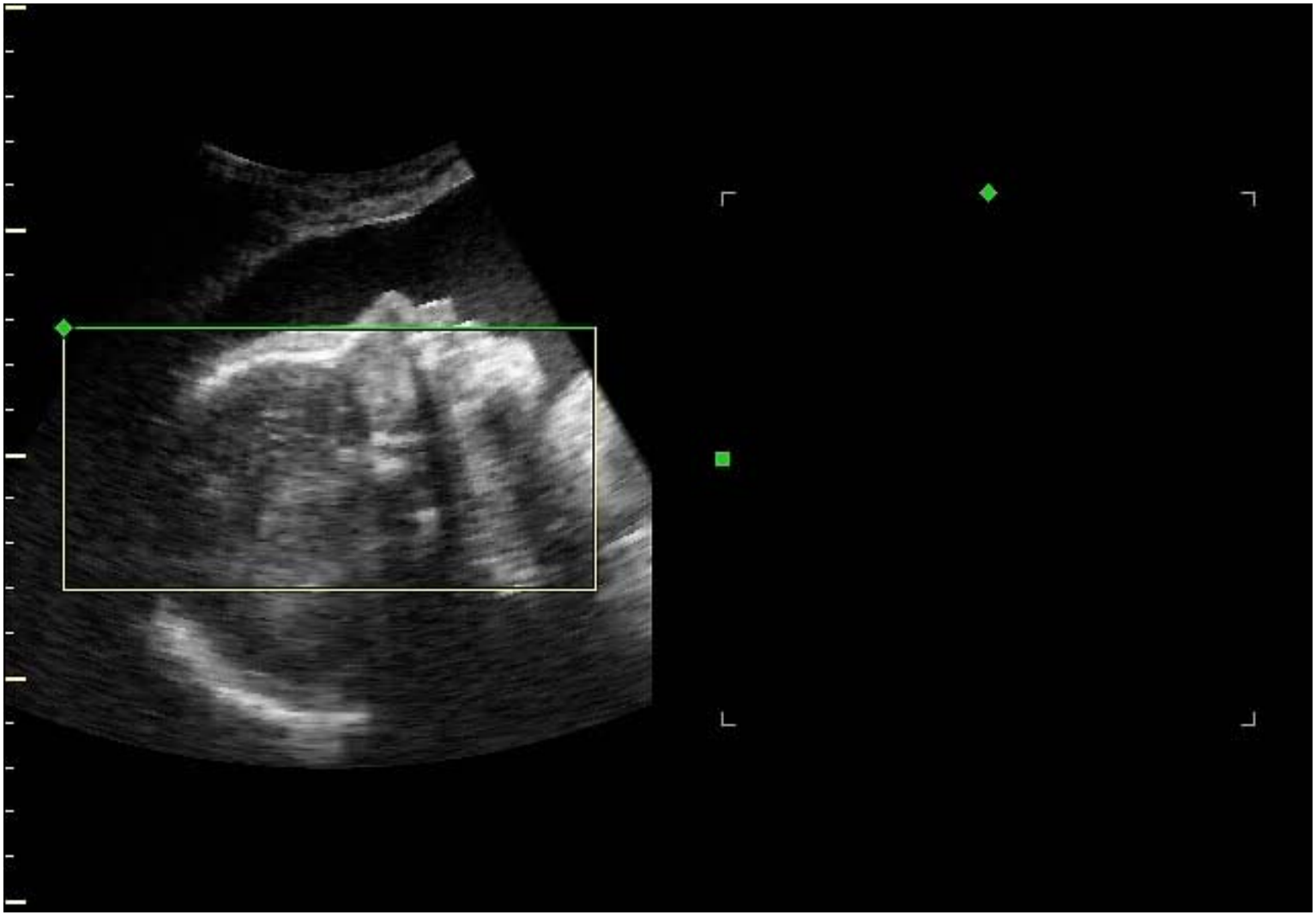
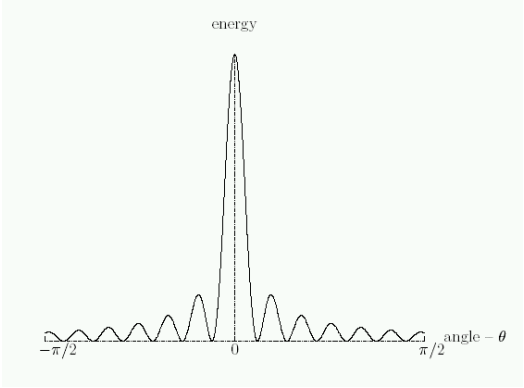
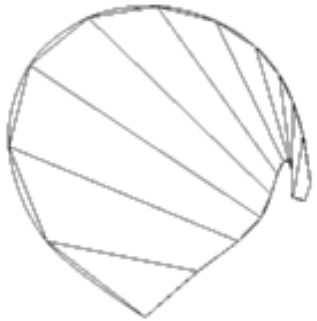
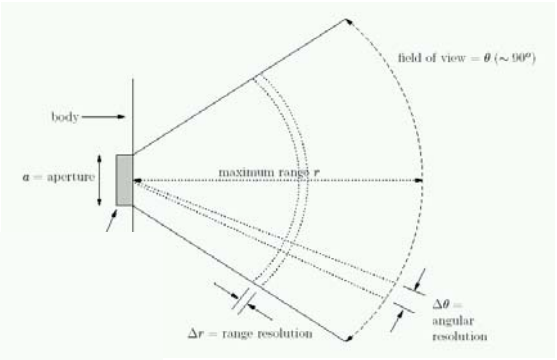


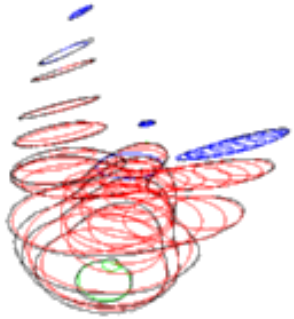


$$S(t) = \mathrm{Re}\int_{-a/2}^{a/2} \mathrm{e}^{-i2\pi f_c\,(t-r(y)/c)}\,dy$$

$$= \mathrm{Re}\;\mathrm{e}^{-i2\pi f_c\,t}\int_{-a/2}^{a/2} \mathrm{e}^{-i2\pi f_c\,r(y)/c}\,dy$$



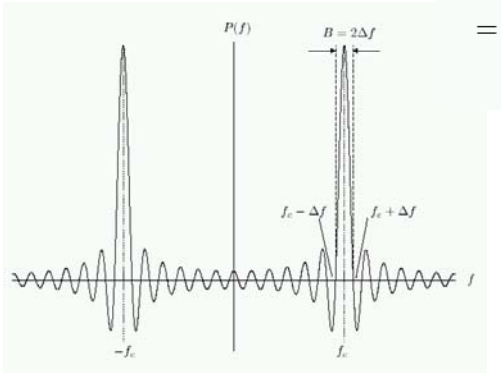




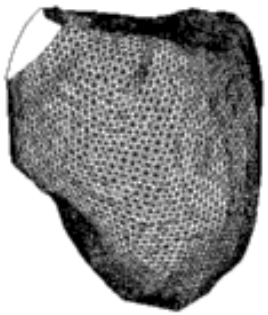
$$= \frac{a}{N}\sum_{n=0}^{N-1} \mathrm{e}^{i\,2\pi f_c\,a\,[n+(1-N)/2](\sin\theta-\sin\theta_0)/(Nc)}$$

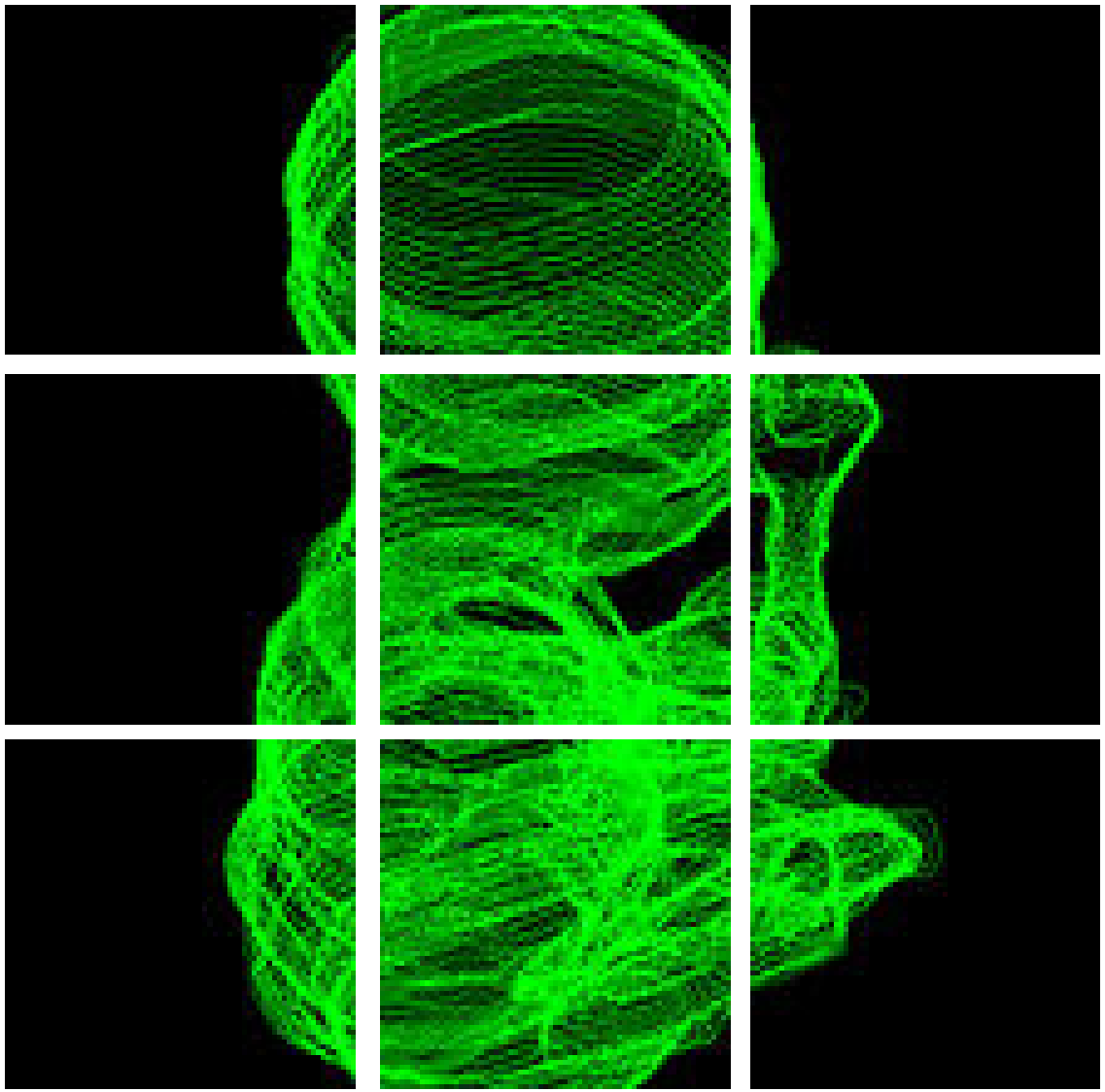
$$= \frac{a}{N}\,\mathrm{e}^{i\,2\pi f_c\,a\,(1-N)(\sin\theta-\sin\theta_0)/(2Nc)}\sum_{n=0}^{N-1} \mathrm{e}^{i\,2\pi f_c\,na(\sin\theta-\sin\theta_0)/(Nc)}$$

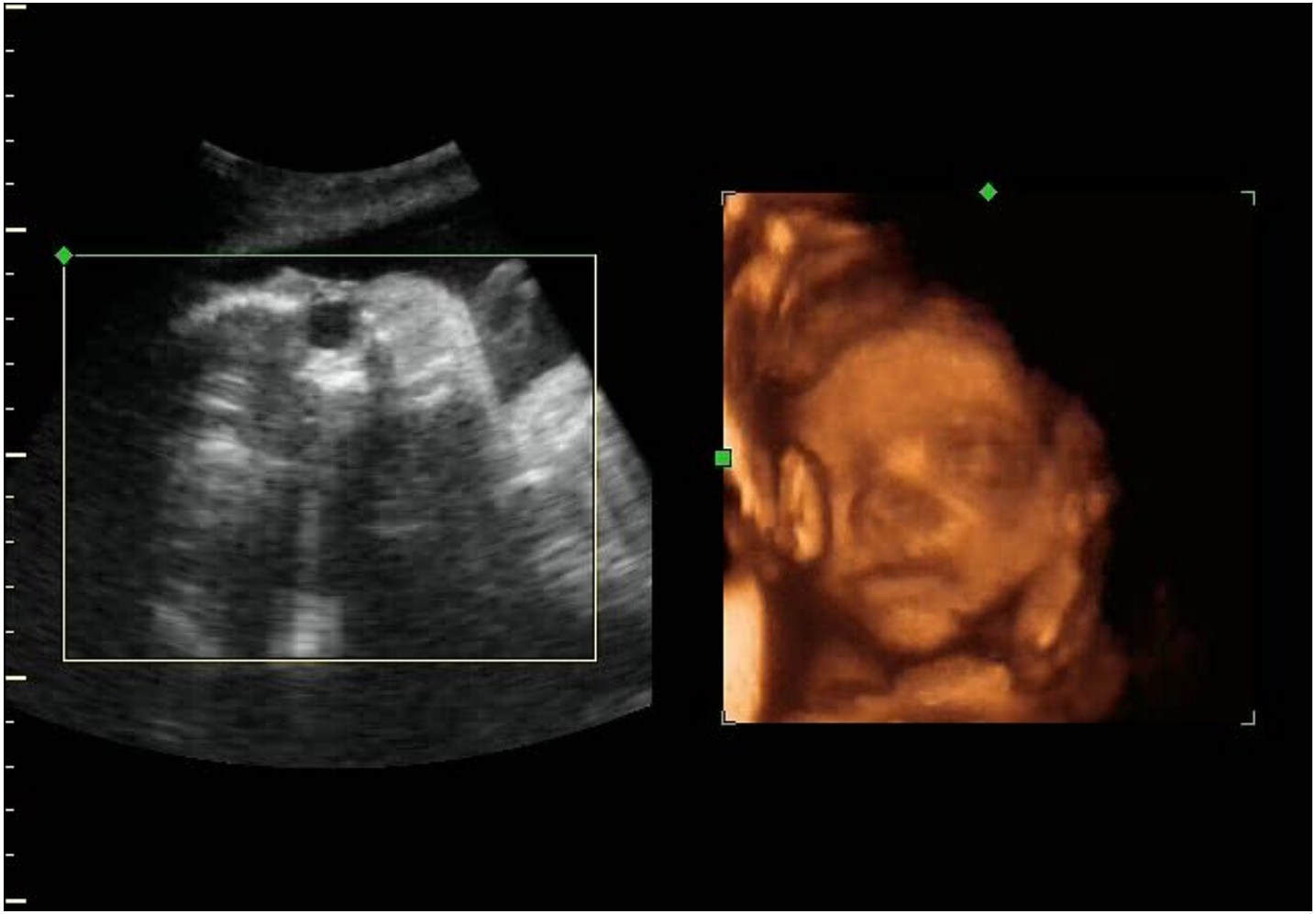
$$= \frac{a}{N}\,\mathrm{e}^{i\,2\pi f_c\,a\,(1-N)(\sin\theta-\sin\theta_0)/(2Nc)}\sum_{n=0}^{N-1} \mathrm{e}^{ikn}$$



$$S'_N = \frac{a}{N}\,\frac{\sin[\pi f_c\,a(\sin\theta-\sin\theta_0)/c]}{\sin[\pi f_c\,a(\sin\theta-\sin\theta_0)/(Nc)]}$$







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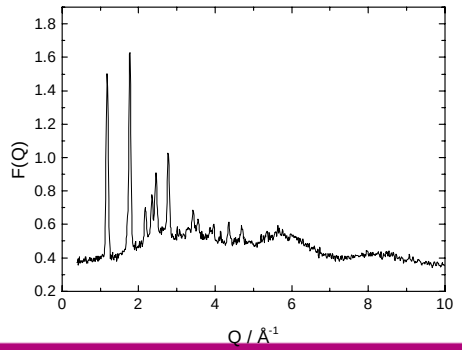
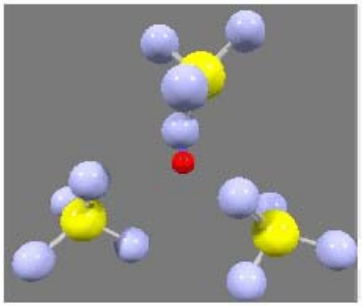
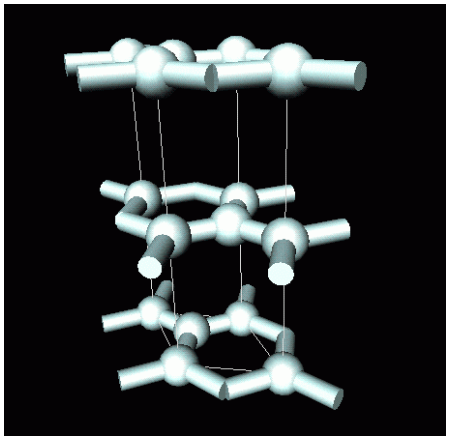
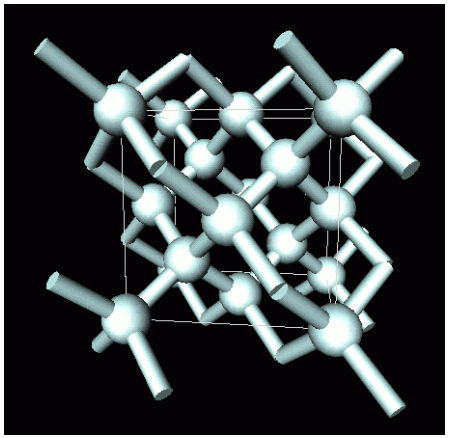
From here …….. to there



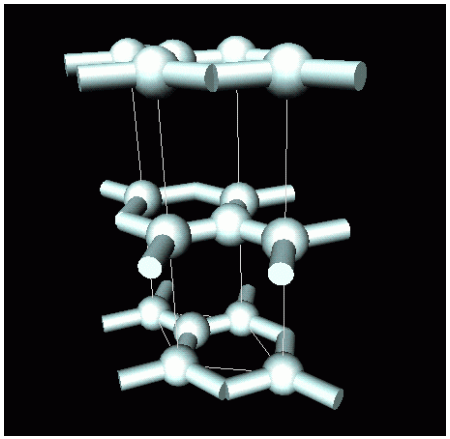




Graphite



Diamond



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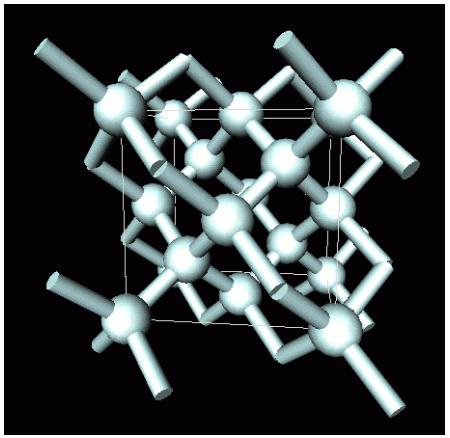

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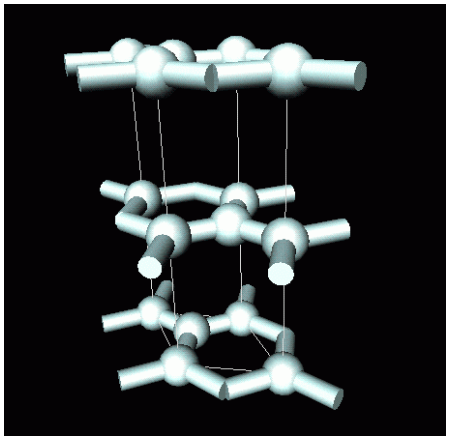

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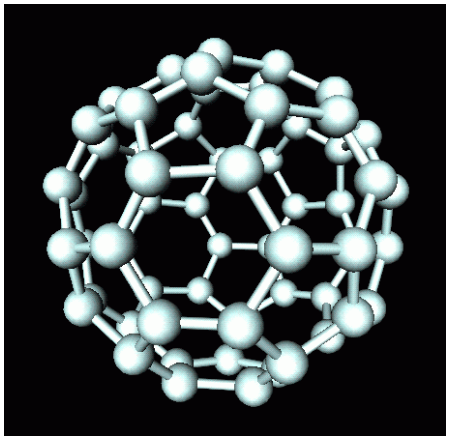
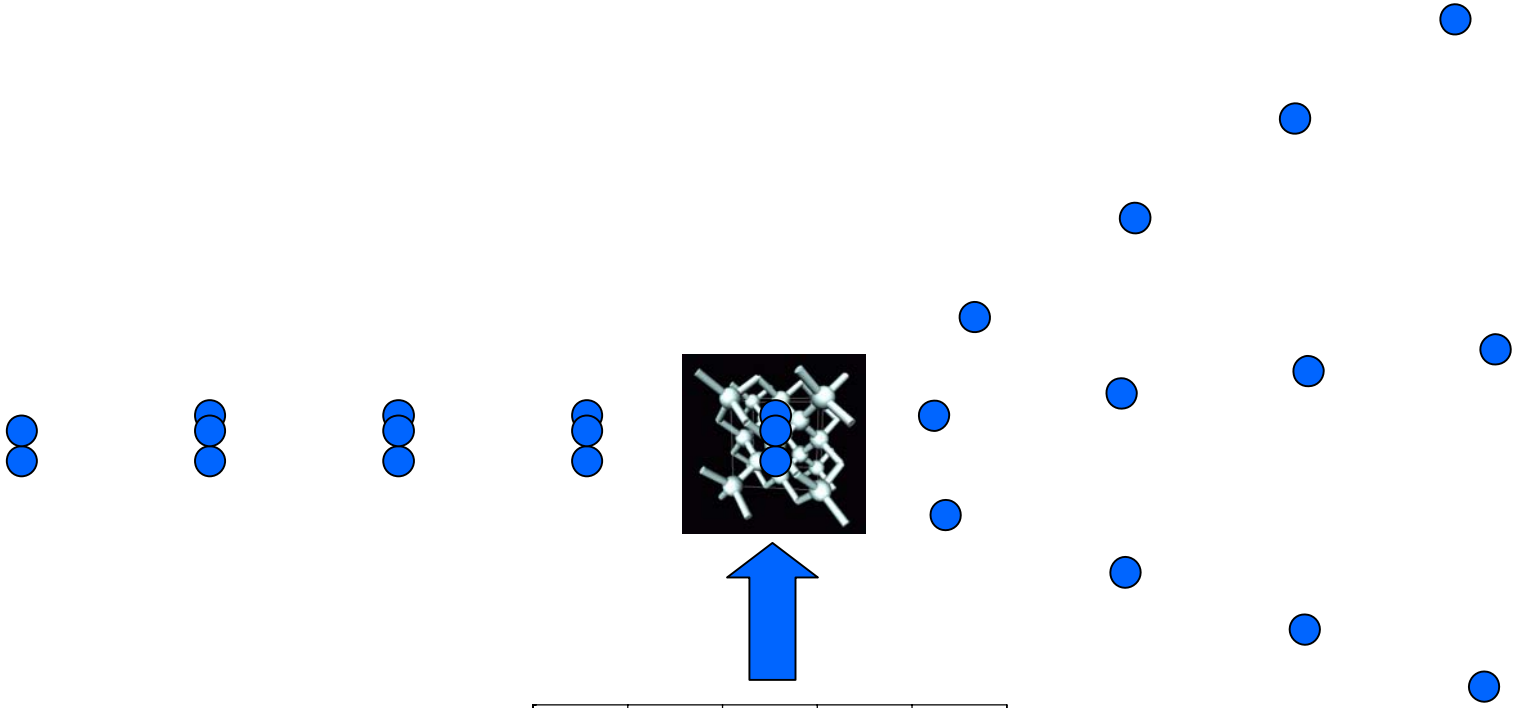
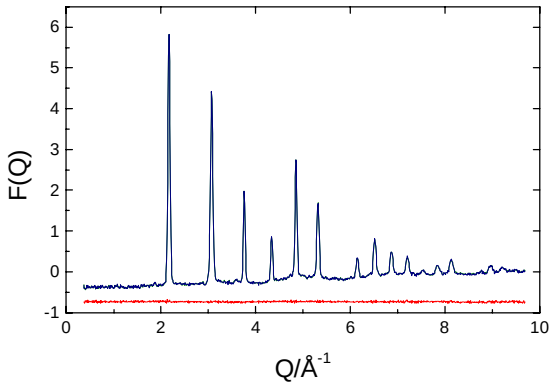
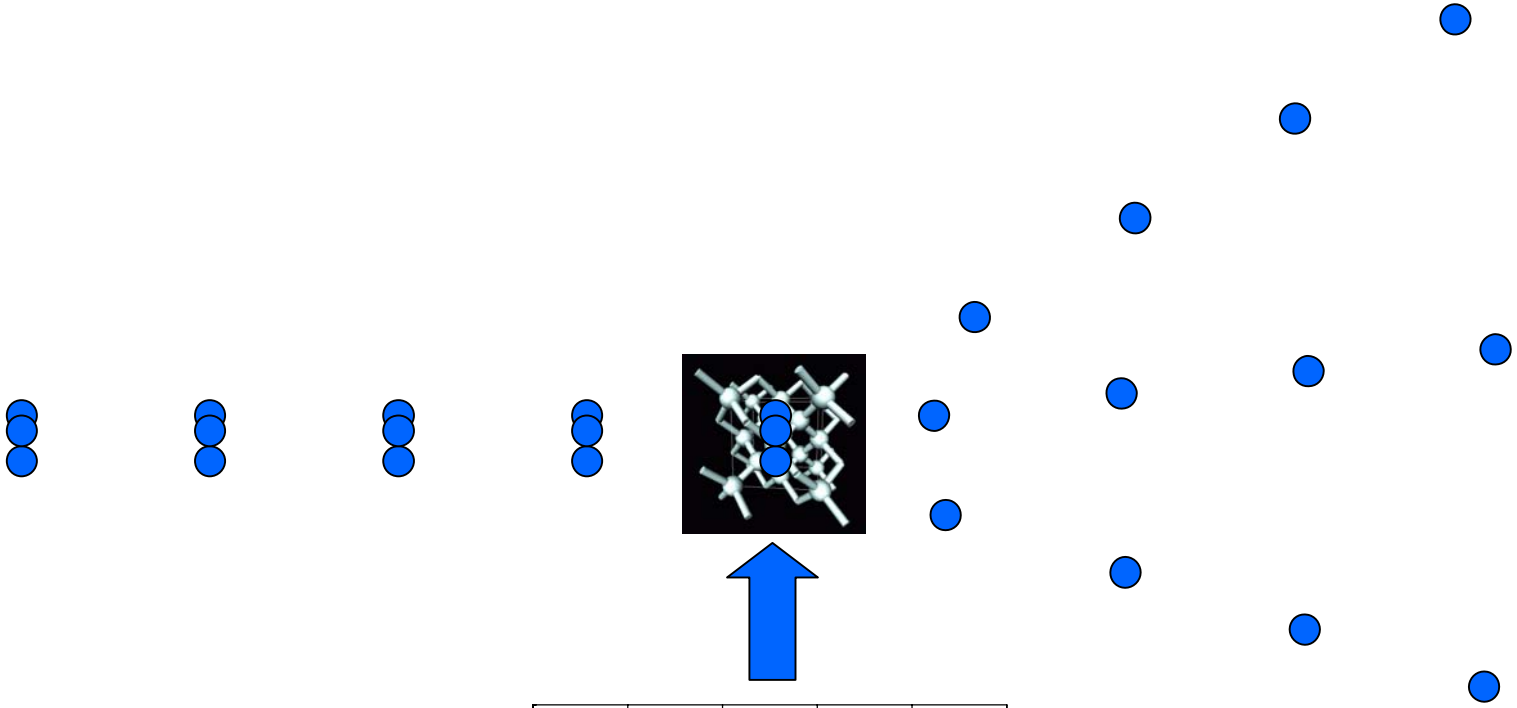


Fullerene



Neutron Diffraction





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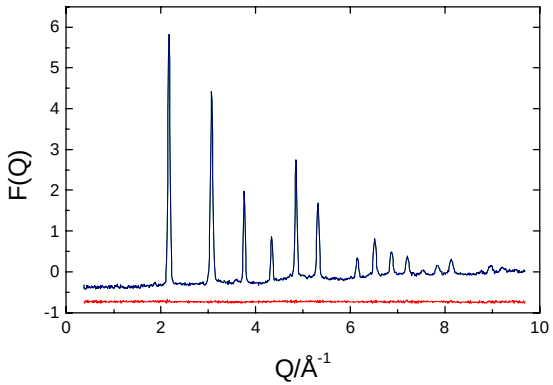

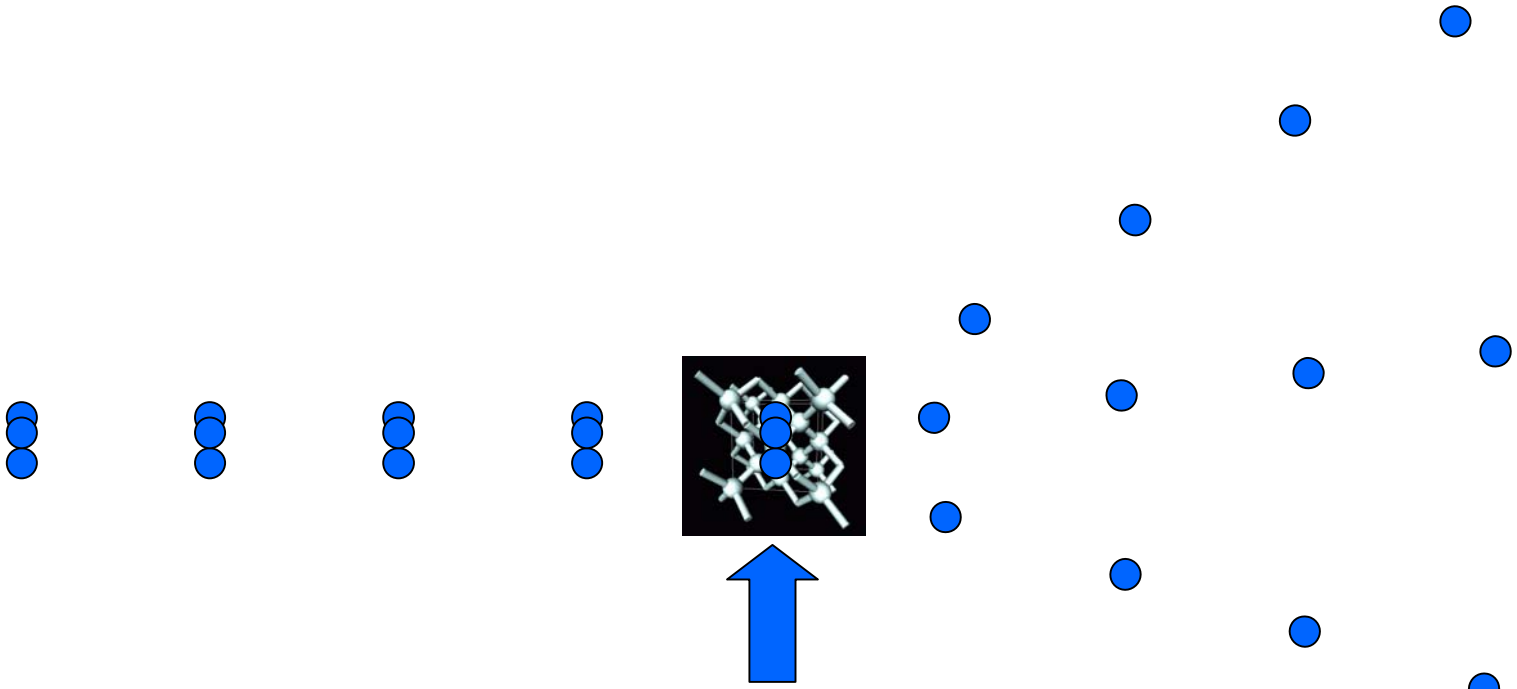

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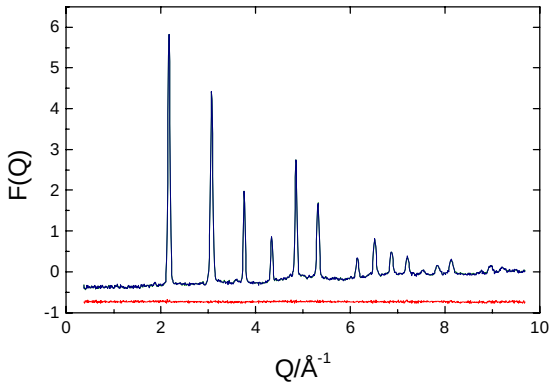
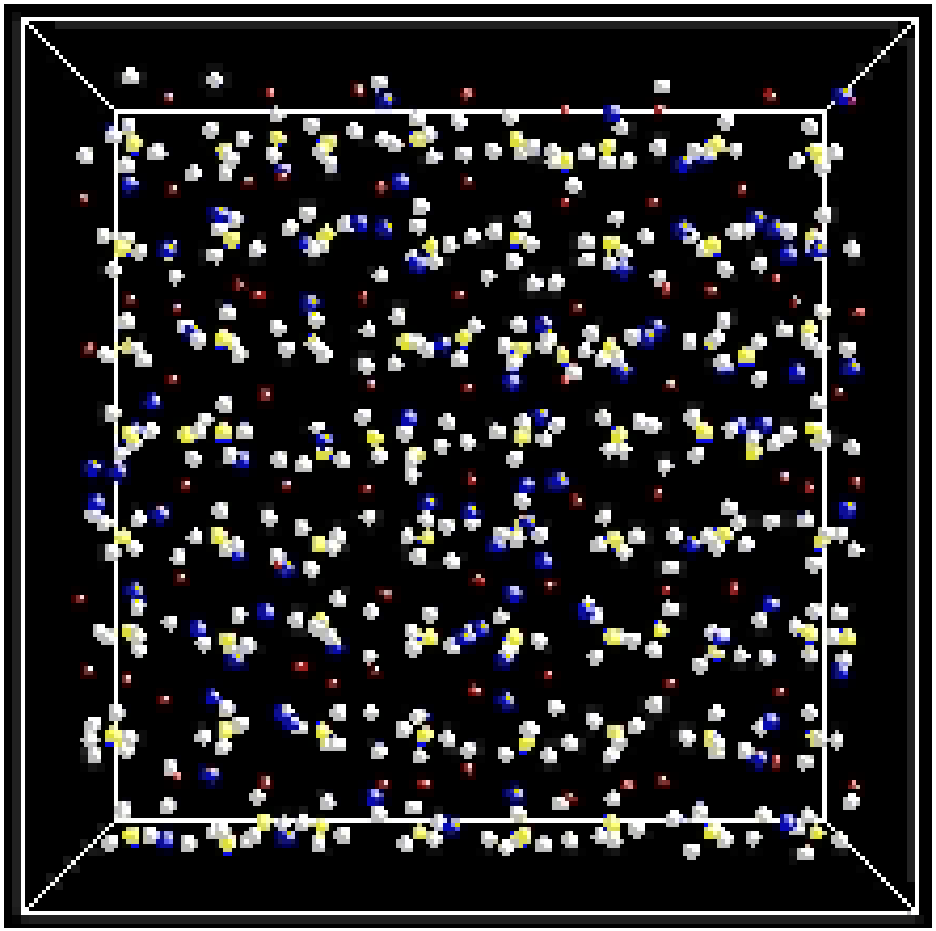
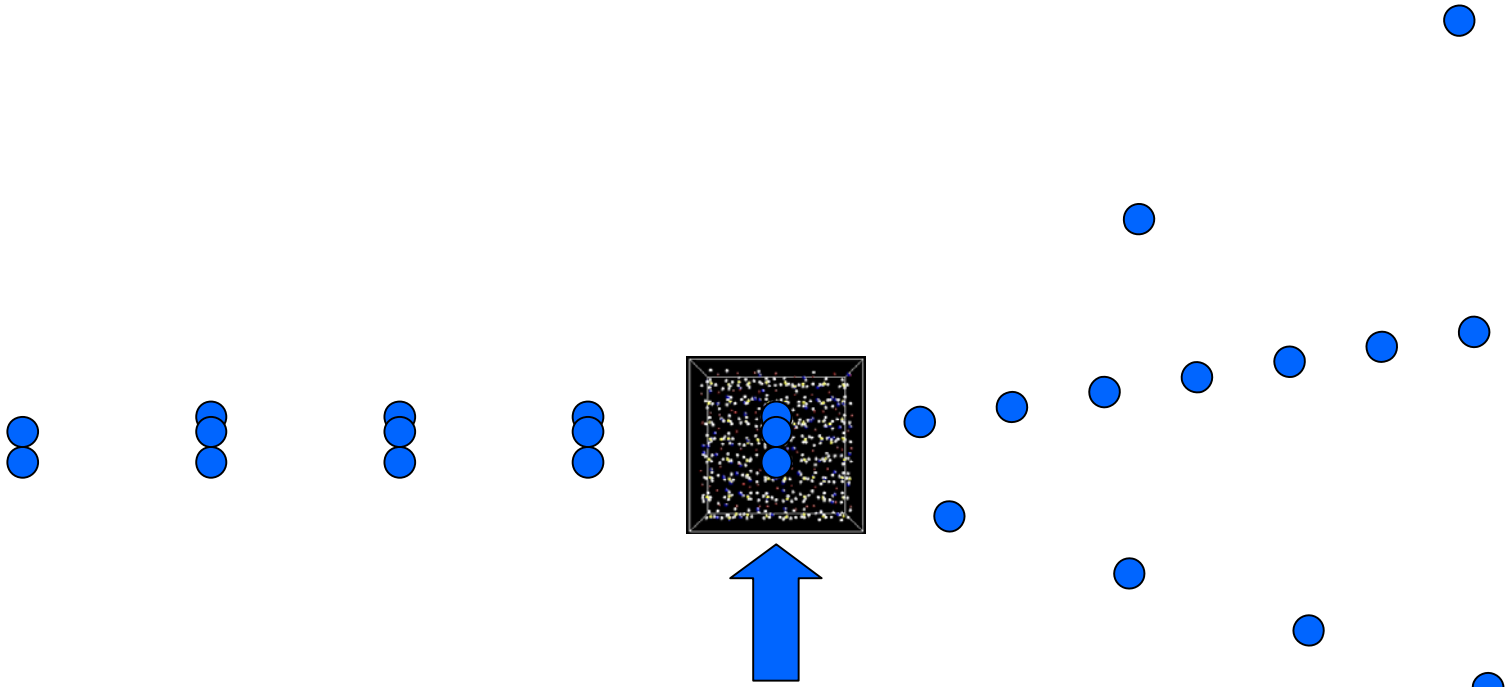
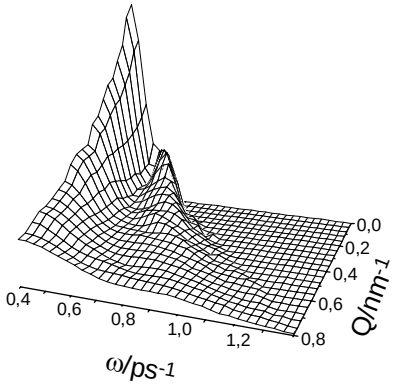
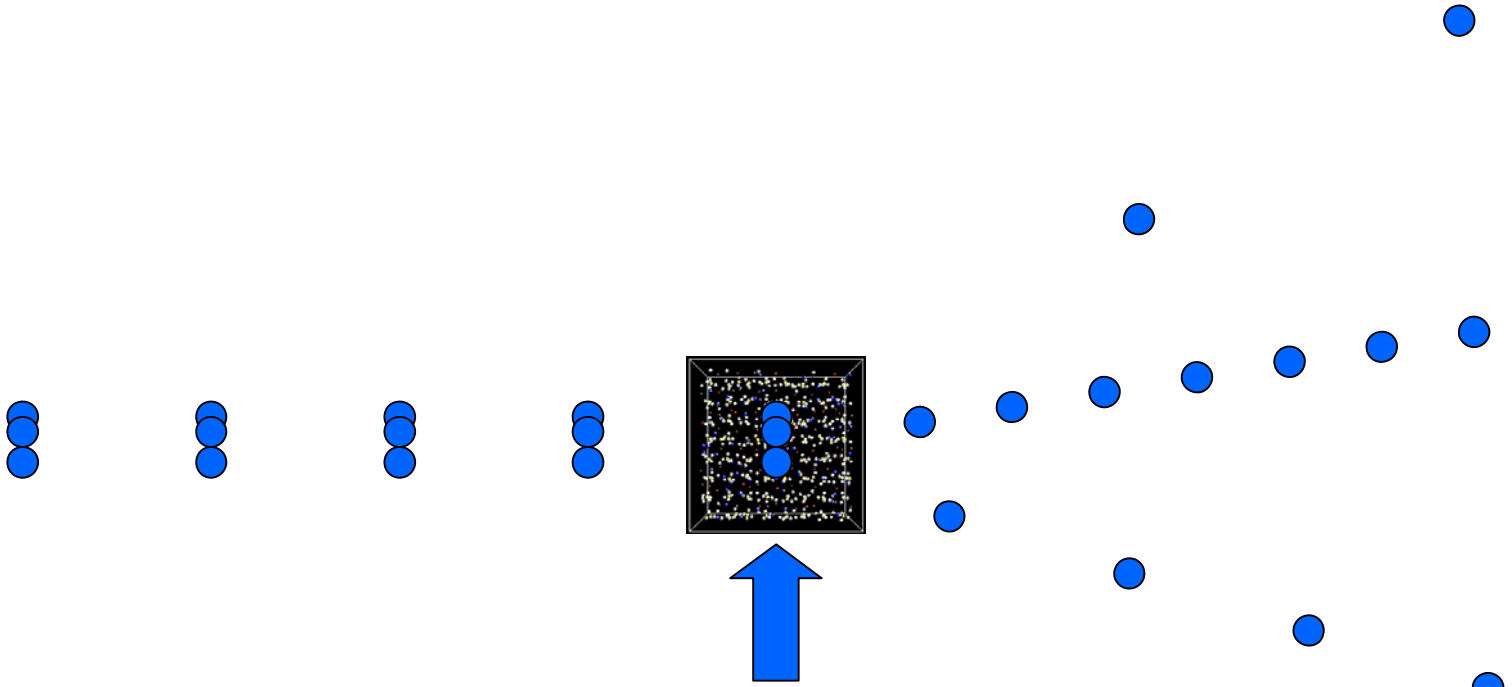






Inelastic Neutron Scattering





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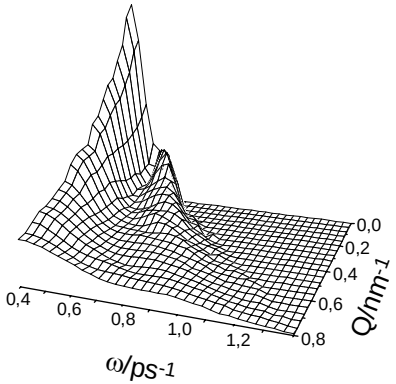

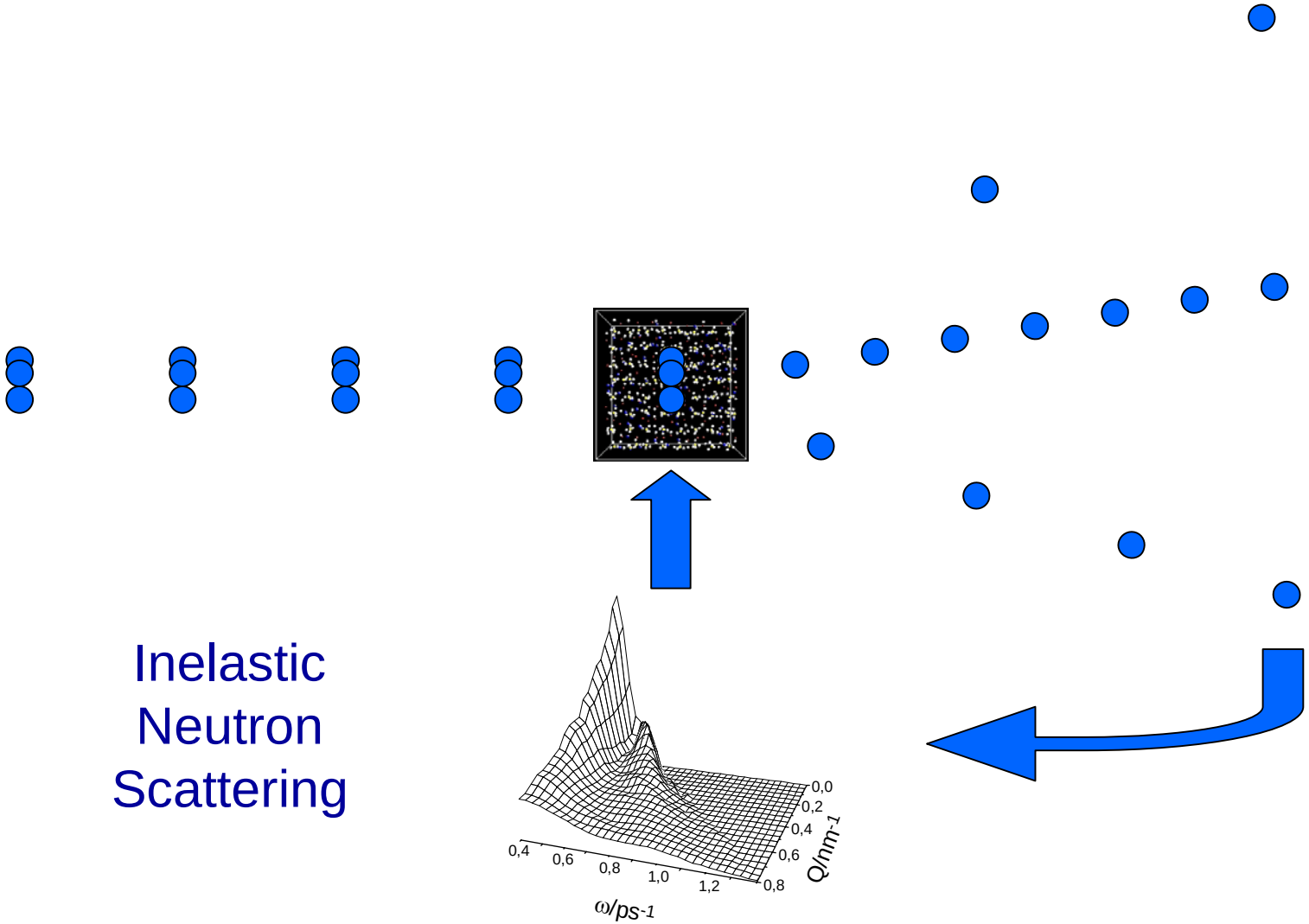

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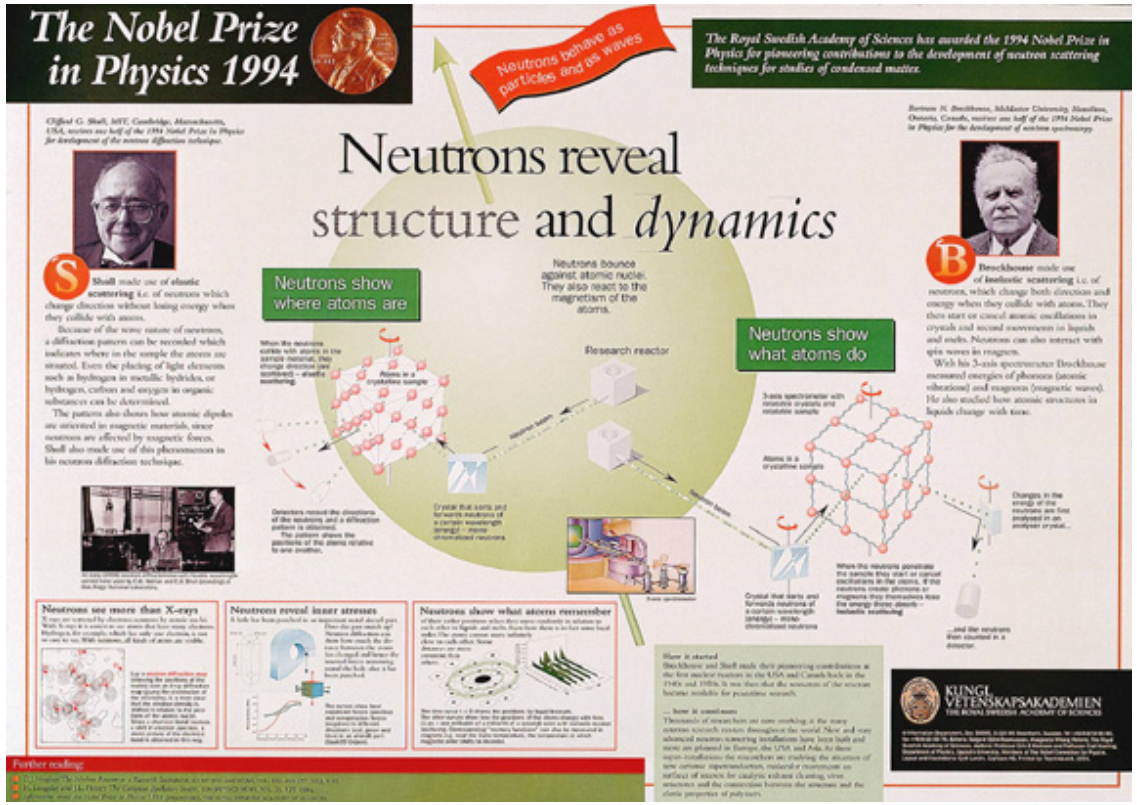
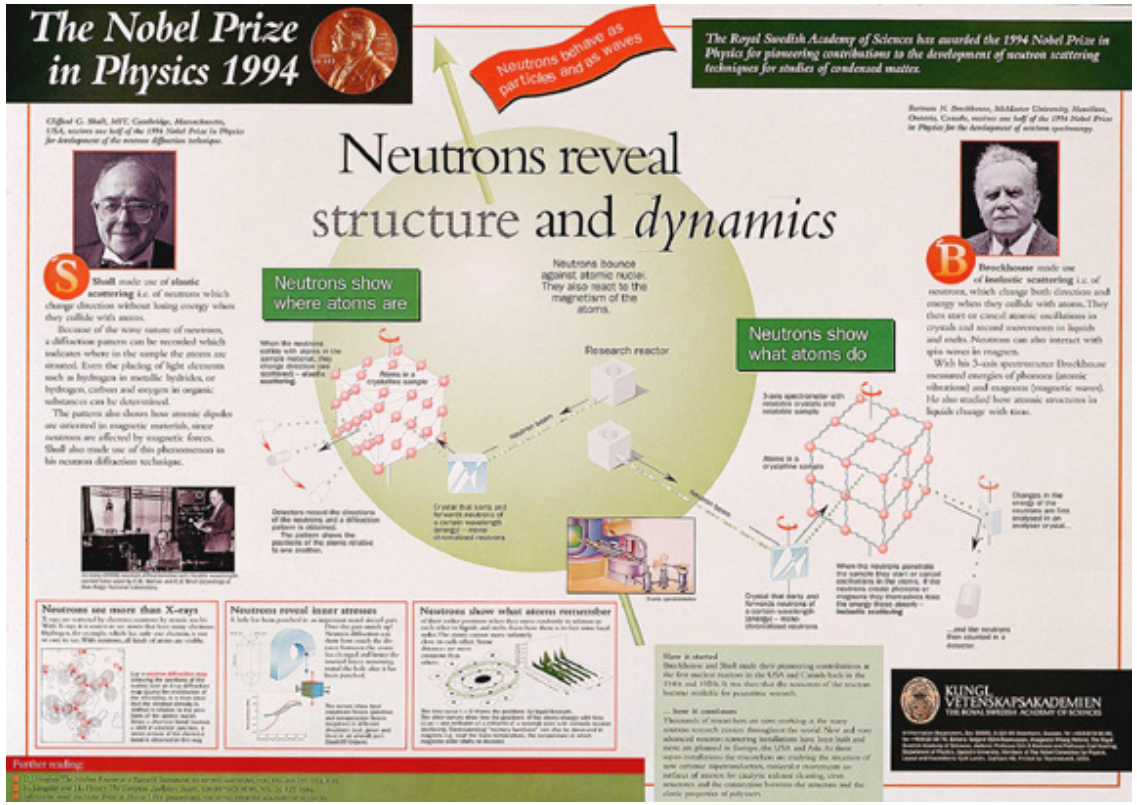
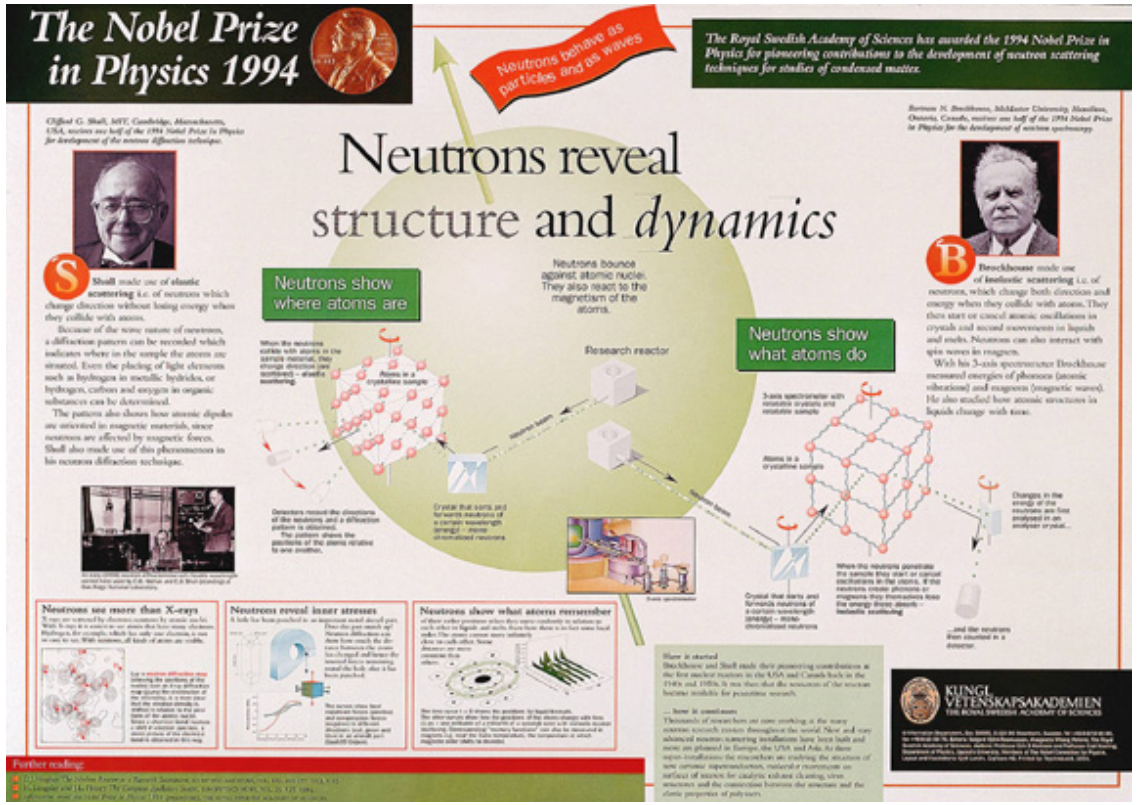

The Nobel Prize in Physics 1994
Neutrons behave as particles and as waves
The Royal Swedish Academy of Sciences has awarded the 1994 Nobel Prize in Physics for pioneering contributions to the development of neutron scattering techniques for studies of condensed matter.
Neutrons reveal structure and dynamics
Neutrons show where atoms are
Neutrons bounce against atomic nuclei. They also react to the magnetism of the atoms.
Neutrons show what atoms do
Research reactor
Neutrons see more than X-rays
Neutrons reveal inner stresses
Neutrons show what atoms remember
Further reading
KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

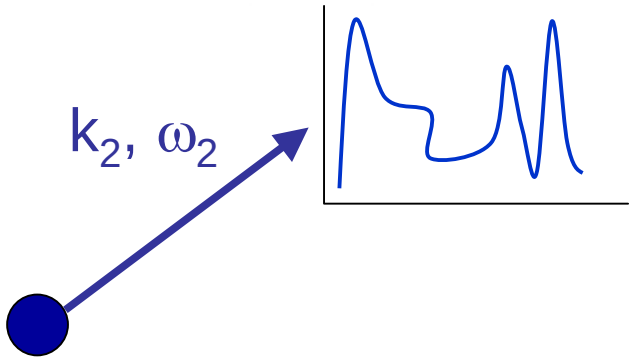


’Neutrons tell you where the atoms are and what the atoms do’



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

No they don’t!



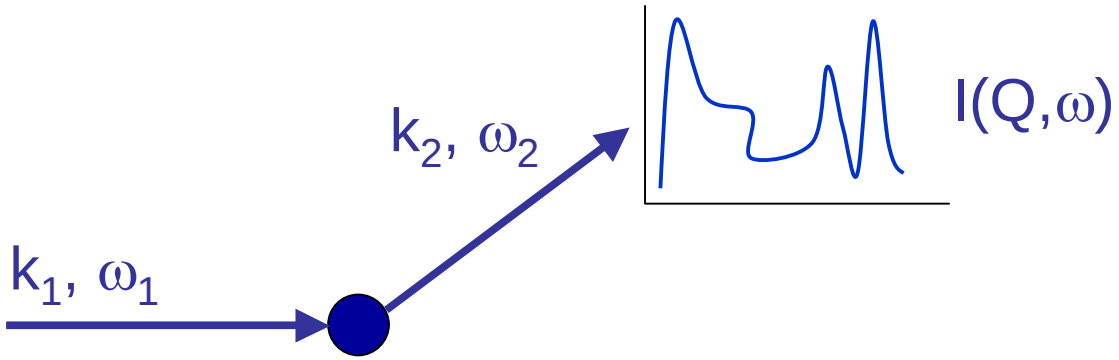
$Q = k_1 - k_2$

$\omega = \omega_1 - \omega_2$

Understanding

- $S(Q,\omega)$
- $G_{AB}(r,t)$
- $r_i(t)$

Constant b	Isotopic substitution	Wide (Q,ω) range
	Under defined Poorly conditioned	Truncation
		Phase problem



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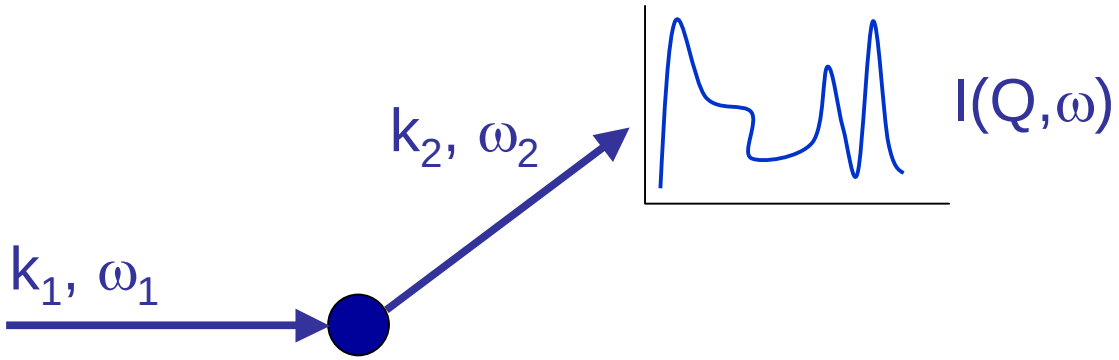

$Q = k_1 - k_2$

$\omega = \omega_1 - \omega_2$

Understanding

$I(Q,\omega)$ · $S(Q,\omega)$ · $G_{AB}(r,t)$ · $r_i(t)$

Constant b	Isotopic substitution	Wide (Q,ω) range
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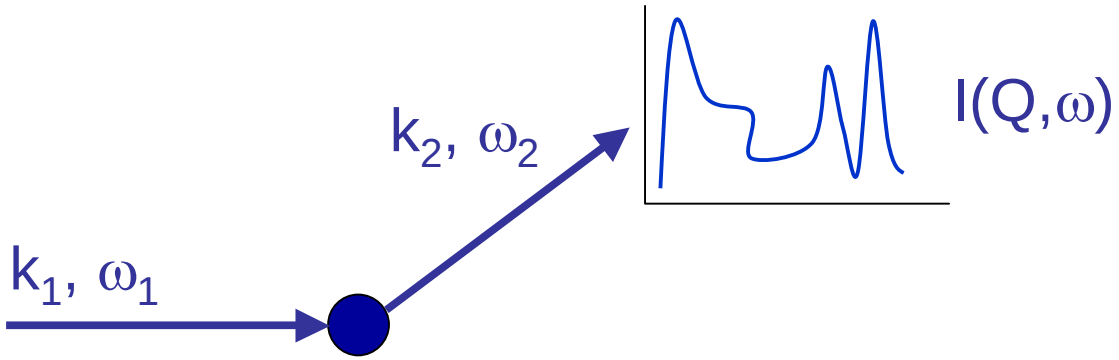


$Q = k_1 - k_2$

$\omega = \omega_1 - \omega_2$

Understanding

$I(Q,\omega) \rightarrow S(Q,\omega)$ · $G_{AB}(r,t)$ · $r_i(t)$

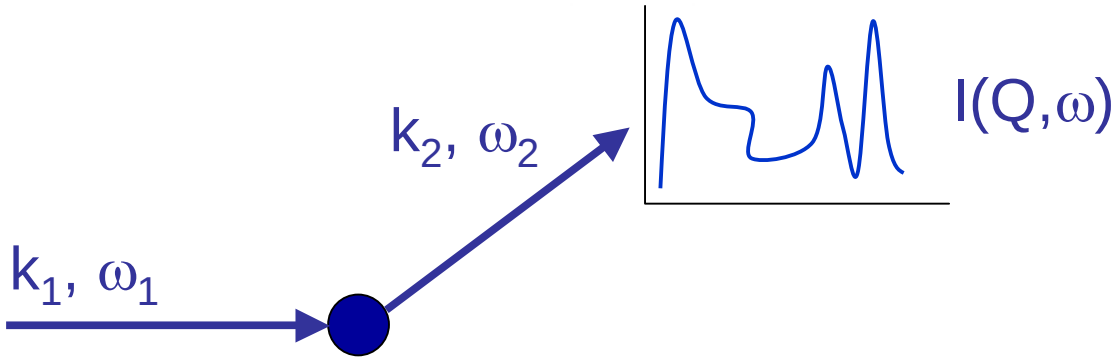
Corrections

Constant b	Isotopic substitution	Wide (Q,ω) range

Under defined
Poorly conditioned

Truncation

Phase problem

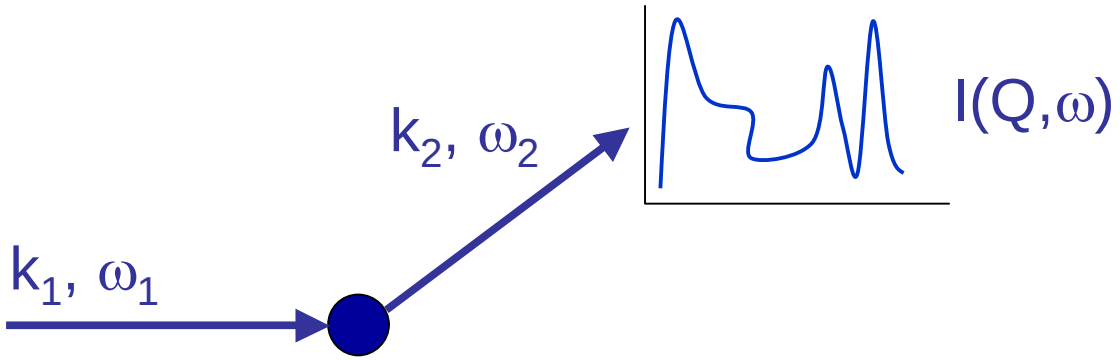


$$Q = k_1 - k_2$$
$$\omega = \omega_1 - \omega_2$$

Understanding

$$I(Q,\omega) \rightarrow S(Q,\omega) = \Sigma S_{AB}(Q,\omega) \cdot G_{AB}(r,t) \cdot r_i(t)$$

Corrections	Separation		
Constant b	Isotopic substitution	Wide (Q,ω) range	
	Under defined Poorly conditioned	Truncation	Phase problem



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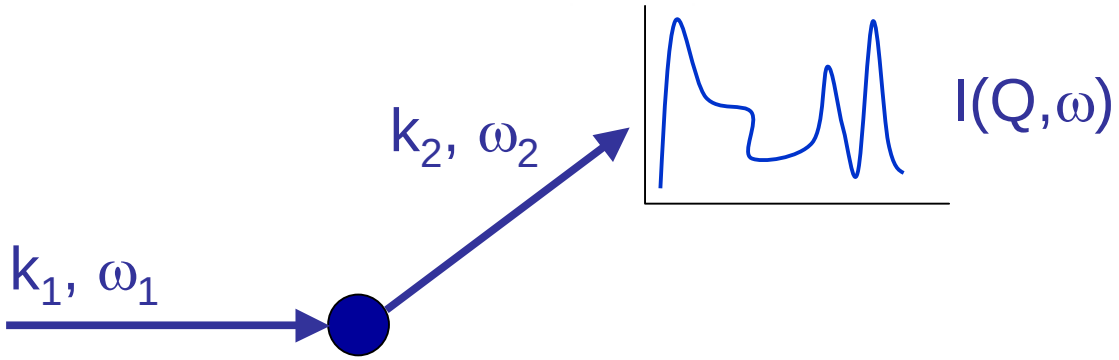
Understanding

$I(Q,\omega) \rightarrow S(Q,\omega) = \Sigma S_{AB}(Q,\omega) \rightarrow G_{AB}(r,t) \cdot r_i(t)$

Corrections	Separation	Transform
Constant b	Isotopic substitution	Wide (Q,ω) range
	Under defined Poorly conditioned	Truncation
		Phase problem



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Understanding

$I(Q,\omega) \rightarrow S(Q,\omega) = \Sigma S_{AB}(Q,\omega) \rightarrow G_{AB}(r,t) - - - - r_i(t)$

Corrections	Separation	Transform	?
Constant b	Isotopic substitution	Wide (Q,ω) range	
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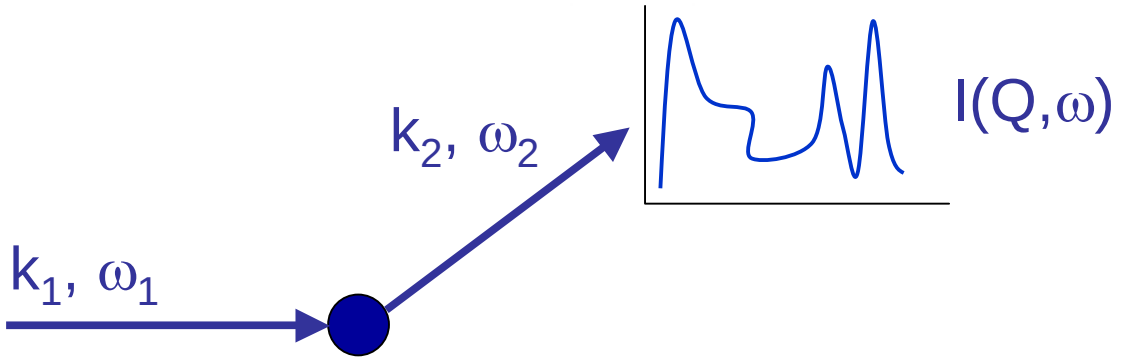

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Measurement → Understanding

$I(Q,\omega) \rightarrow S(Q,\omega) = \Sigma S_{AB}(Q,\omega) \rightarrow G_{AB}(r,t) - - - - r_i(t)$

Corrections	Separation	Transform	?
Constant b	Isotopic substitution	Wide (Q,ω) range	
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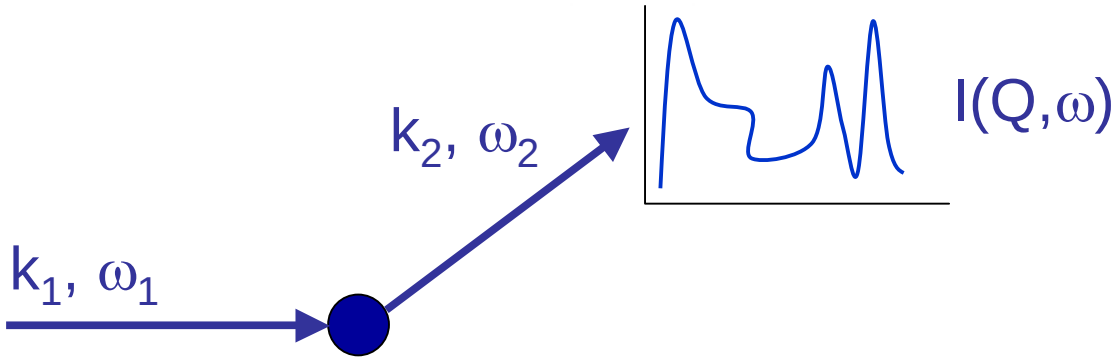

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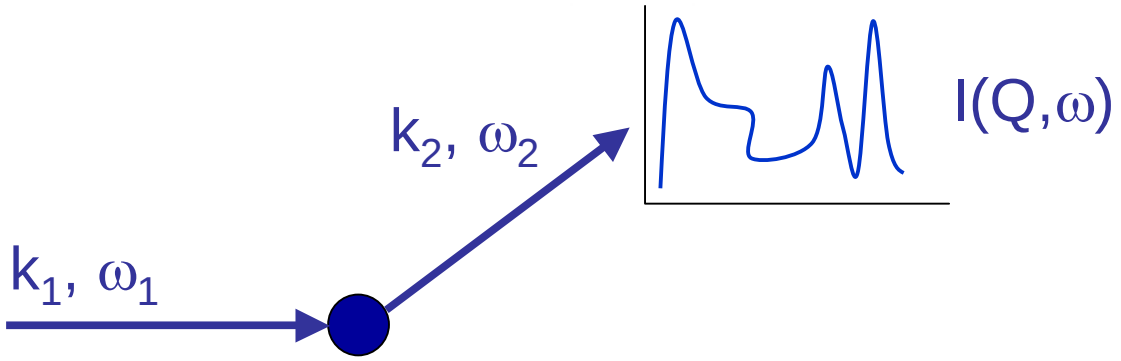
Corrections	Separation	Transform	?
Constant b	Isotopic substitution	Wide (Q,ω) range	
Weak probe			
	Under defined Poorly conditioned	Truncation	Phase problem



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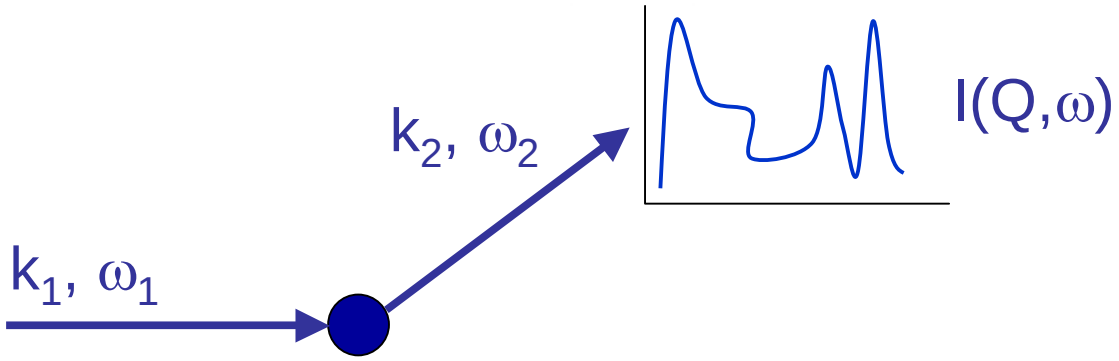
Corrections	Separation	Transform	?
Constant b	Isotopic substitution	Wide (Q,ω) range	
Weak probe			
Errors	Under defined Poorly conditioned	Truncation	Phase problem



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Measurement → Understanding

$I(Q,\omega) \rightarrow S(Q,\omega) = \Sigma S_{AB}(Q,\omega) \rightarrow G_{AB}(r,t) - - - - r_i(t)$

Corrections	Separation	Transform	?
Constant b	Isotopic substitution	Wide (Q,ω) range	
Weak probe			
Errors	Under defined Poorly conditioned	Truncation	Phase problem

SO …

Neutron scattering data analysis

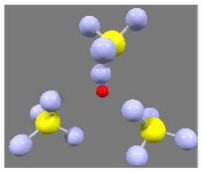
is an

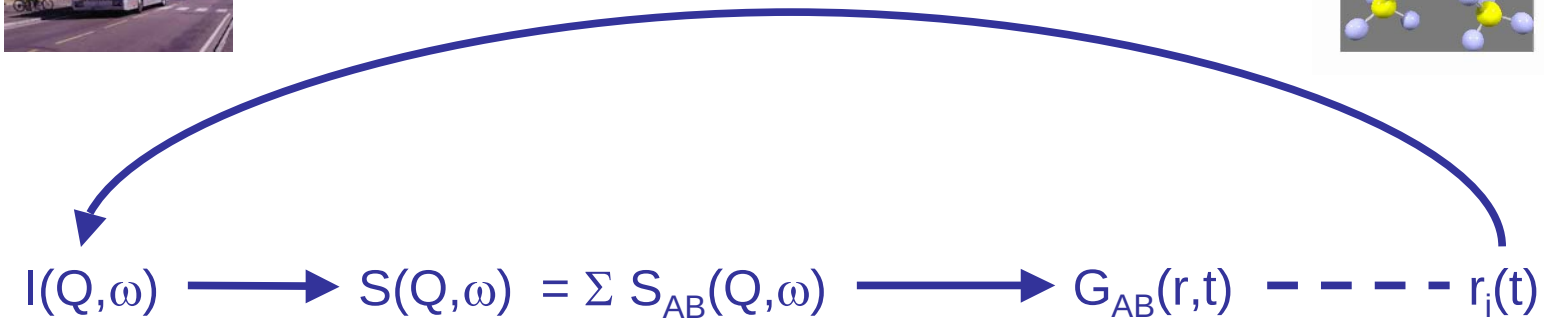
problem

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

Corrections Separation Transform

Errors Under defined Poorly conditioned Truncation Phase problem





Errors

Under defined
Poorly conditioned

Truncation

Phase problem

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

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

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

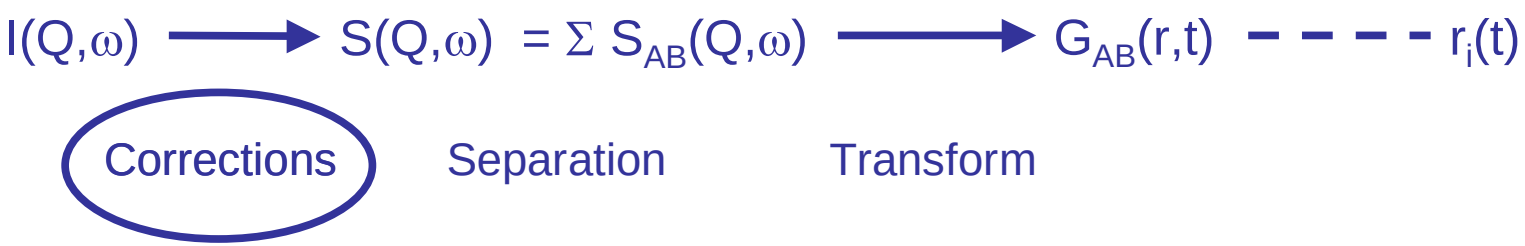
$$I(\theta) \propto F(\mathbf{Q}) = \int_{-\infty}^{\infty} S(\mathbf{Q},\omega)\,d\omega = S(\mathbf{Q},t=0) = \int e^{i\mathbf{Q}.\mathbf{r}}\ G(\mathbf{r},t=0)\,d\mathbf{r}$$

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

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

Corrections Separation Transform

Errors Under defined Poorly conditioned Truncation Phase problem

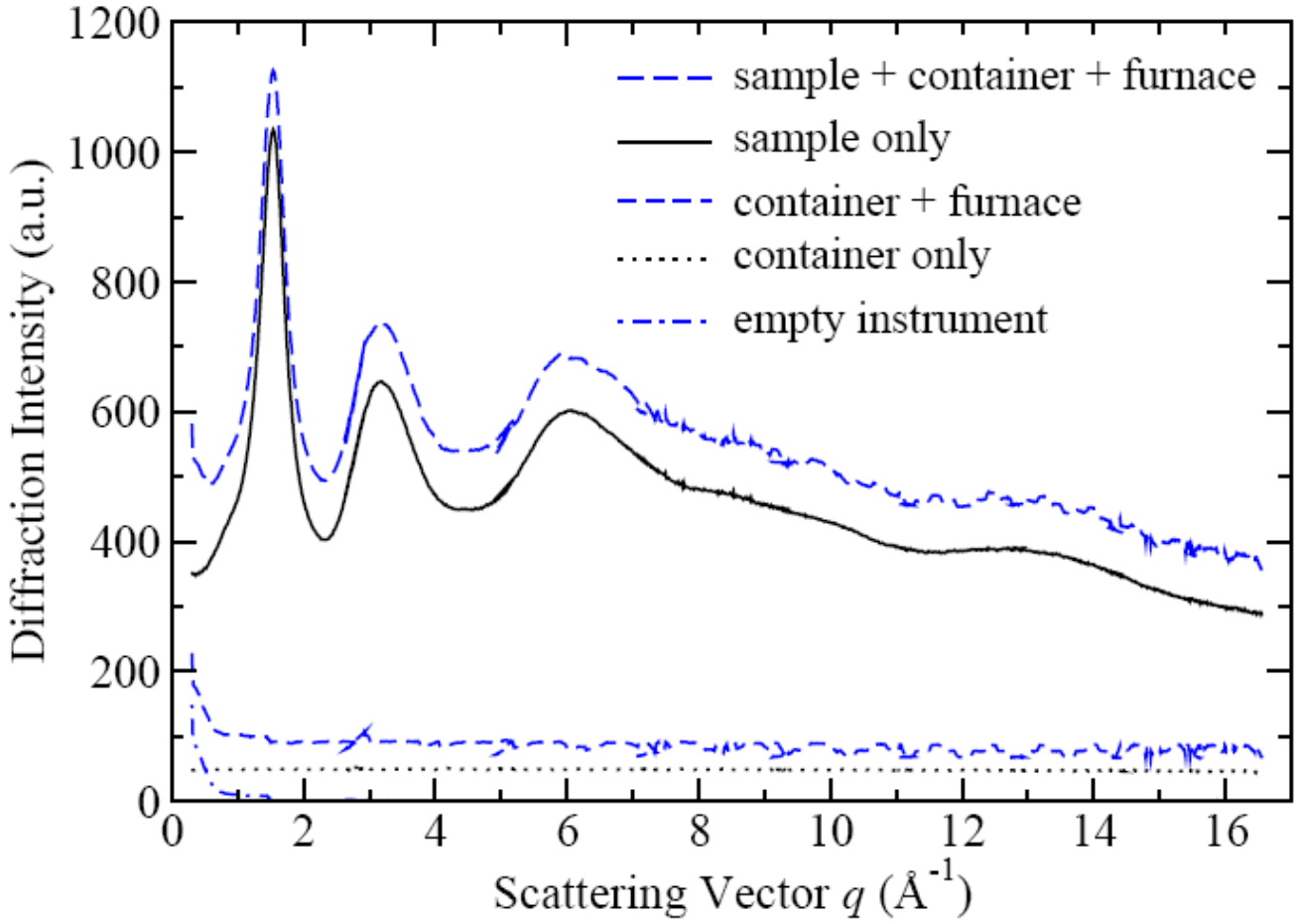


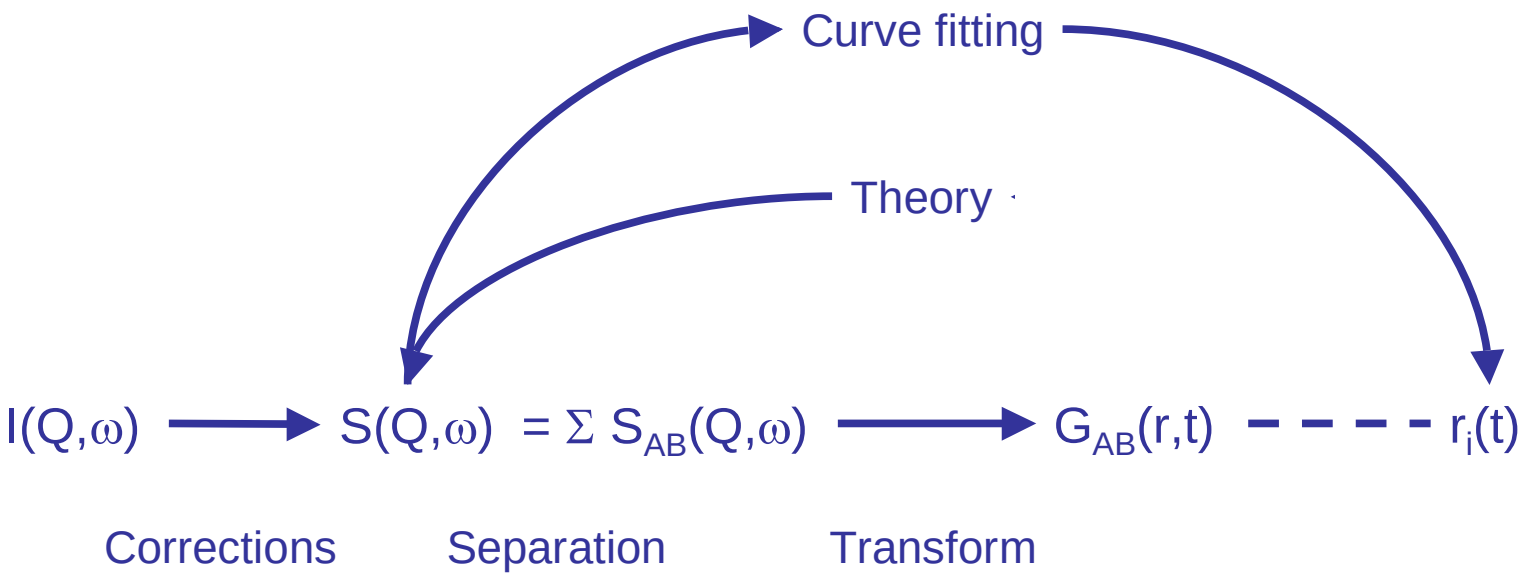
Errors

Under defined
Poorly conditioned

Truncation

Phase problem


sample + container + furnace
sample only
container + furnace
container only
empty instrument
Diffraction Intensity (a.u.)
Scattering Vector q (Å-1)
0
200
400
600
800
1000
1200
0
2
4
6
8
10
12
14
16

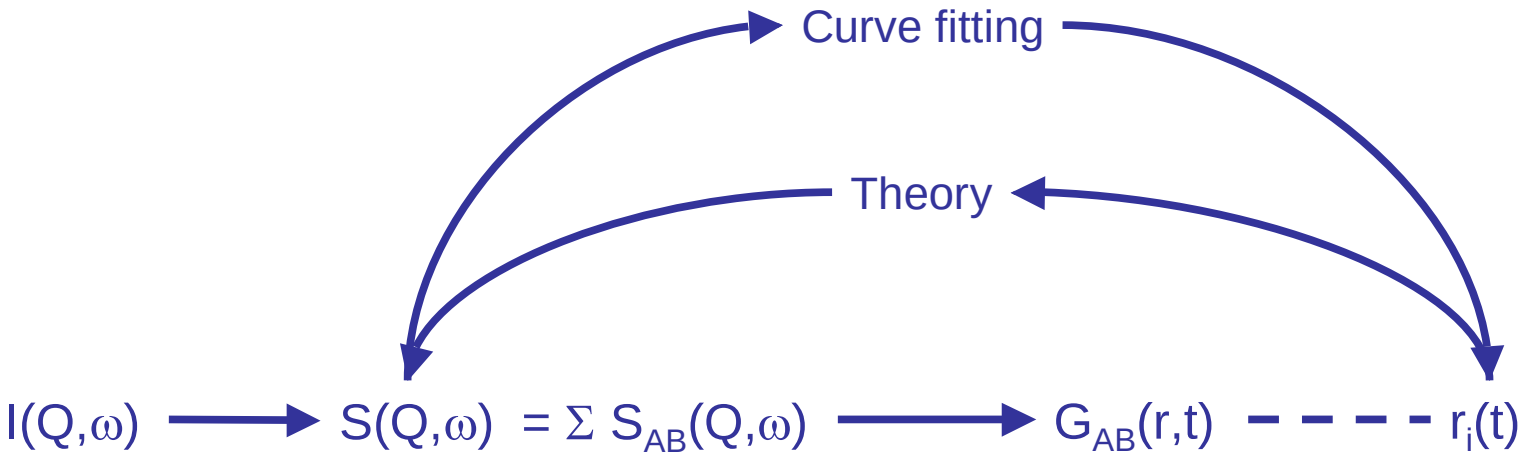


Errors

Under defined
Poorly conditioned

Truncation

Phase problem

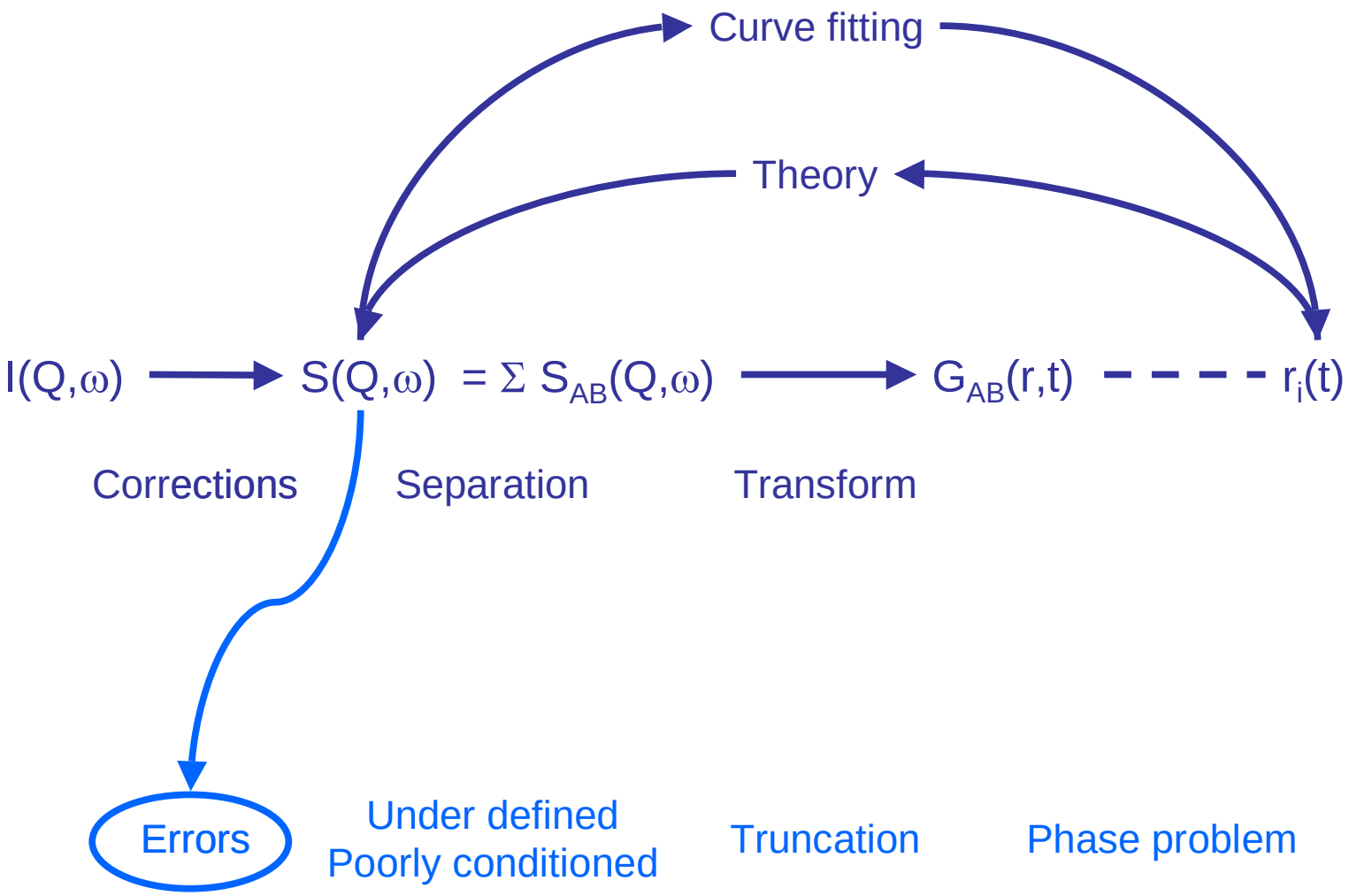


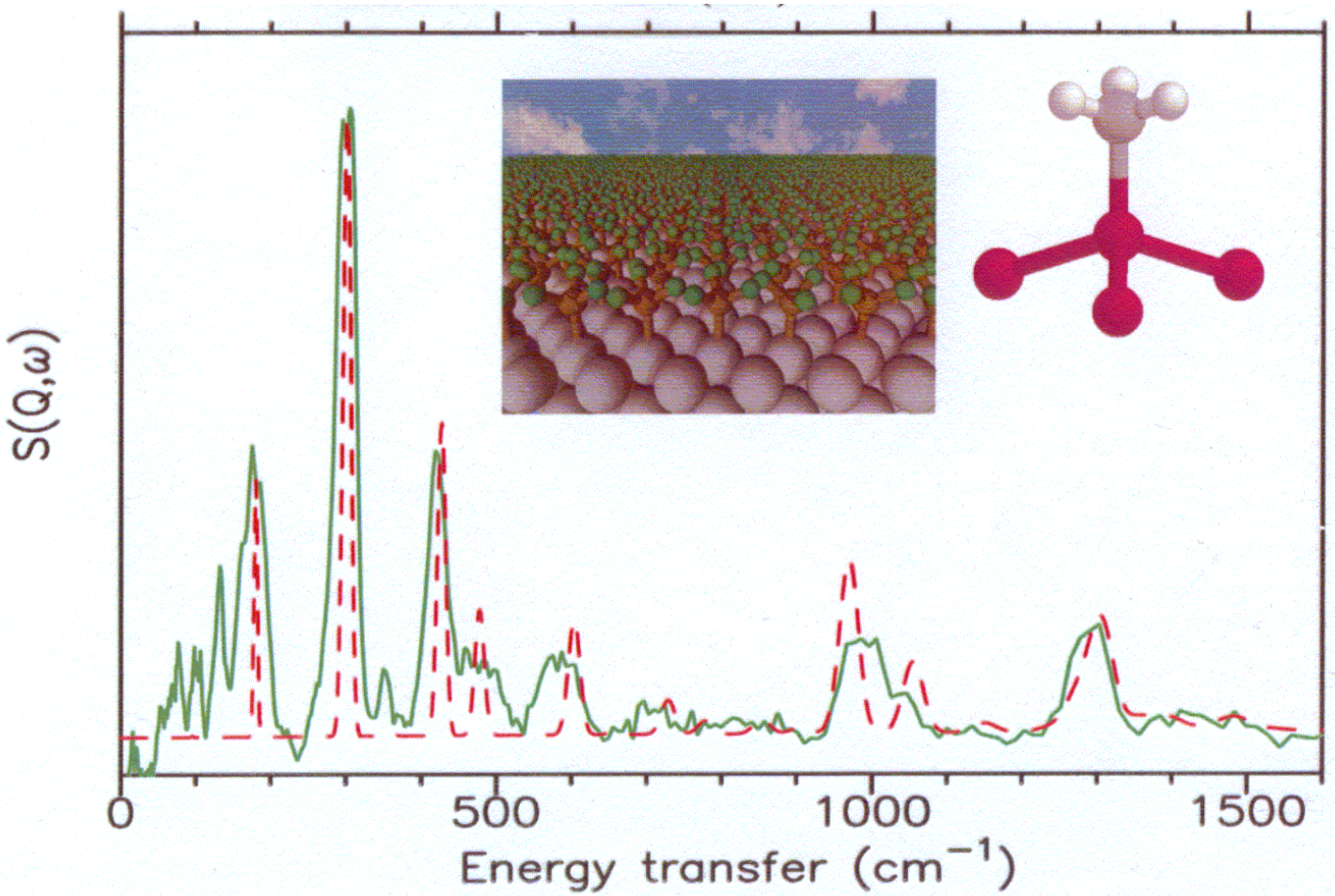
Errors

Under defined
Poorly conditioned

Truncation

Phase problem


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


S(Q,ω)
0
500
1000
1500
Energy transfer (cm^{-1})

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

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

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

What is *N* ?

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

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

What is *N* ?

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

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Bayes theorem

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

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

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

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

If we assume no knowledge of N then

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

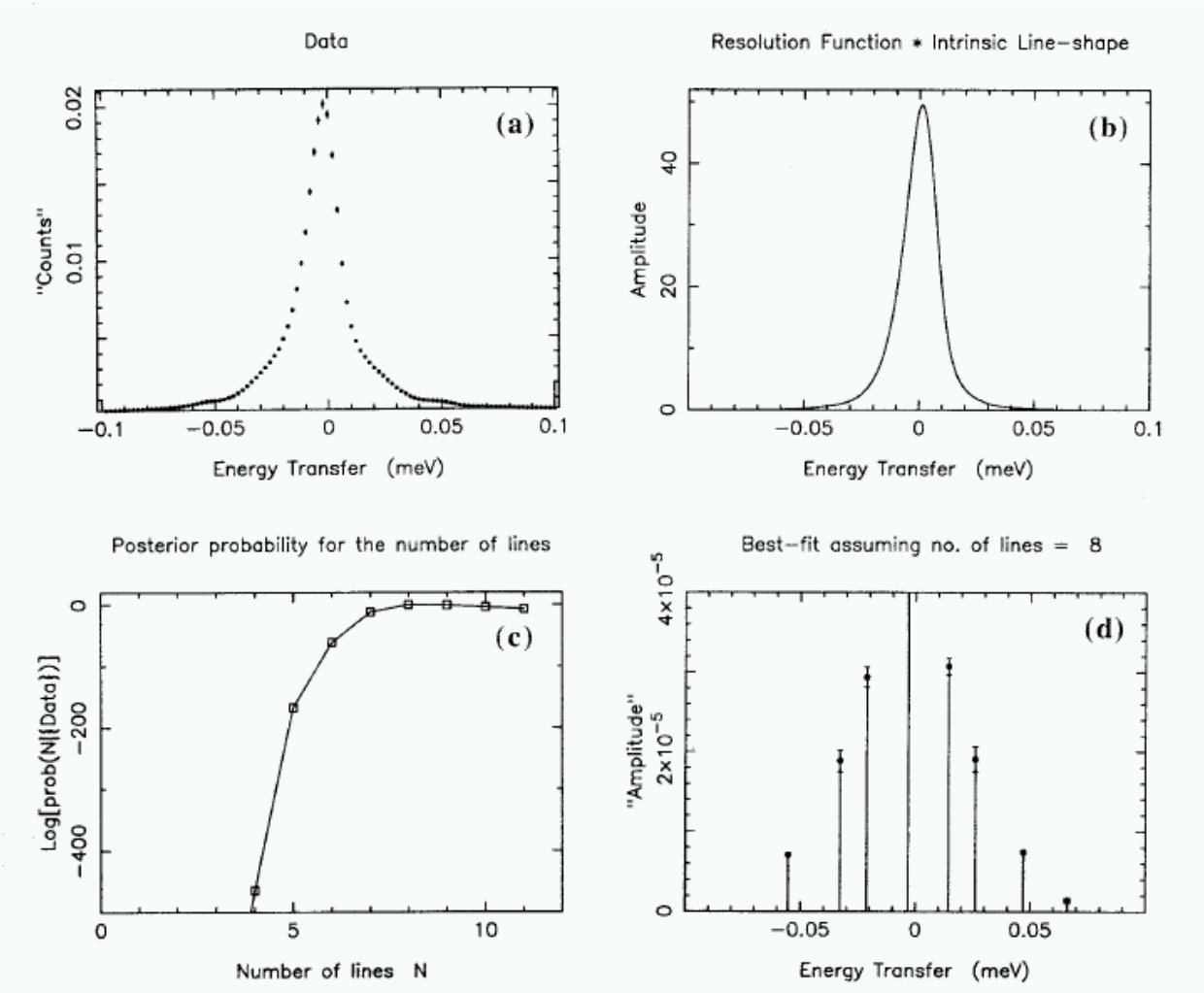
so

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

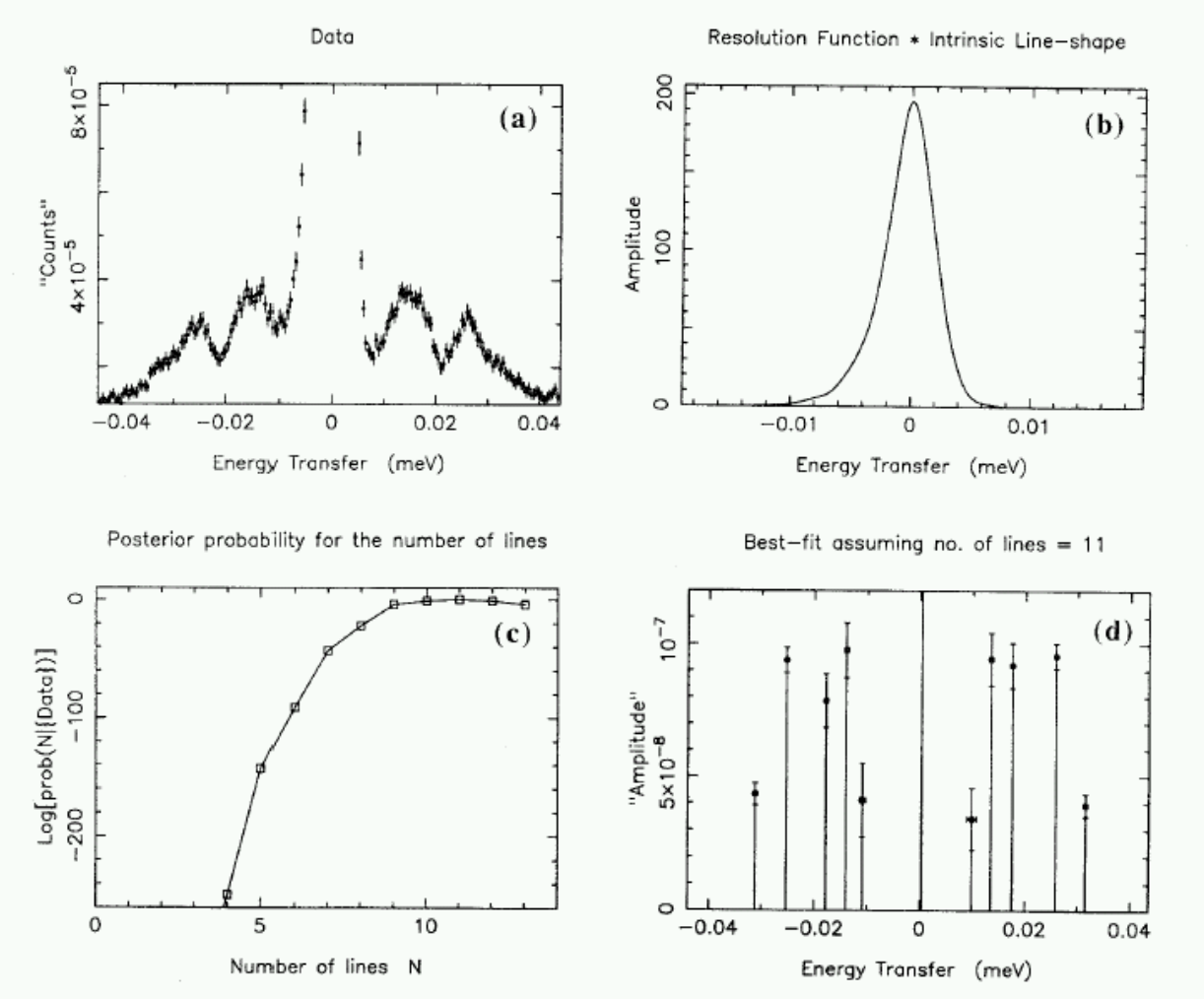
so calculate the integral above and then maximise

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

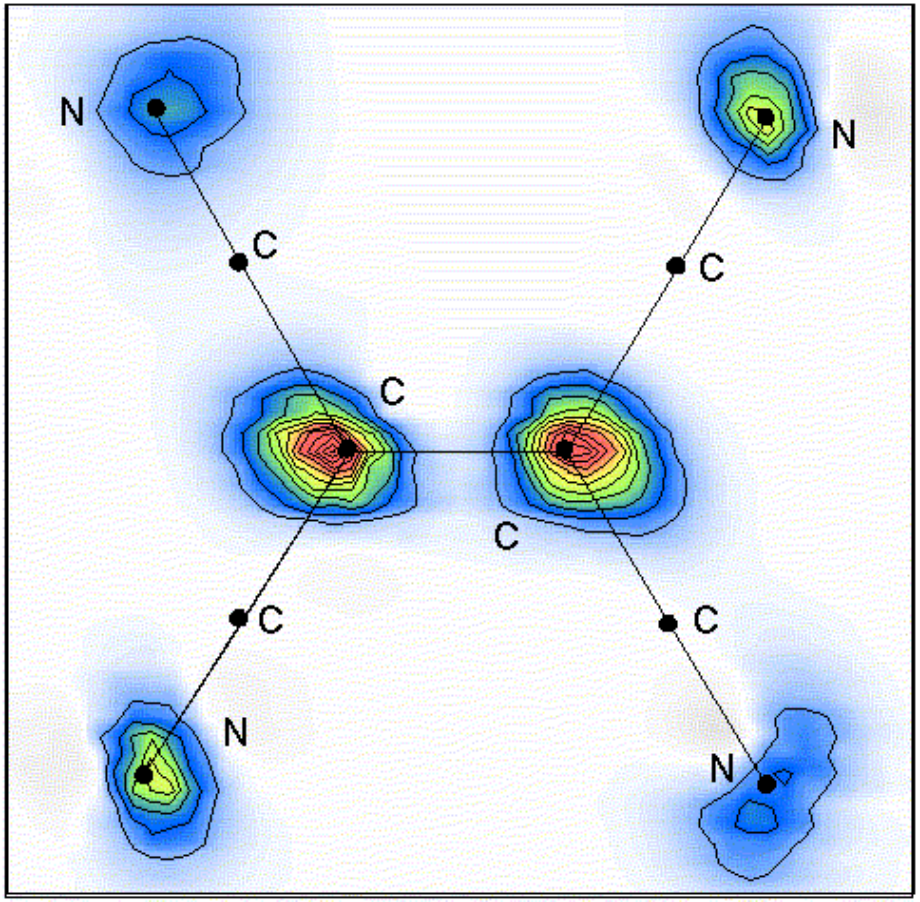
D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992



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

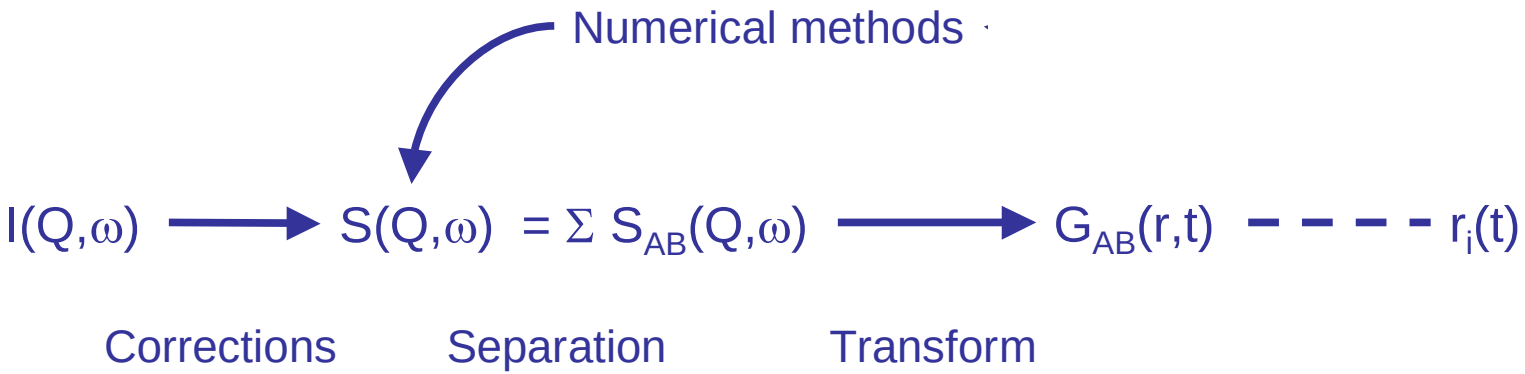


D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992



What not to do ….

Choose the prior to get the answer you want

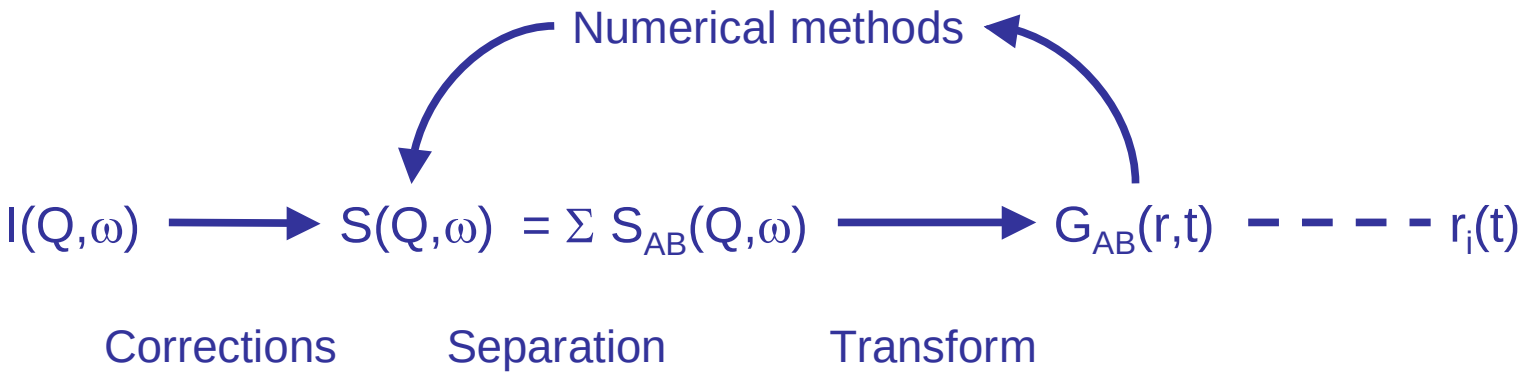


Errors

Under defined
Poorly conditioned

Truncation

Phase problem



Errors

Under defined
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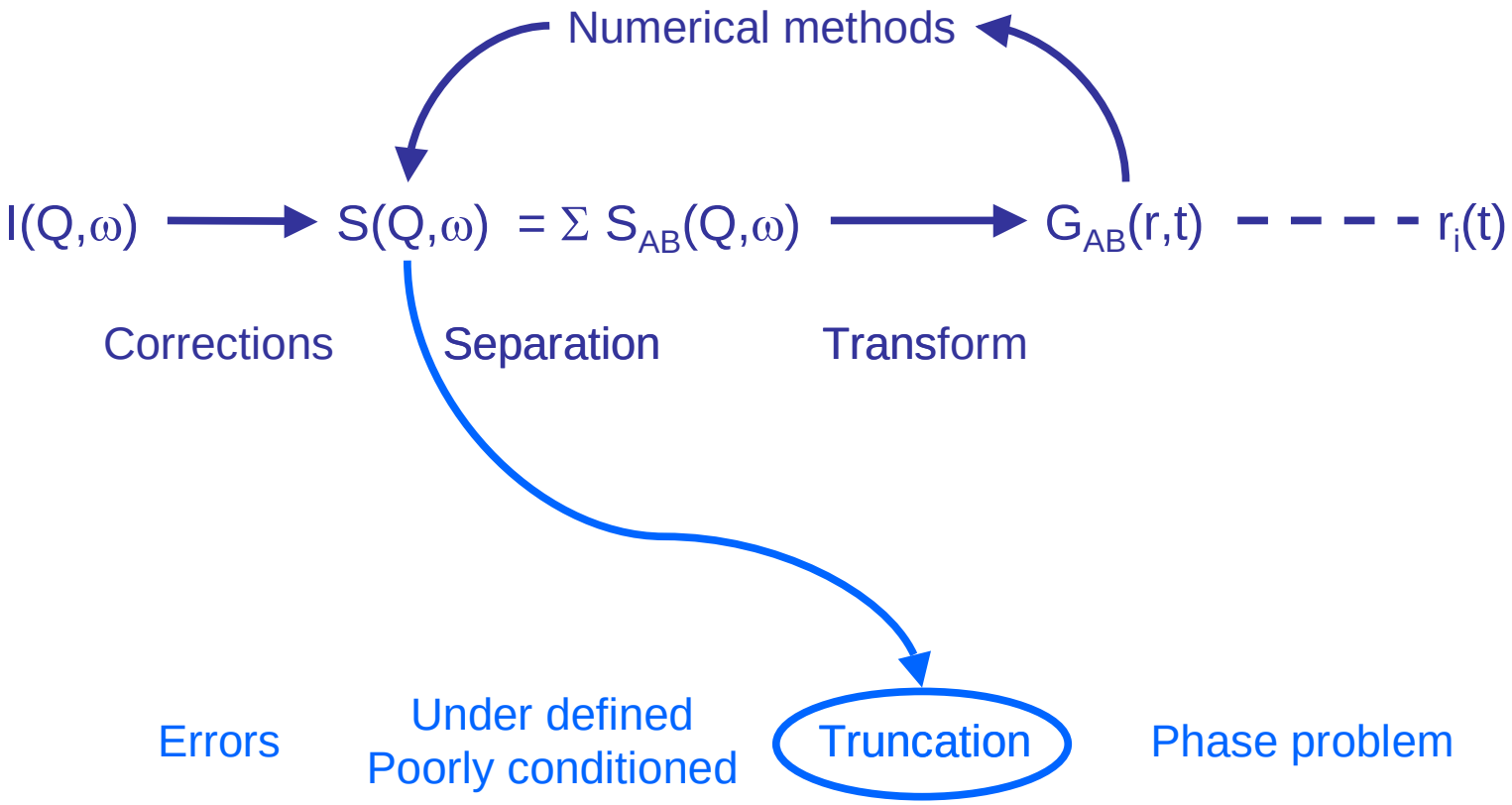
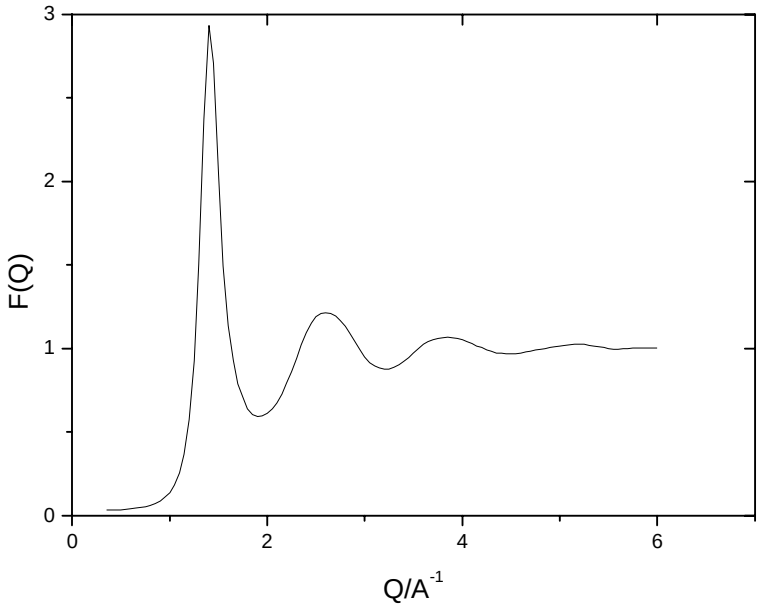
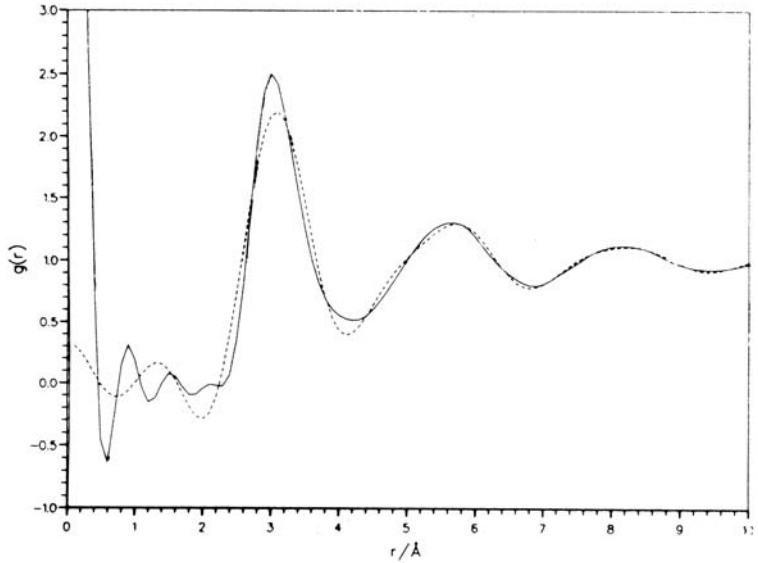
Truncation

Phase problem


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’

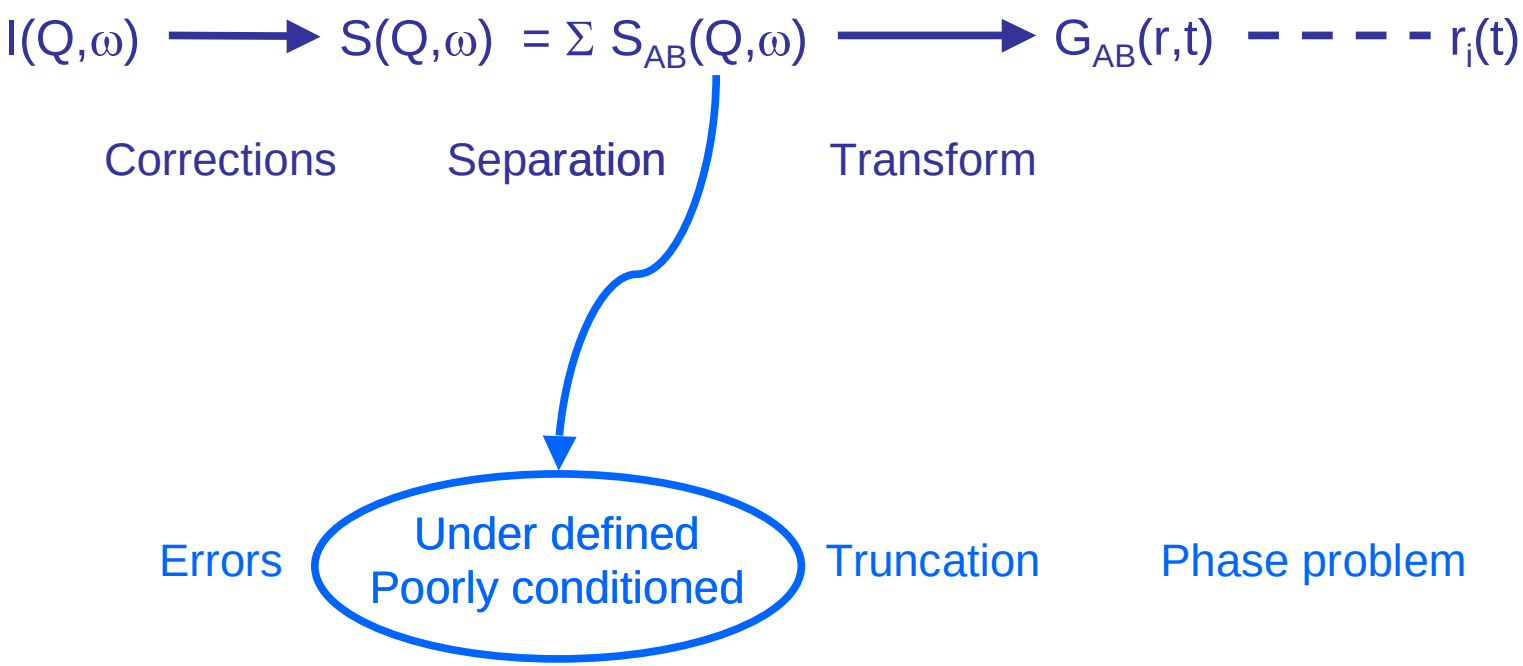
$$I = \int (1 + d'^2(r))^{1/2} \, \partial r$$

‘Shortest line’

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

Corrections Separation Transform

Errors Under defined Poorly conditioned Truncation Phase problem


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

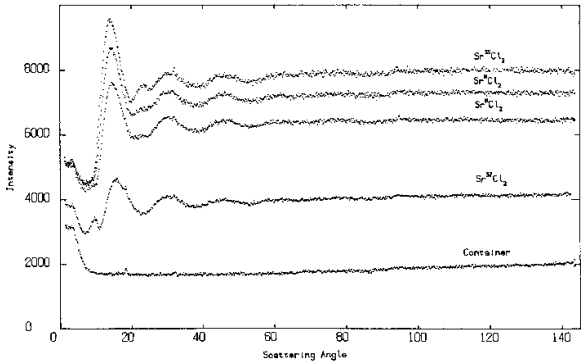
$$F^{(k)}(Q) = \sum_{\alpha} \sum_{\beta} c_{\alpha\beta}^{(k)} \left(A_{\alpha\beta}(Q) - 1 \right)$$

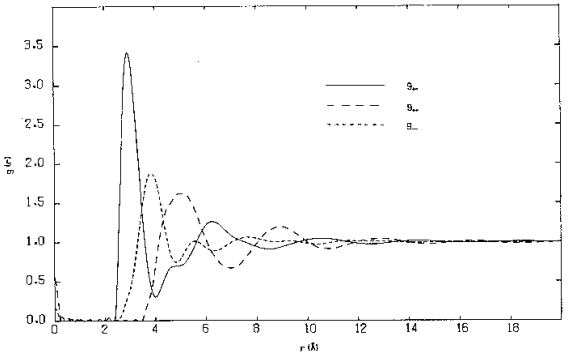
$$\vec{F} = \mathbf{C}\,\vec{A} \qquad \vec{A} = \mathbf{C}^{-1}\,\vec{F}$$

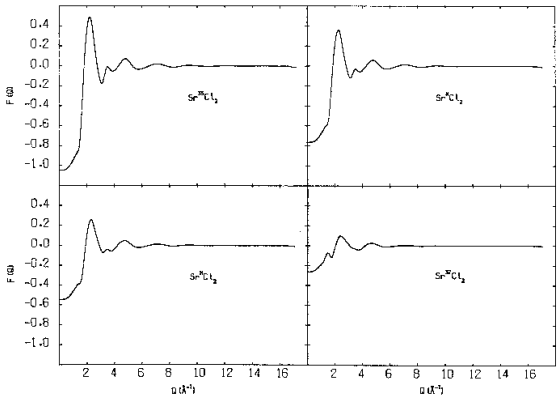
Make a set of measurements with varying coefficients $c_{\alpha\beta}^{(k)}$ (isotopic substitution, anomalous scattering, EXAFS) and solve

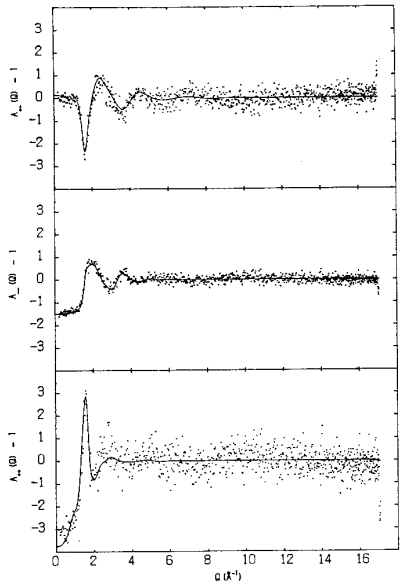
C is poorly conditioned (nearly singular), so small errors in F lead to large errors in A

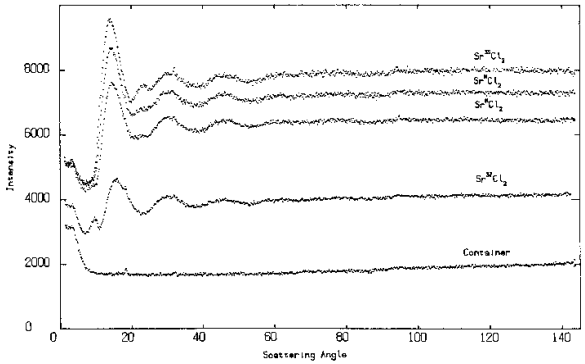
The Turing M conditioning number is a measure of the conditioning of matrix $\mathbf{C}$

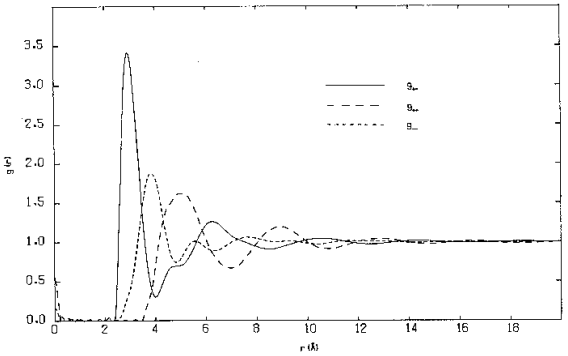

Intensity
Scattering Angle
Container

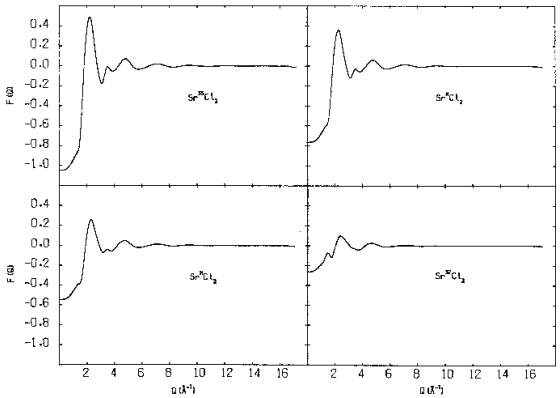

g(r)
r (Å)

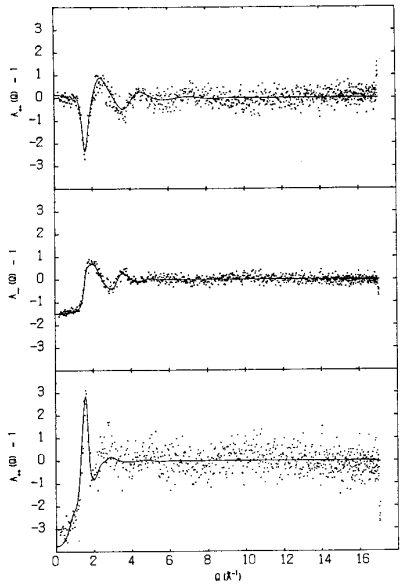

F(Q)
Q (Å⁻¹)

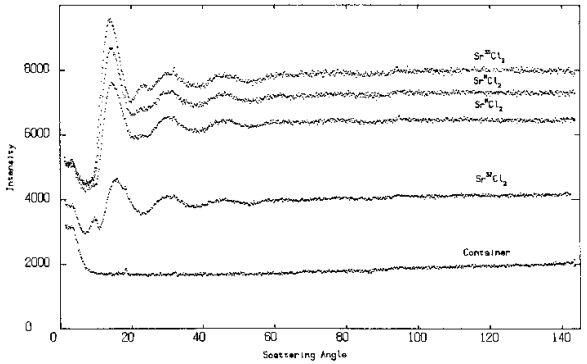

A_αβ (Q) − 1
Q (Å⁻¹)

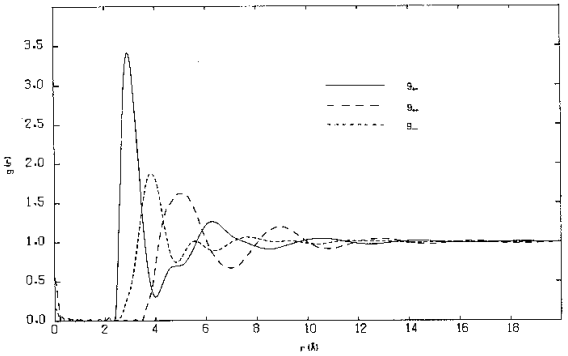

Intensity
Scattering Angle
Container

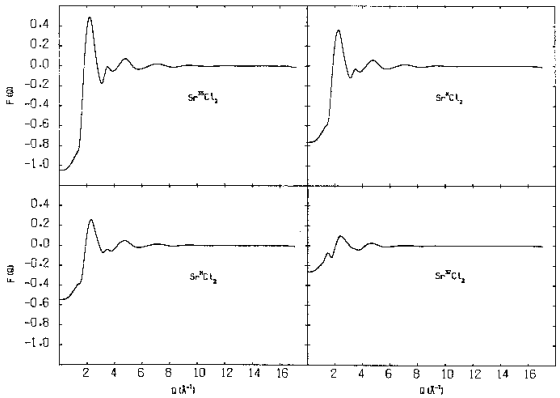

g(r)
r (Å)


F(Q)
Q (Å⁻¹)

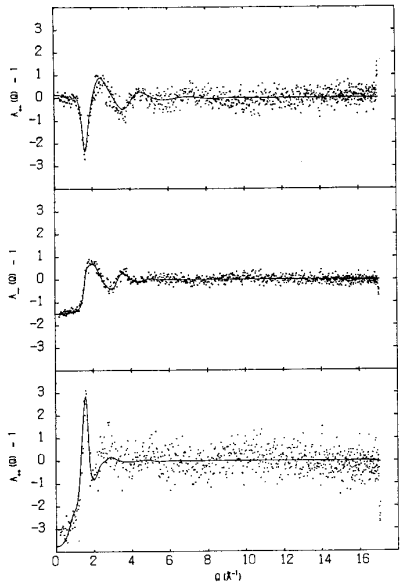

A_αβ (Q) − 1
Q (Å⁻¹)

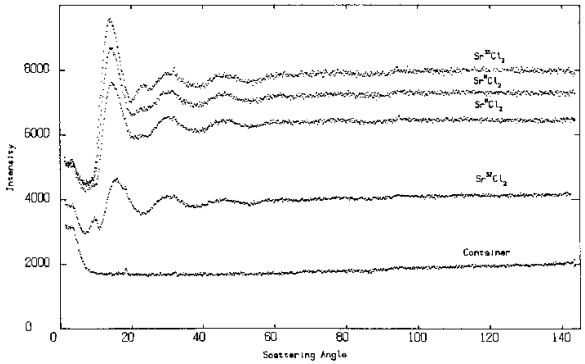


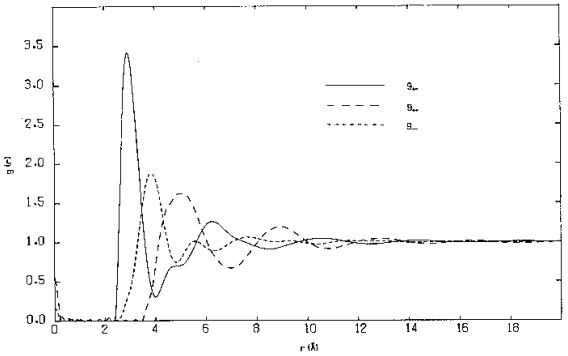


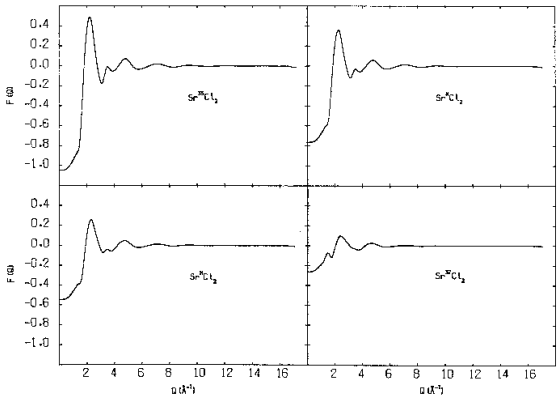


M=35

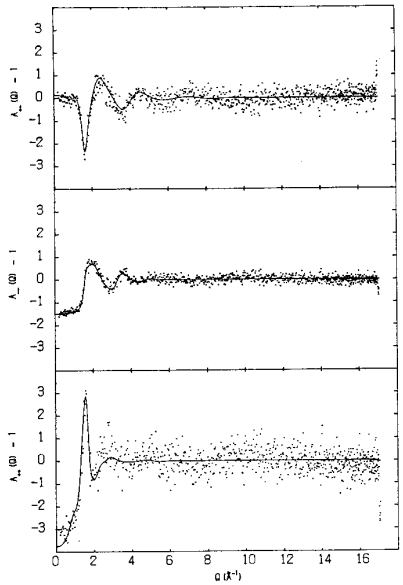


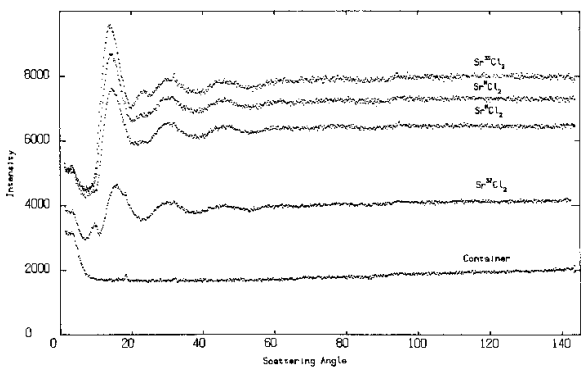


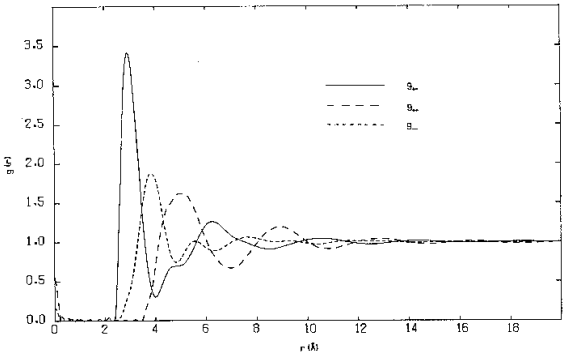


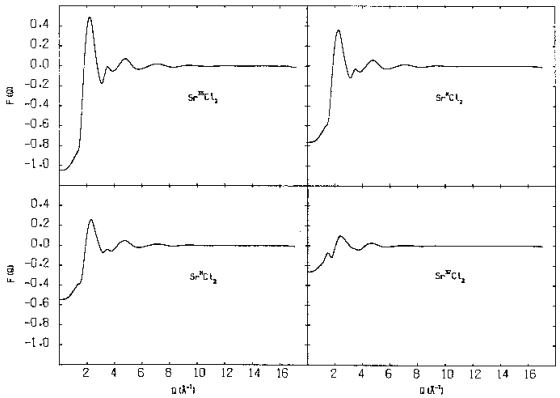


M=35

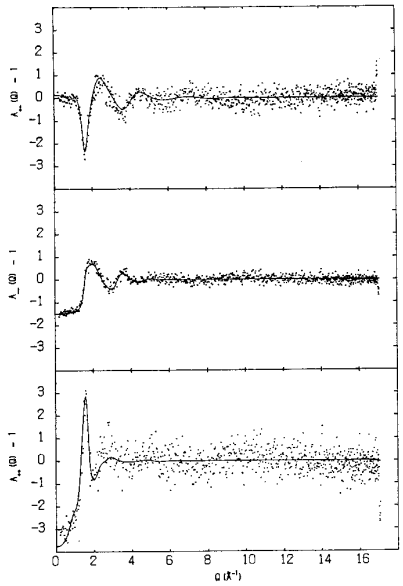


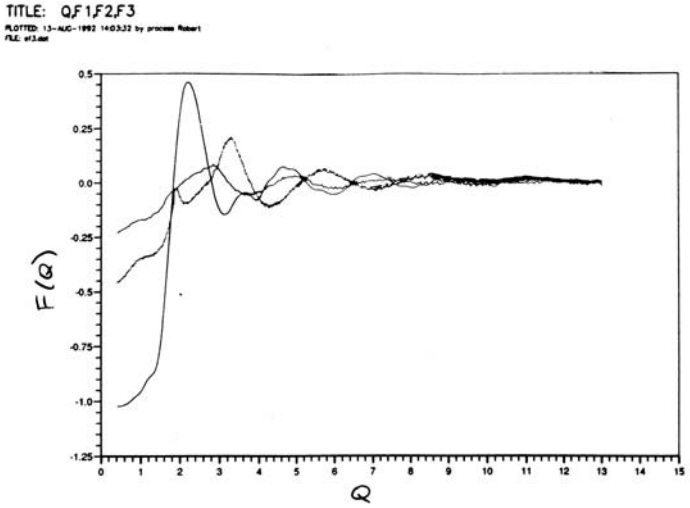


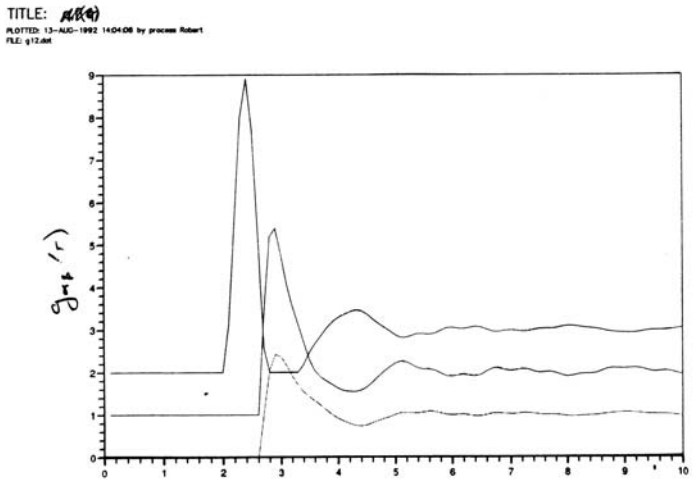


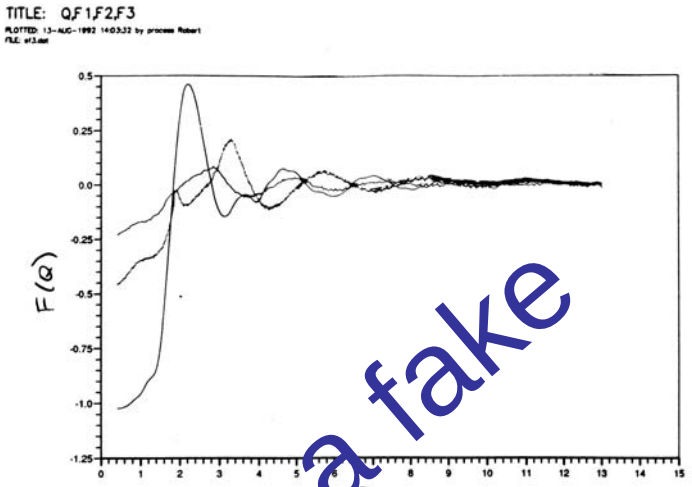


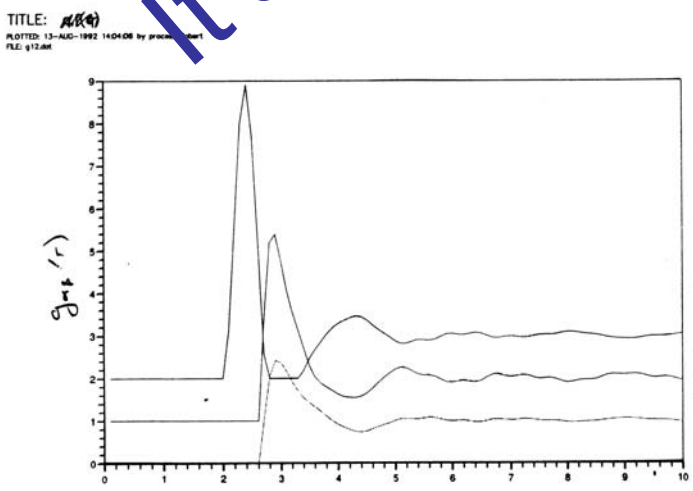
M=35



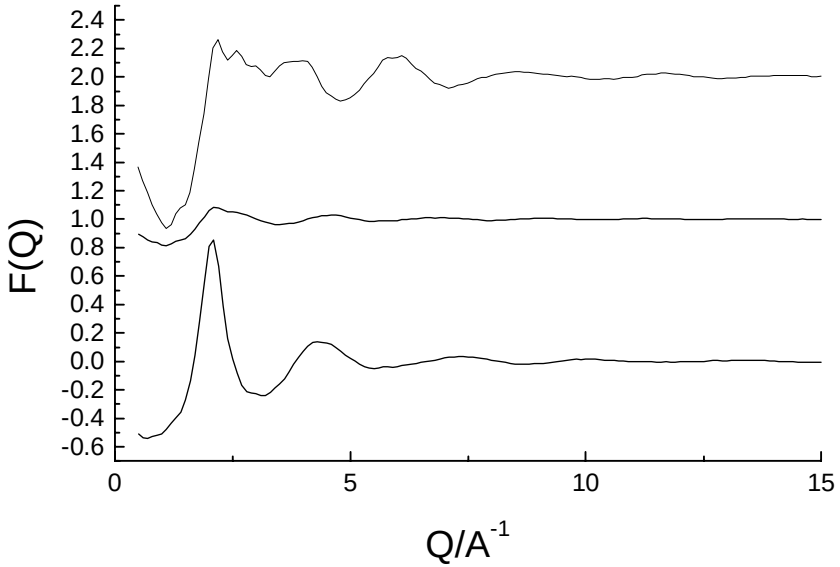

TITLE: Q,F1,F2,F3
F(Q)
Q


TITLE:



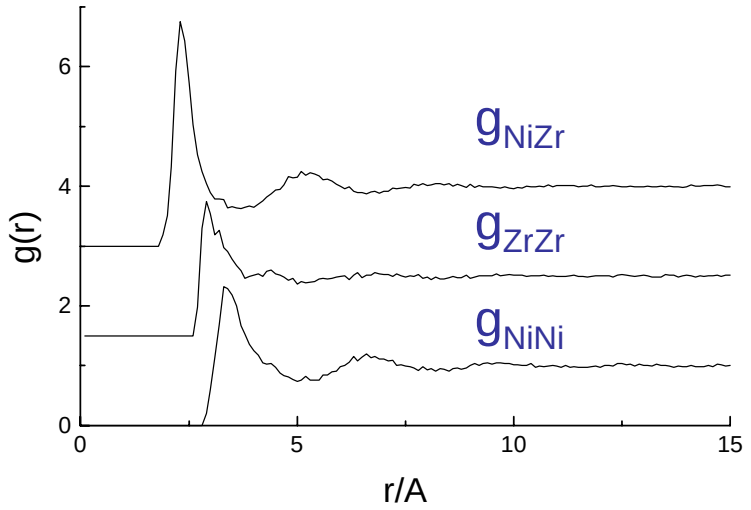


It's a fake



M=11

Metallic glass: NiZr



^{63}CuZr

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

^{65}CuZr

Metallic glass: CuZr

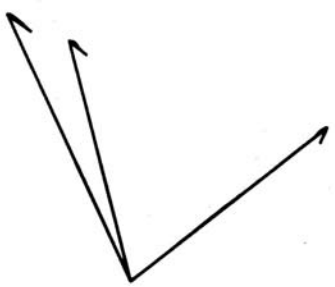
$$c^{(k)} = \begin{pmatrix} c_{11} \\ c_{12} \\ . \\ . \\ c_{nn} \end{pmatrix} \qquad \hat{c}^{(k)} = c^{(k)} / \sum c_{\alpha\beta}^2$$

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

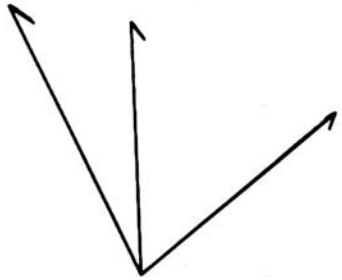
θ_{jk} is a measure of the relative information content in $F^{(j)}(Q)$ and $F^{(k)}(Q)$

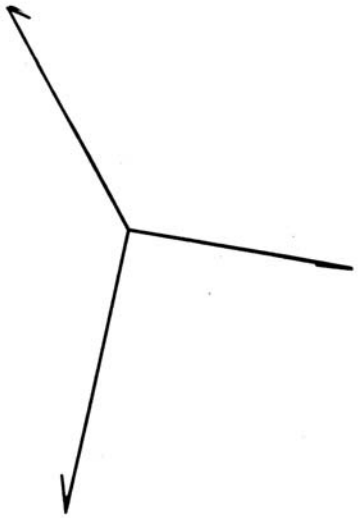
(90° is good!)

NiZr neutron + Ni/Zr EXAFS



CuZr neutron + Cu/Zr EXAFS





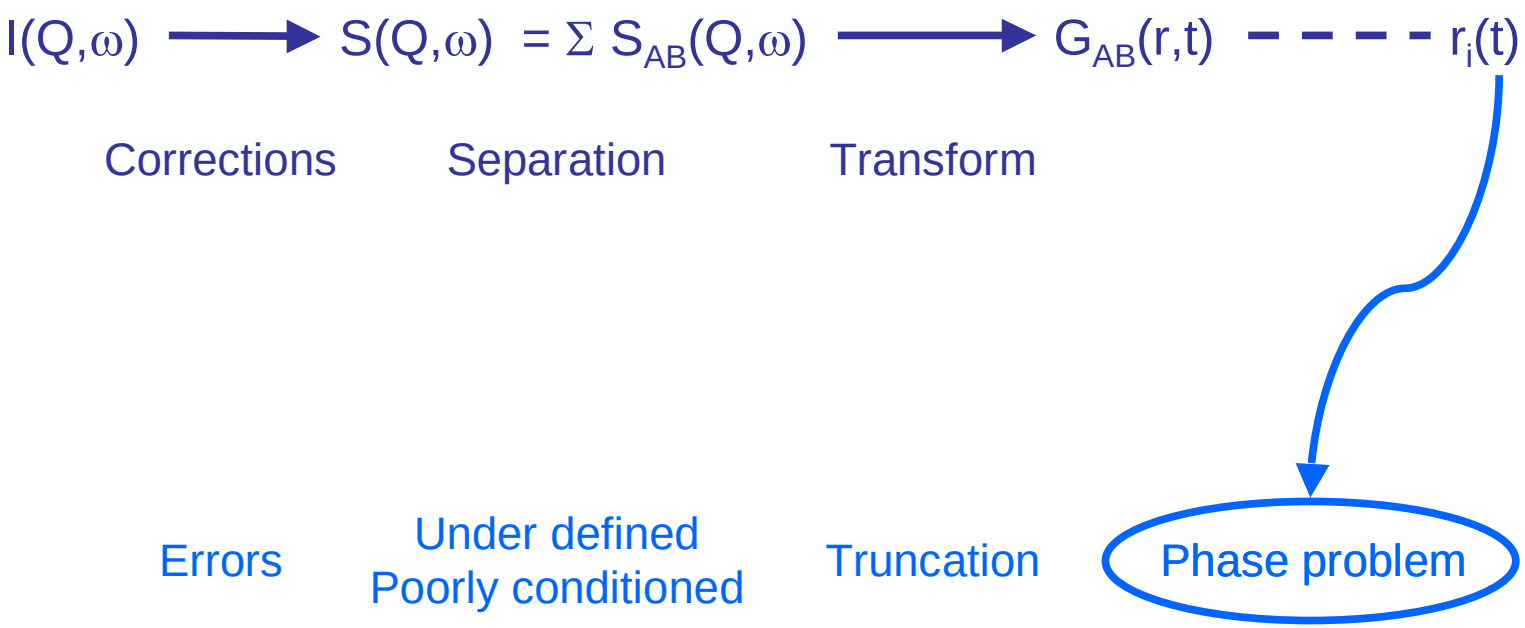
NiZr neutron isotopes

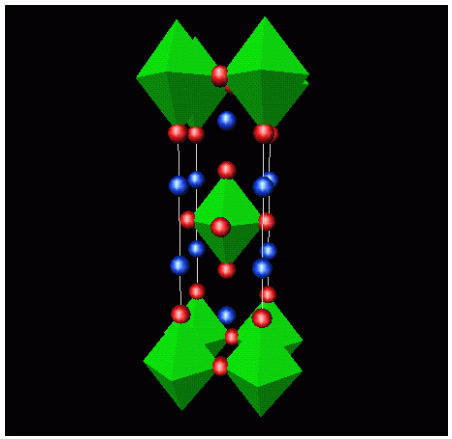
CuZr neutron isotopes

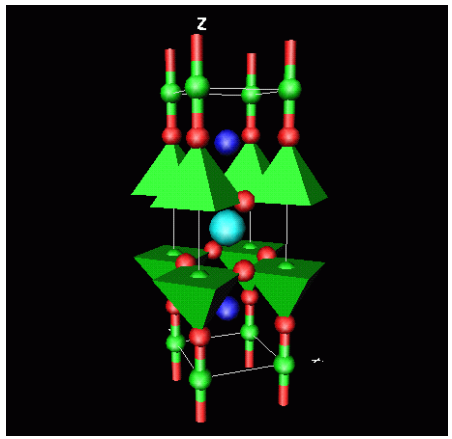
$$I(Q,\omega) \longrightarrow S(Q,\omega) = \Sigma\, S_{AB}(Q,\omega) \longrightarrow G_{AB}(r,t) \;\text{- - - -}\; r_i(t)$$

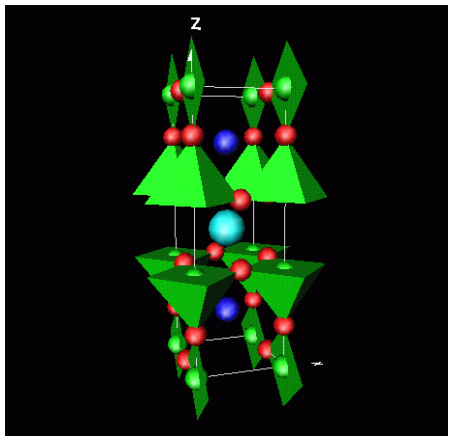
Corrections Separation Transform

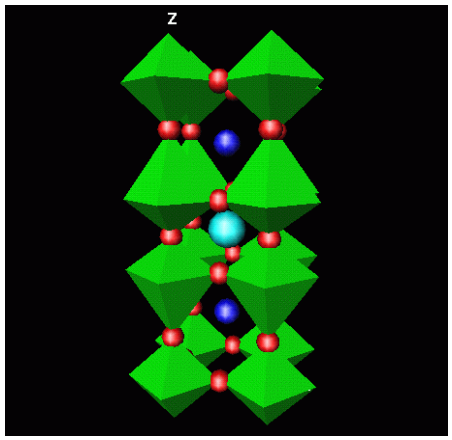
Errors Under defined Poorly conditioned Truncation Phase problem

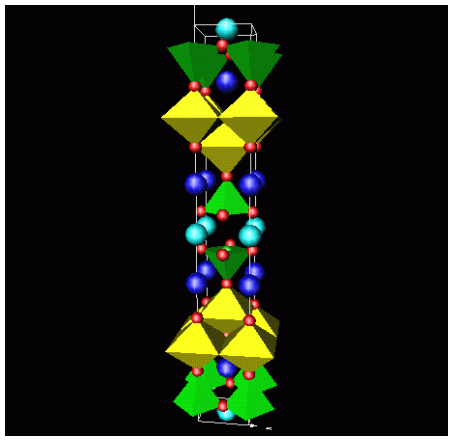

I(Q,ω)
S(Q,ω) = Σ S_AB(Q,ω)
G_AB(r,t)
r_i(t)
Corrections
Separation
Transform
Errors
Under defined
Poorly conditioned
Truncation
Phase problem



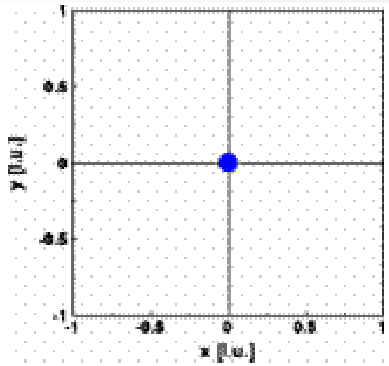


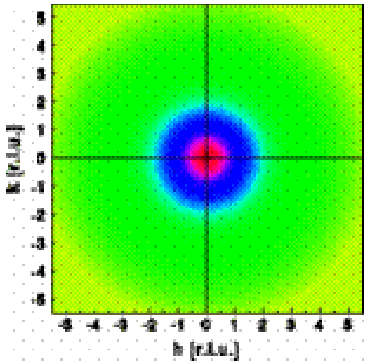






High temperature superconductors


y [l.u.]
x [l.u.]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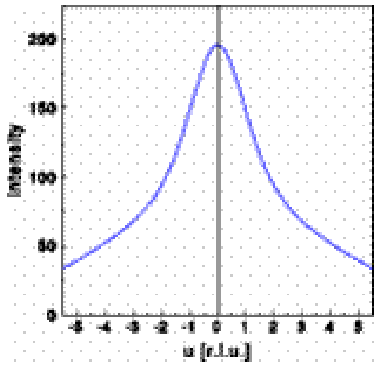
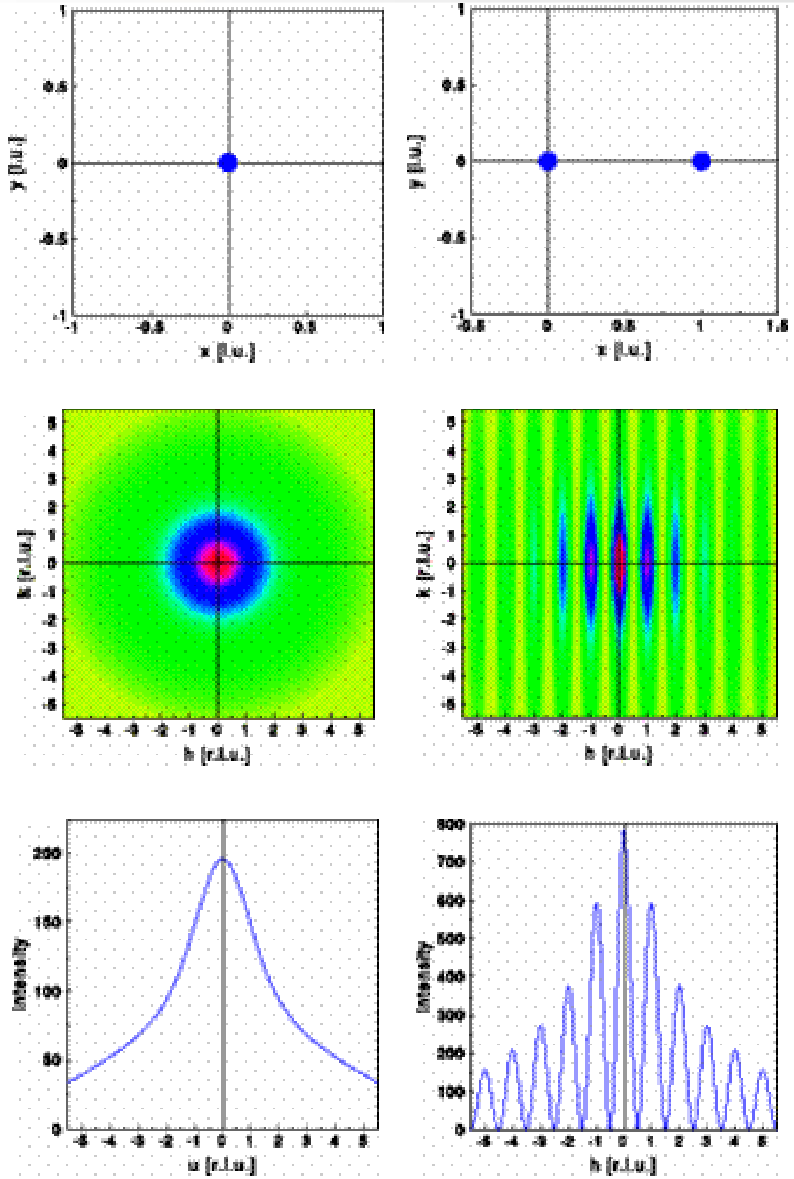
h [r.l.u.]


Intensity
u [r.l.u.]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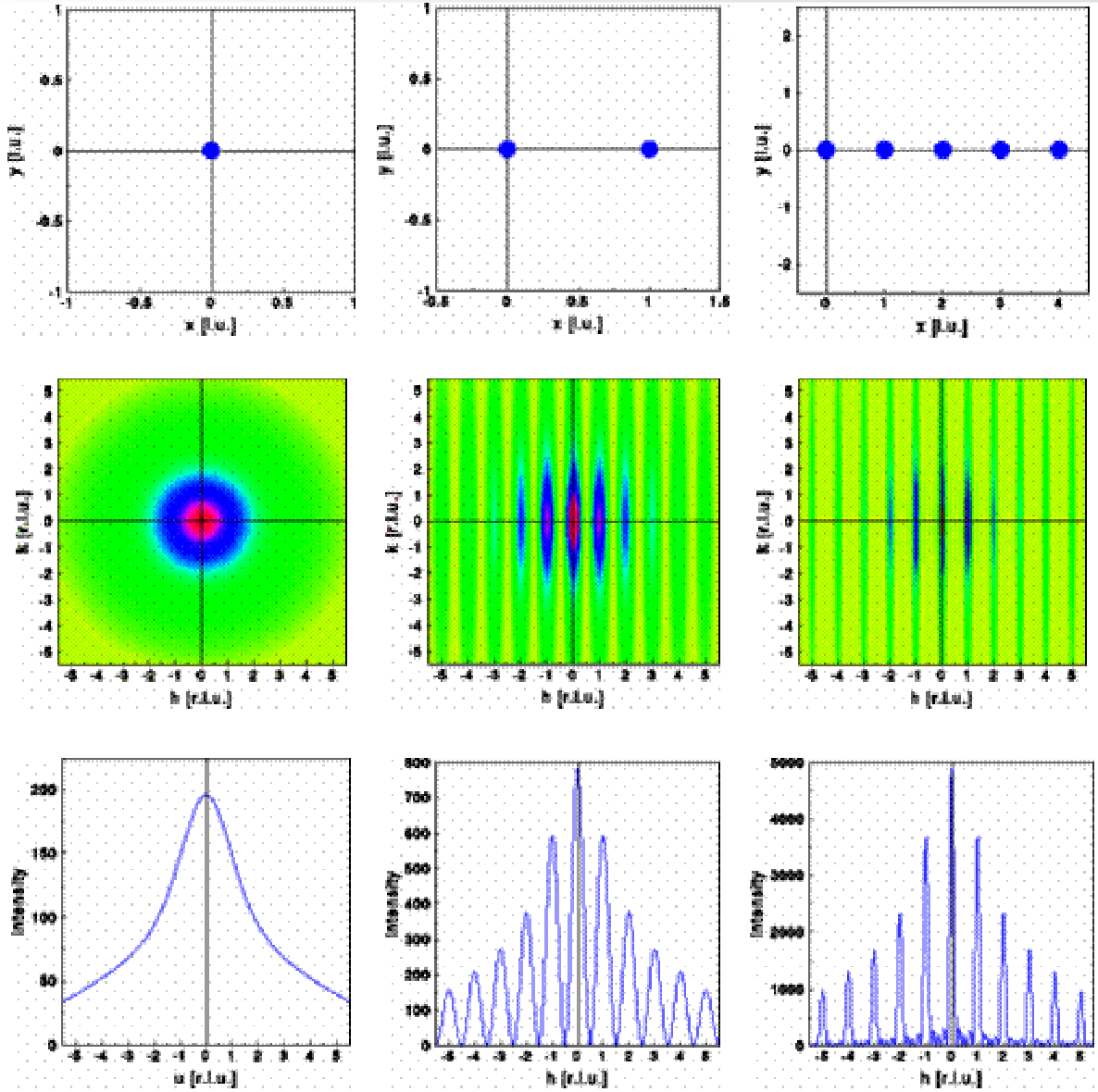
x [l.u.]
k [r.l.u.]
h [r.l.u.]
Intensity
u [r.l.u.]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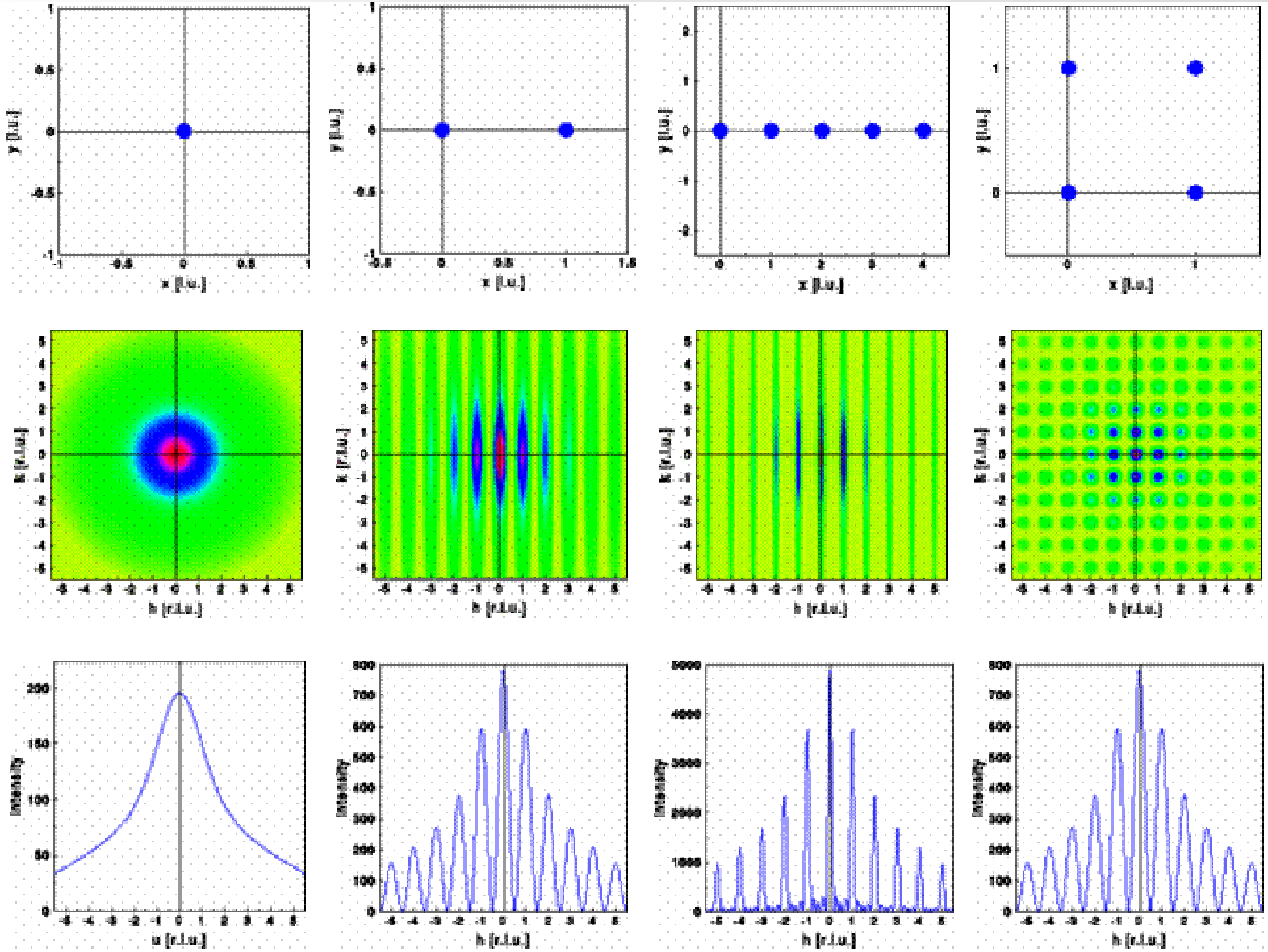
x [l.u.]
k [r.l.u.]
h [r.l.u.]
Intensity
u [r.l.u.]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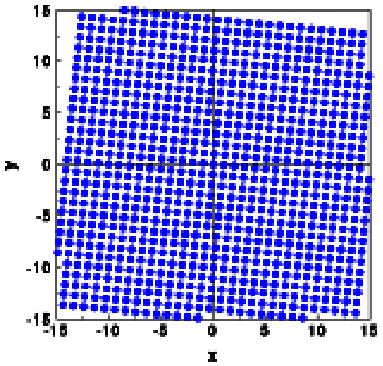
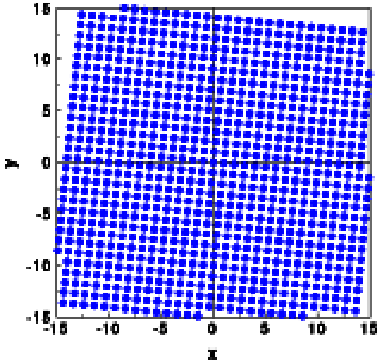
x [l.u.]
k [r.l.u.]
h [r.l.u.]
Intensity
u [r.l.u.]


15
10
5
0
-5
-10
-15
y
-15
-10
-5
0
5
10
15
x


15
10
5
0
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-10
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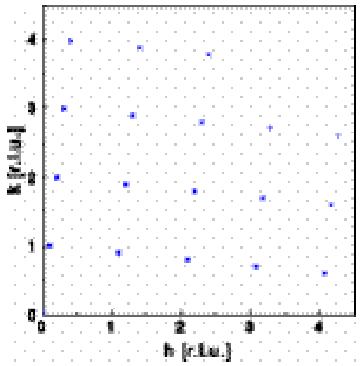
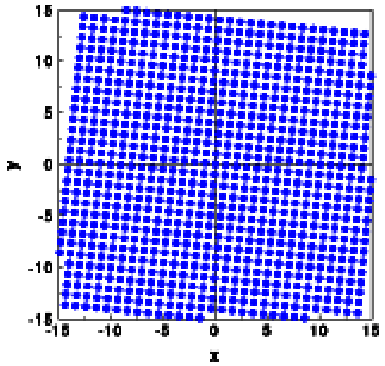
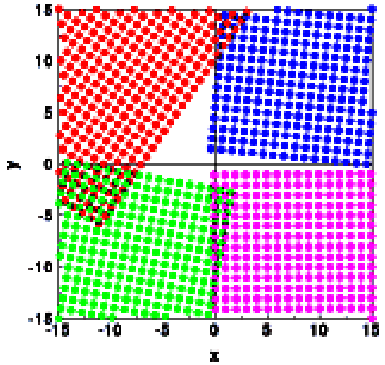
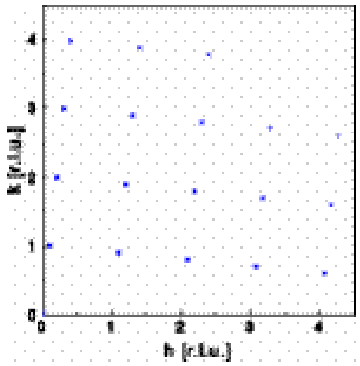
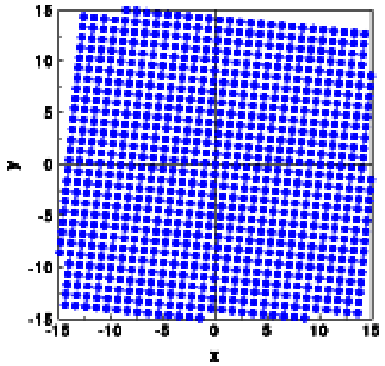
y
-15
-10
-5
0
5
10
15
x

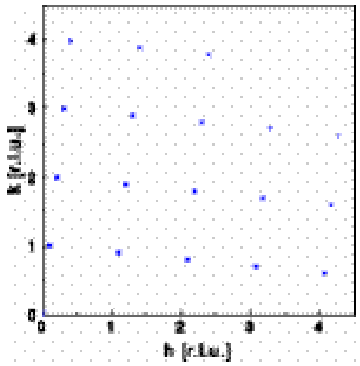

4
3
2
1
0
k [r.l.u.]
0
1
2
3
4
h [r.l.u.]


15
10
5
0
-5
-10
-15
y
-15 -10 -5 0 5 10 15
x


15
10
5
0
-5
-10
-15
y
-15 -10 -5 0 5 10 15
x


4
3
2
1
0
0 1 2 3 4
h [r.l.u.]


y
x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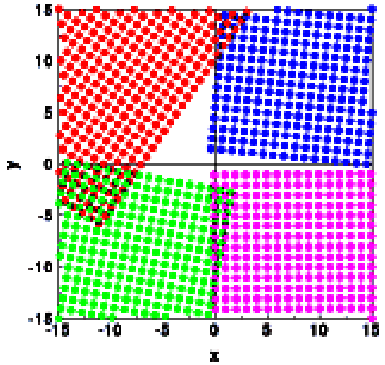
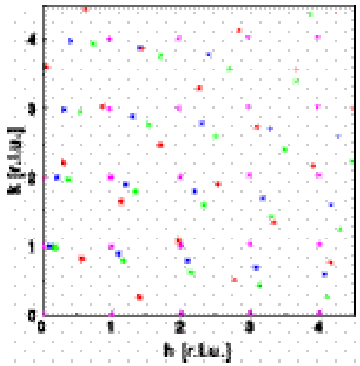

y
x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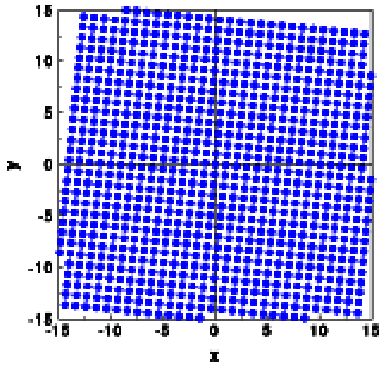
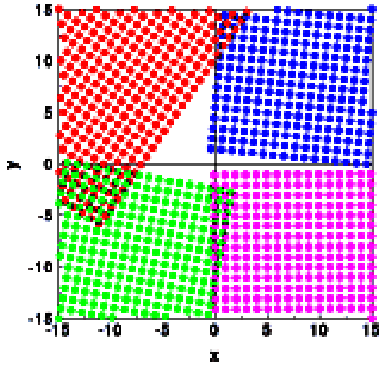
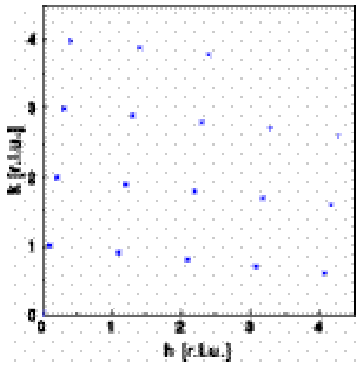

y
x


y
x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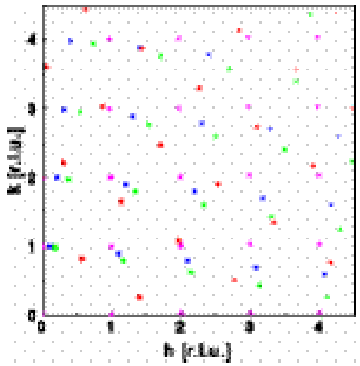
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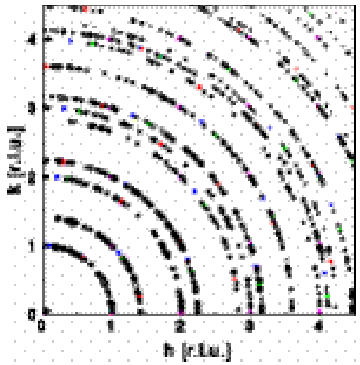
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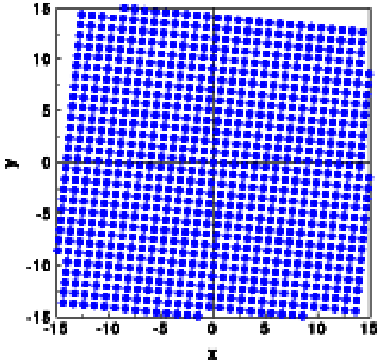
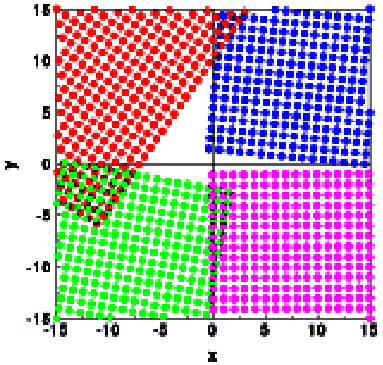
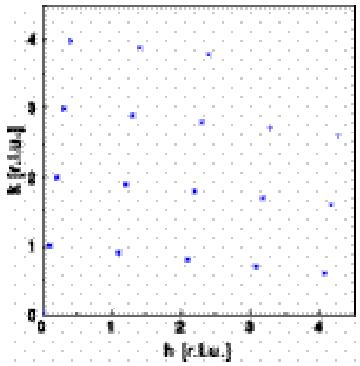

y
x


y
x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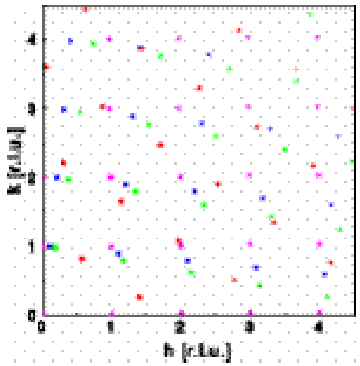
h [r.l.u.]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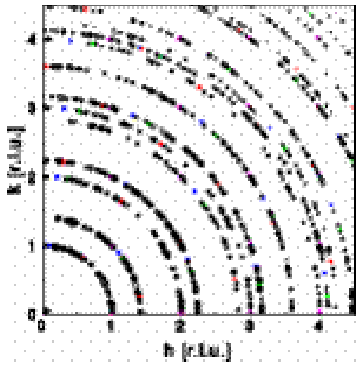
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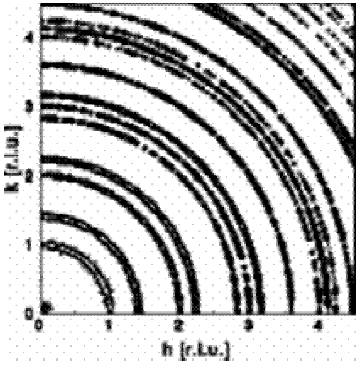
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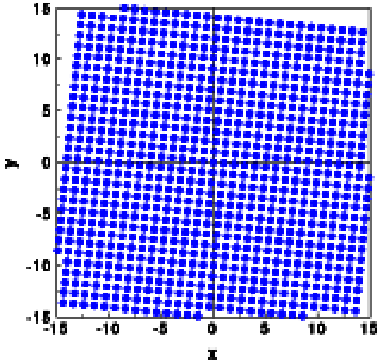
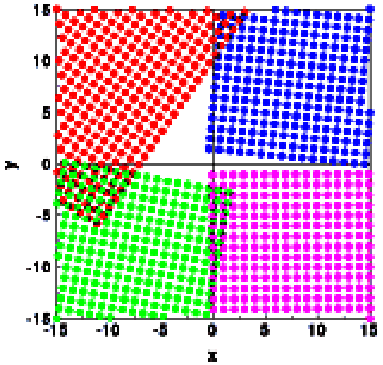
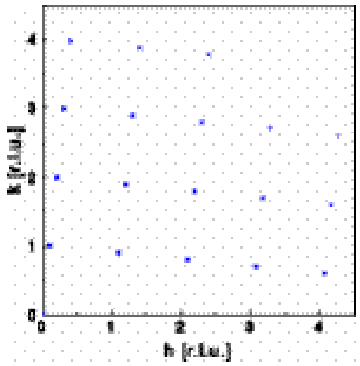

y
x


y
x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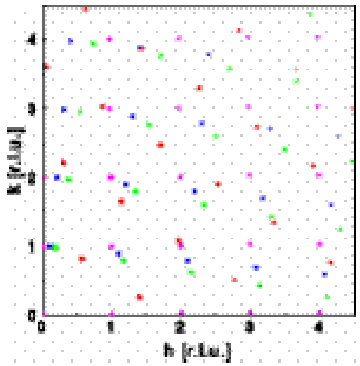
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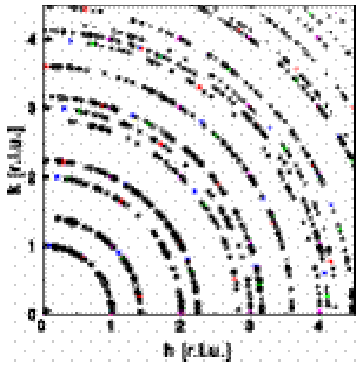
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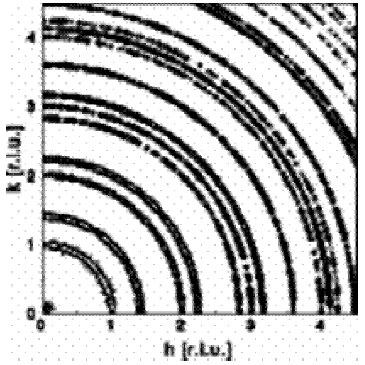
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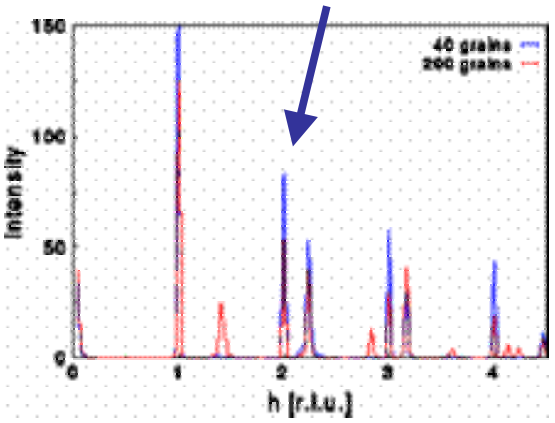
40 grains
200 grains
Intensity
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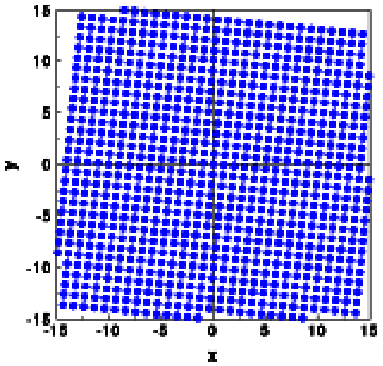
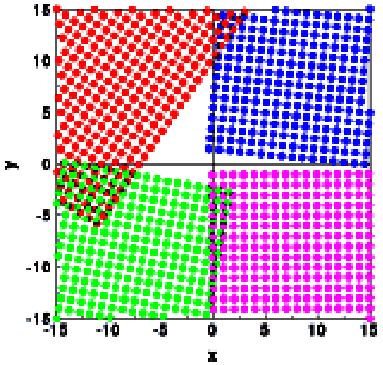
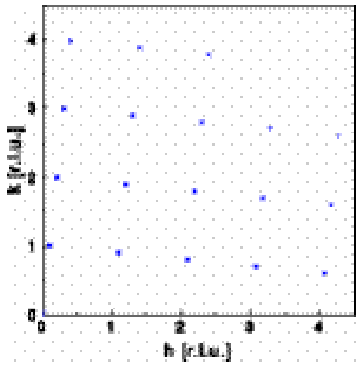

y
x


y
x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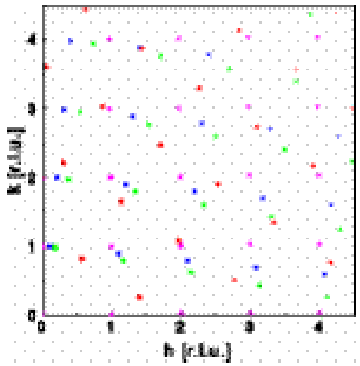
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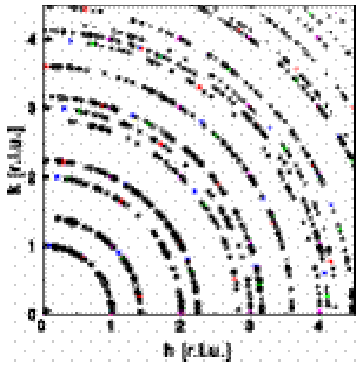
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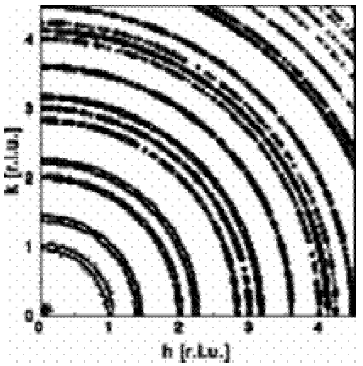
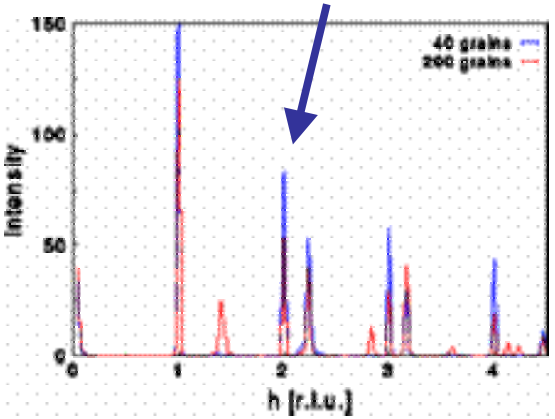
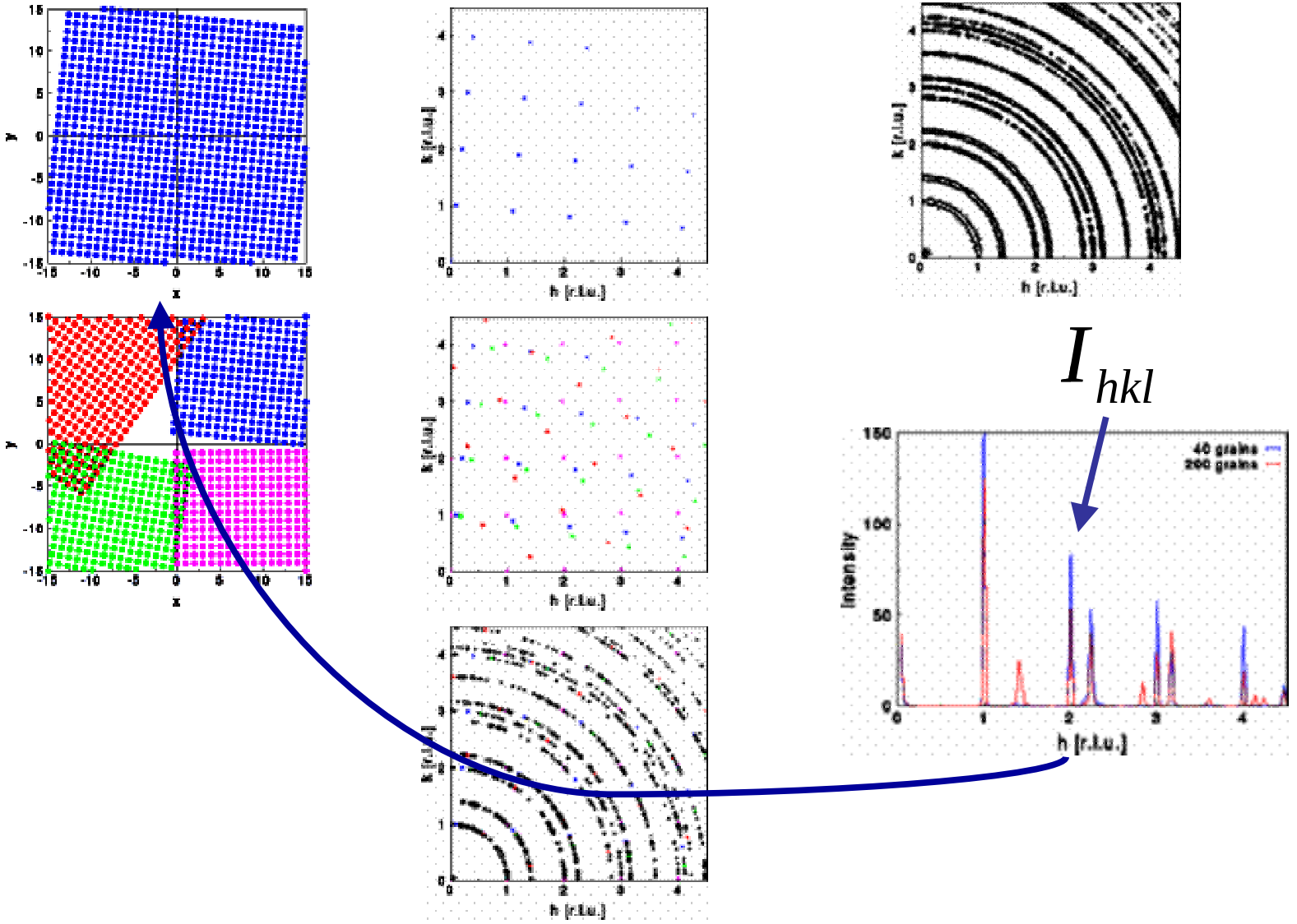
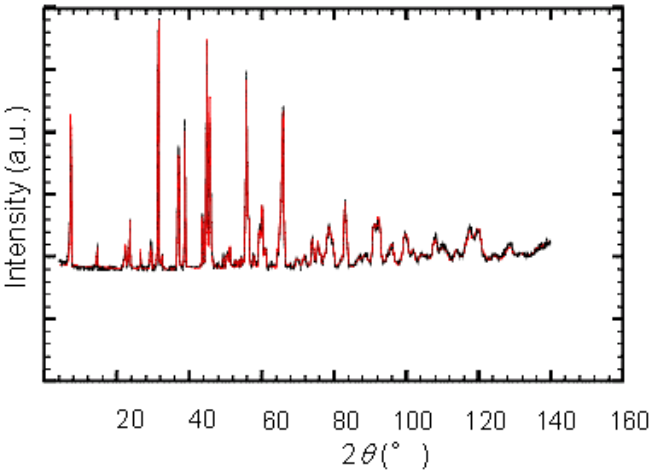

k [r.l.u.]
h [r.l.u.]

I_{hkl}


40 grains
200 grains
Intensity
h [r.l.u.]


x
y
h [r.l.u.]
k [r.l.u.]
I_{hkl}
intensity
40 grains
200 grains

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



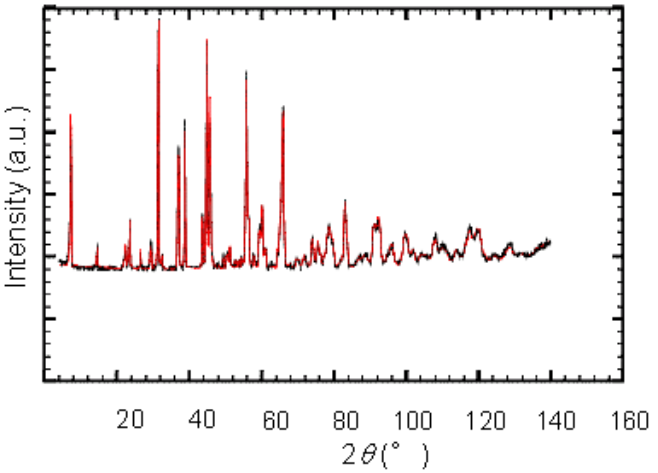
$$F_{hkl} = \sum_{j=1}^{N_j} b_j \exp\left(2\pi i(hx_j + ky_j + lz_j)\right)$$

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

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

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

Rietveld refinement (parametric modeling)



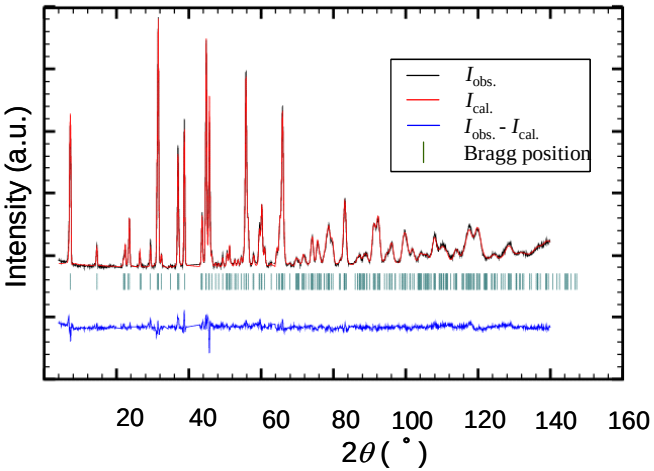
$$y_i^c = s\sum_{hkl} L_{hkl}\left|F_{hkl}\right|^2 \phi(2\theta_i - 2\theta_{hkl})P_{hkl}A + y_i^b$$

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

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

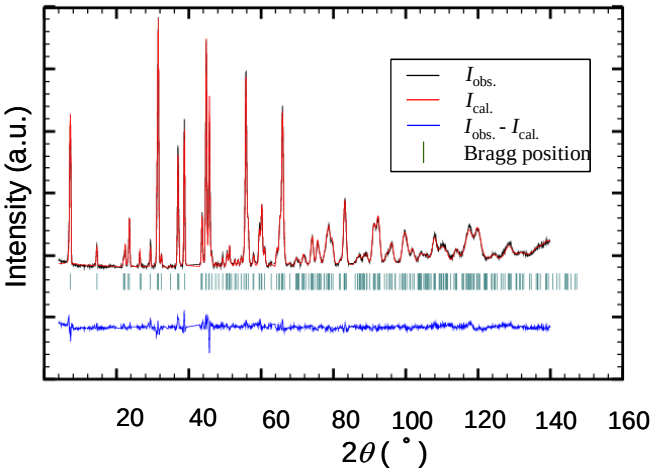


$R_p = 4.17$, $R_{wp} = 5.47$, $\chi^2 = 3.68$

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)

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

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

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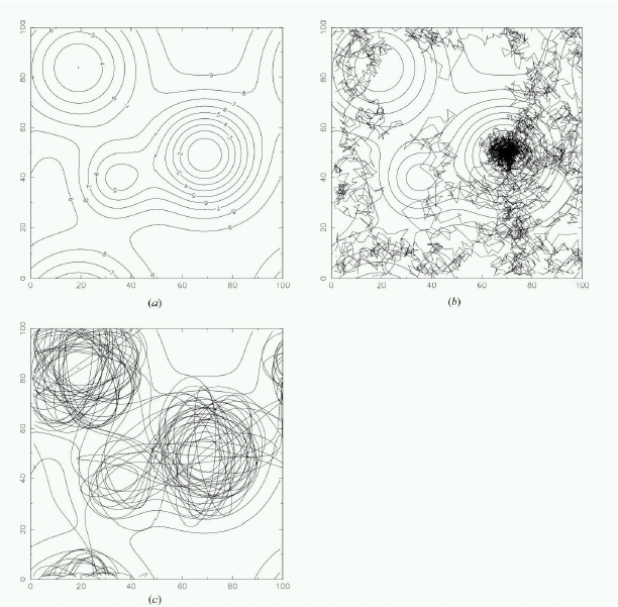

Johnston, David, Markvardsen, Shankland. Acta Cryst A 58 441 2002

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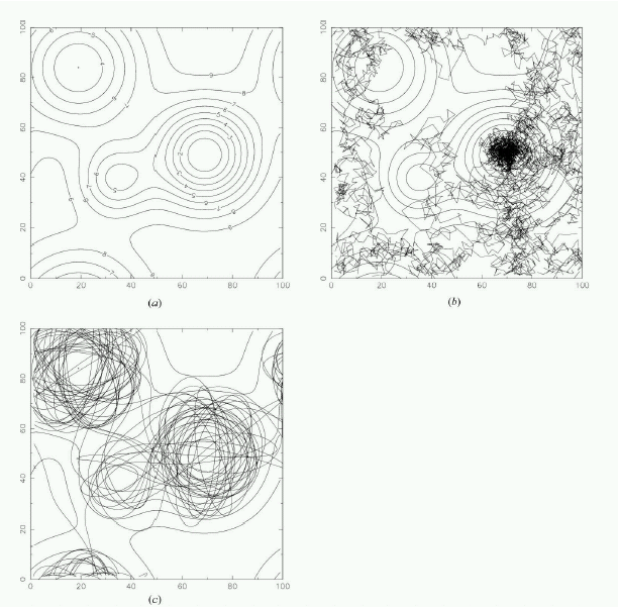
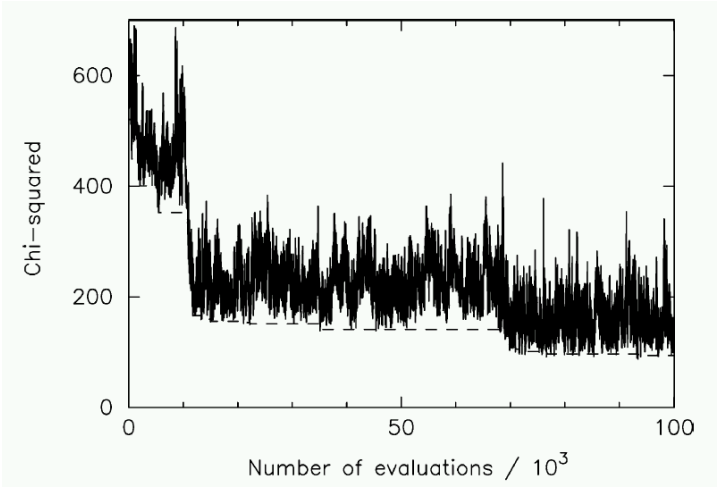
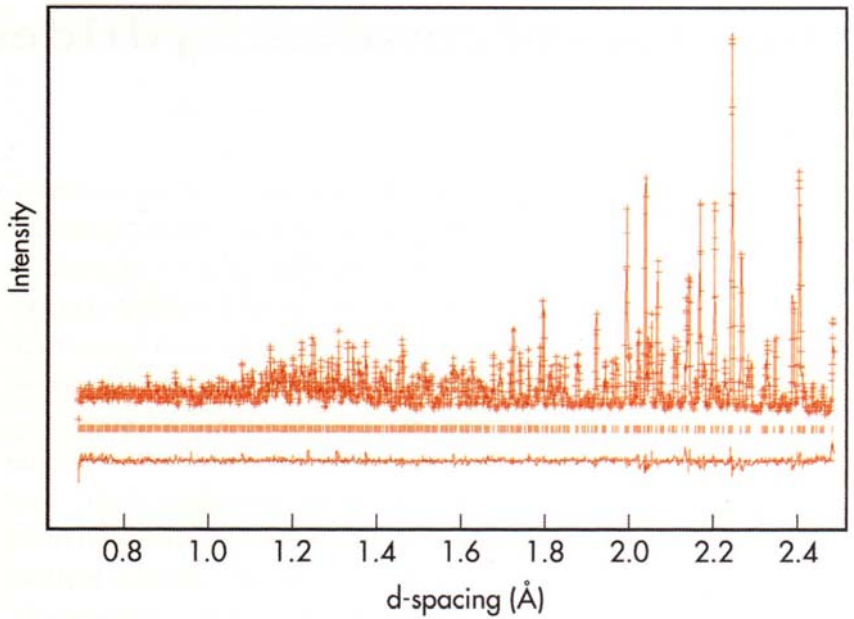
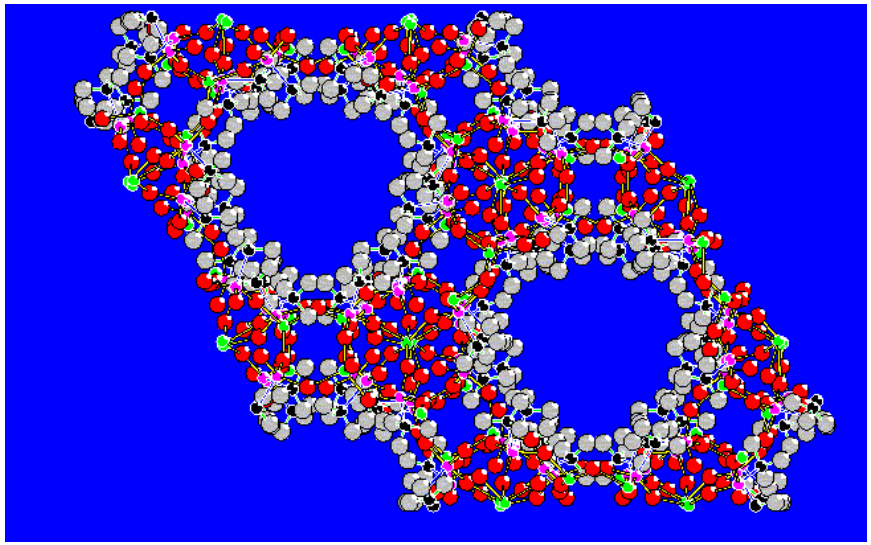




Johnston, David, Markvardsen, Shankland. Acta Cryst A 58 441 2002



Pushing the 100 atom limit



α-AgI

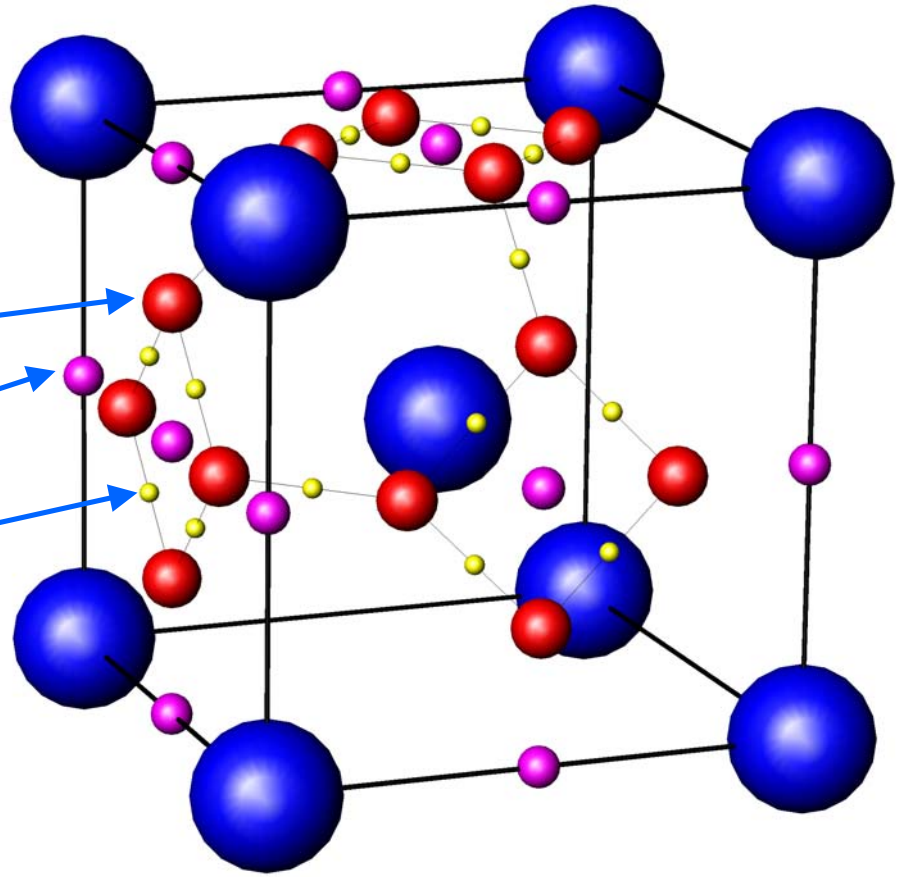
b.c.c. I^-

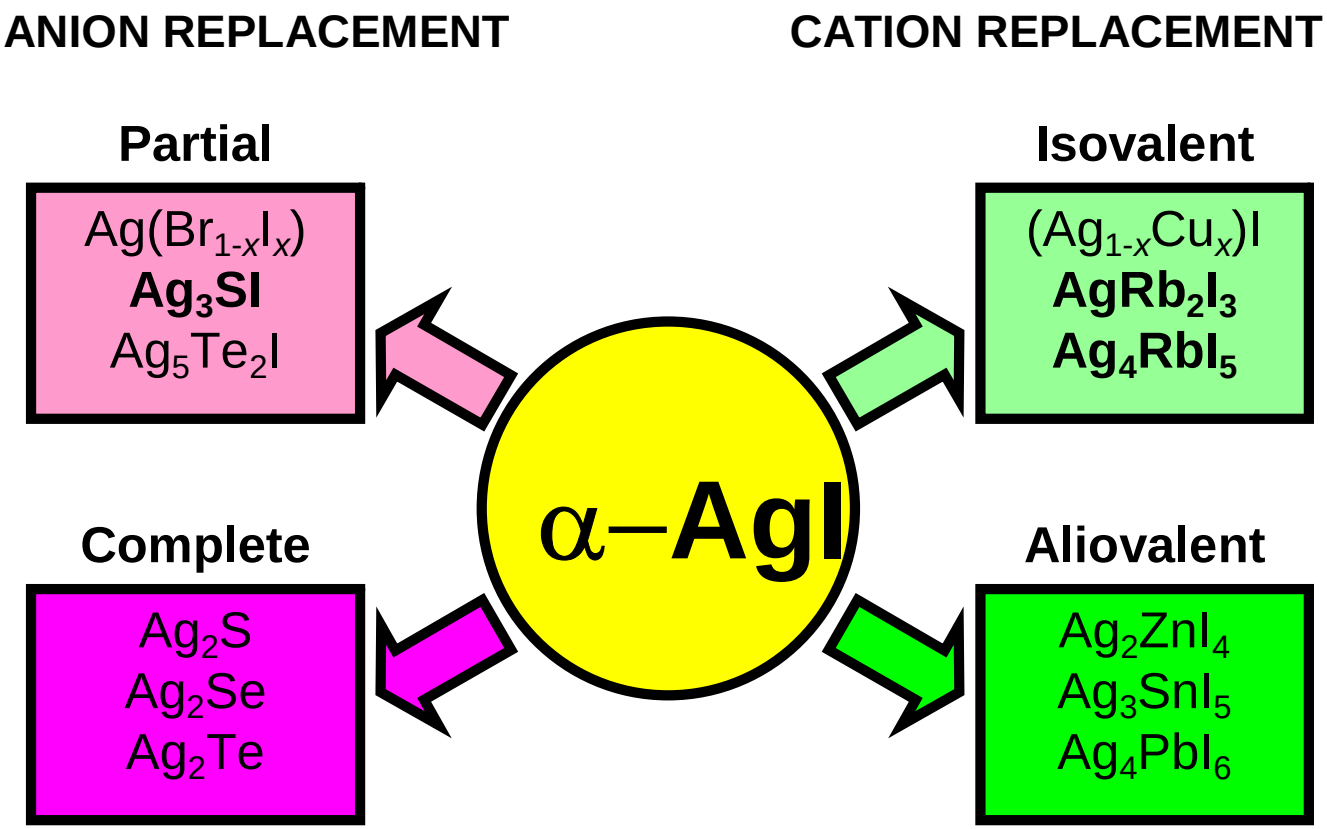
Ag^+ sites.....

12 × tetrahedral

6 × octahedral

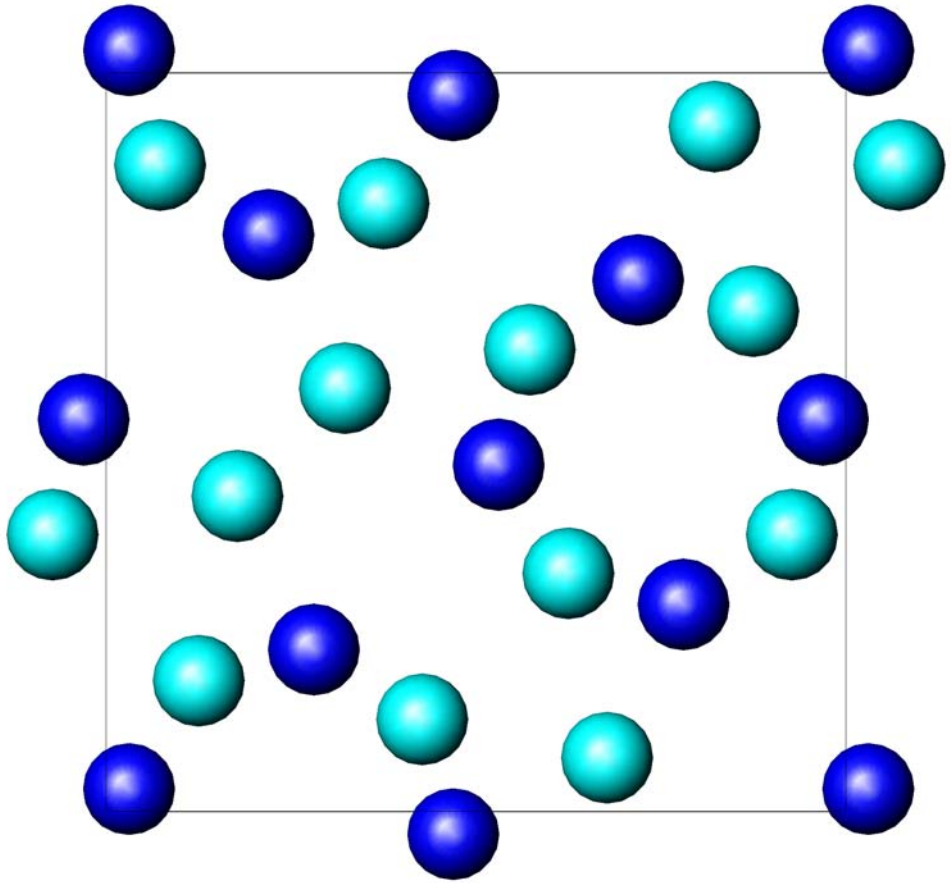
24 × trigonal





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

Ag_4RbI_5 : IODINE SUBSTRUCTURE



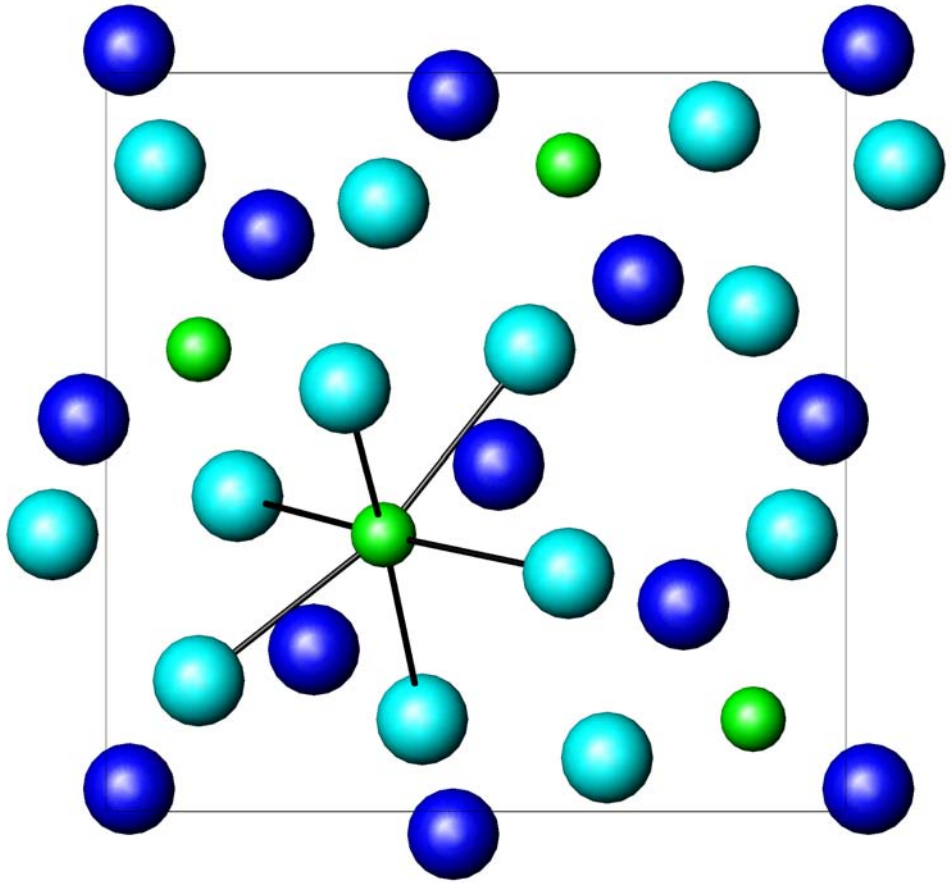
P $4_1$32
a ~11.24Å

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

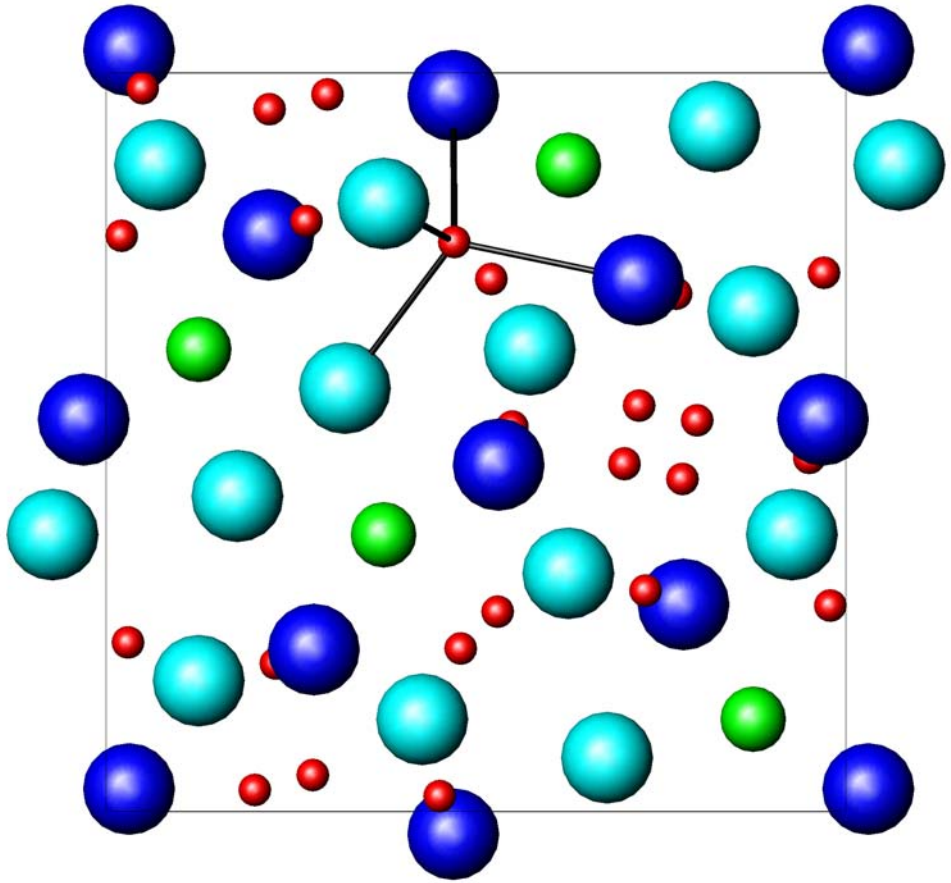


P $4_1$32
a ~11.24Å

Rb in 4(*a*)
$^3I_8$,$^3I_8$,$^3I_8$

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

Ag_4RbI_5 : Ag1 SITES

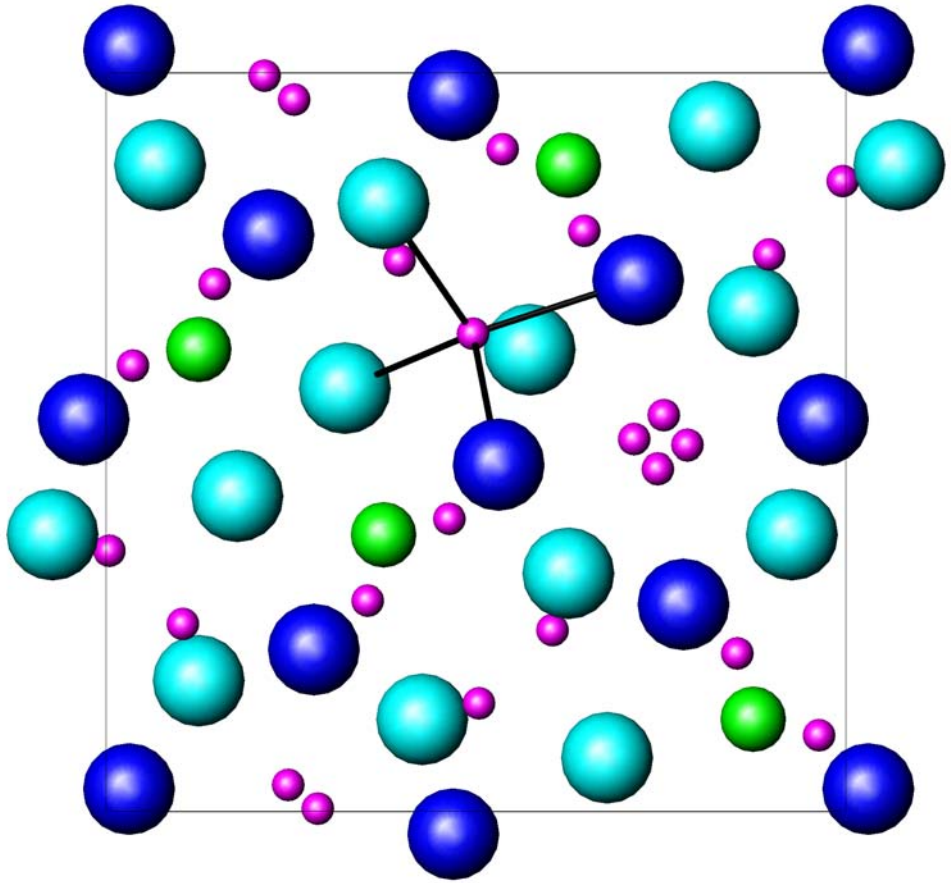


P $4_1$32
a ~11.24Å

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

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

Ag_4RbI_5 : Ag2 SITES

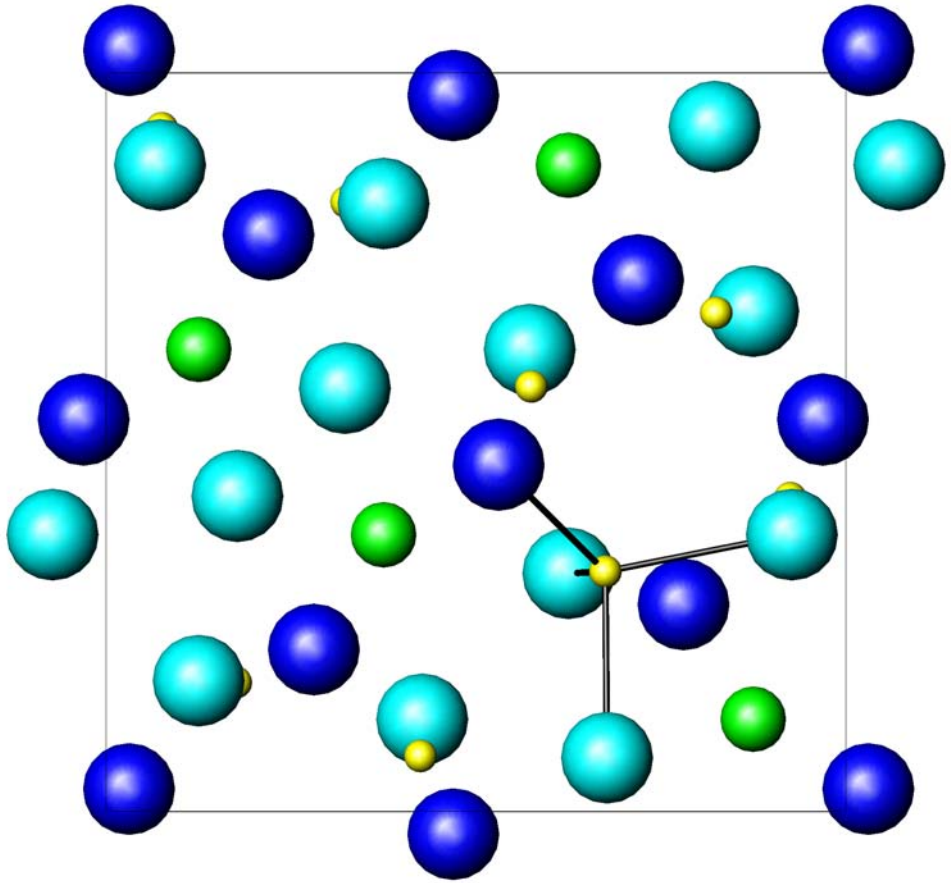


P $4_1$32
a ~11.24Å

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

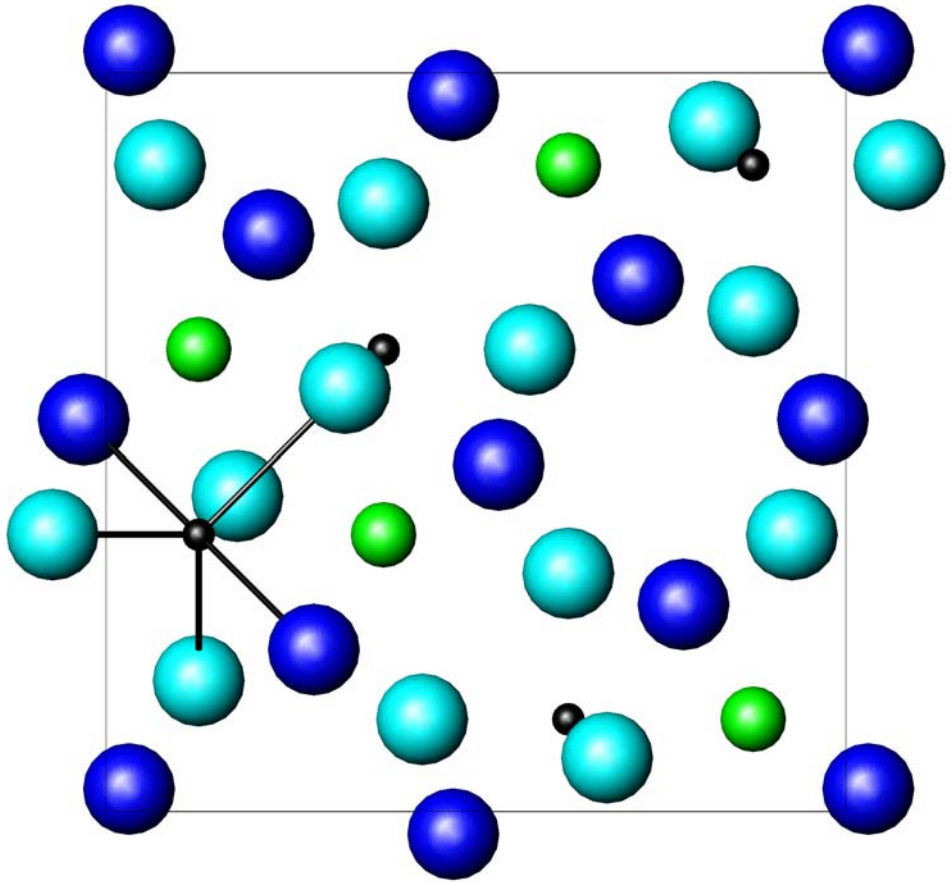


P $4_1$32
a ~11.24Å

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

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

Ag_4RbI_5 : Ag4 SITES

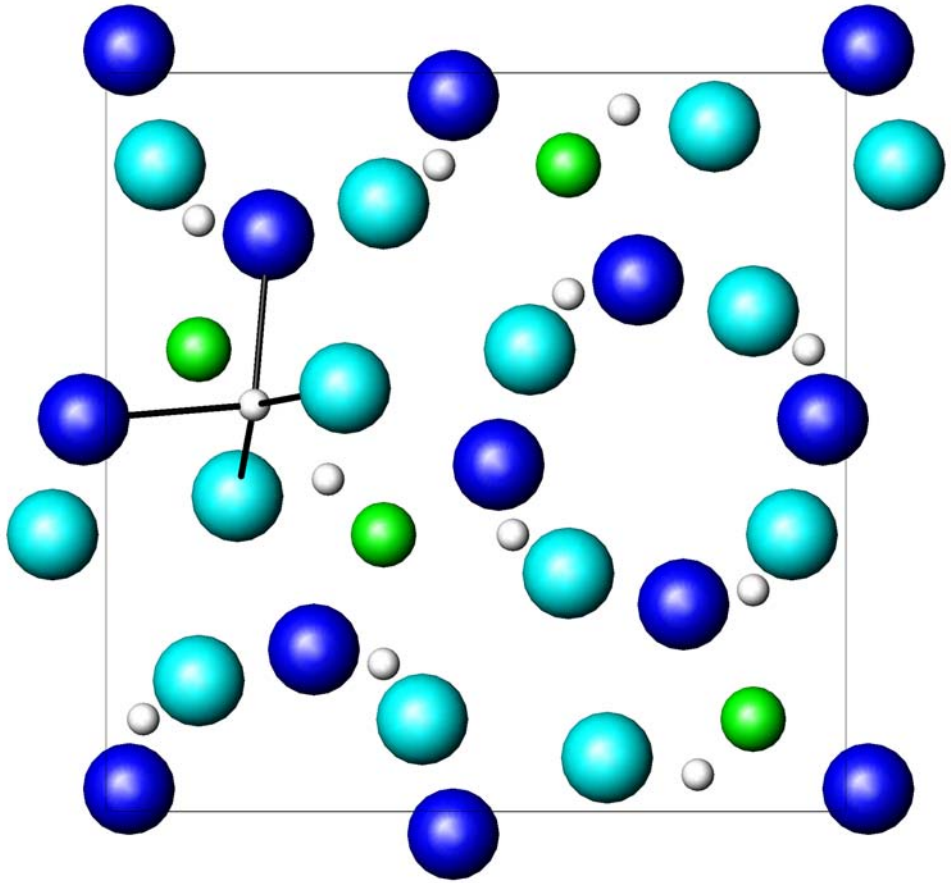


P $4_1$32
a ~11.24Å

Ag4 in 4(*b*)
$^7I_8$,$^7I_8$,$^7I_8$

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

Ag_4RbI_5 : Ag5 SITES

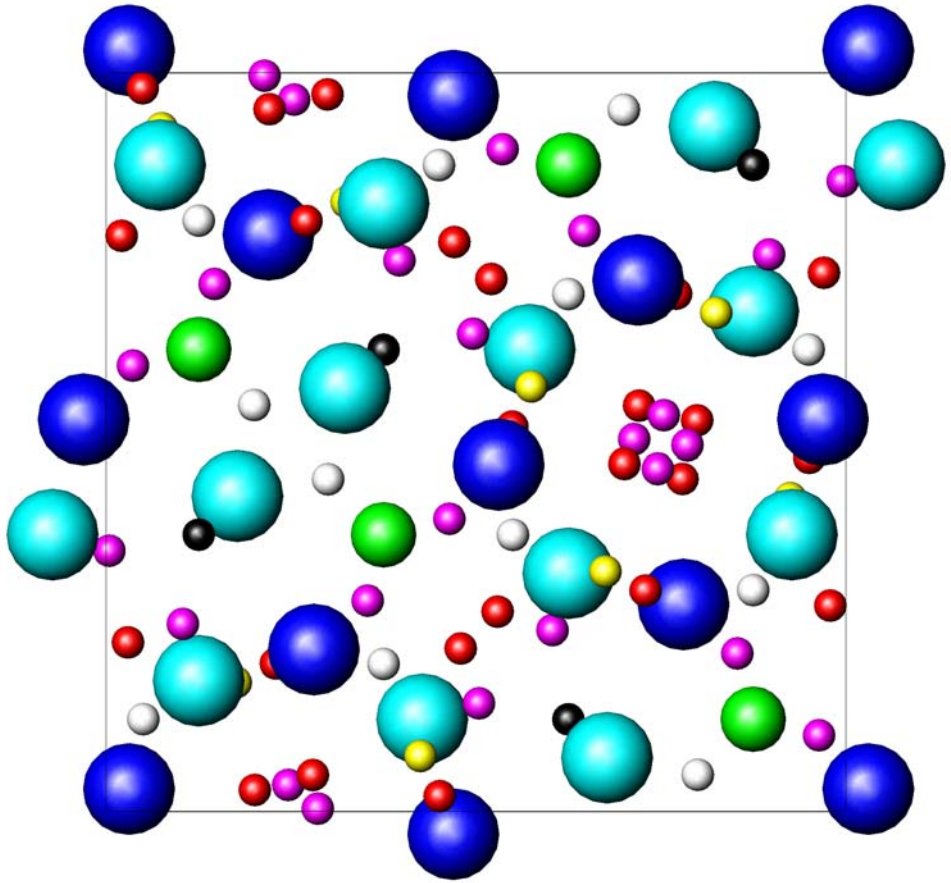


P $4_1$32
a ~11.24Å

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



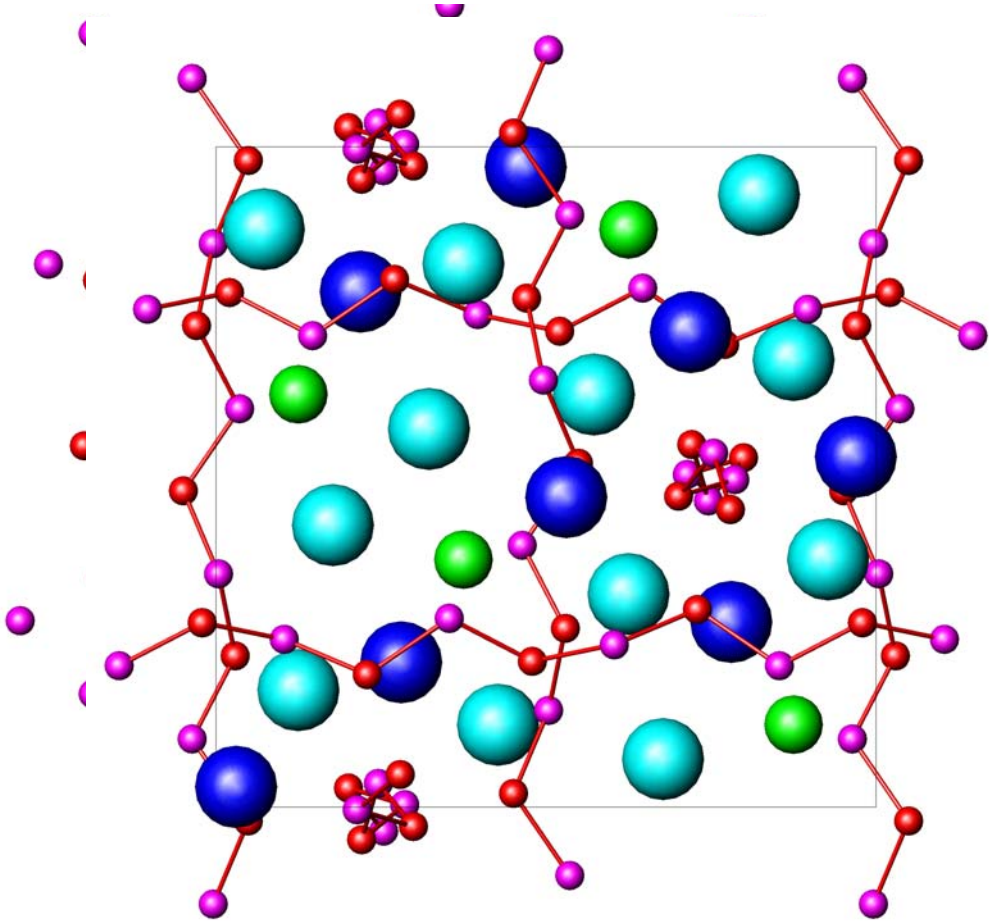
P $4_1$32
a ~11.24Å

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.

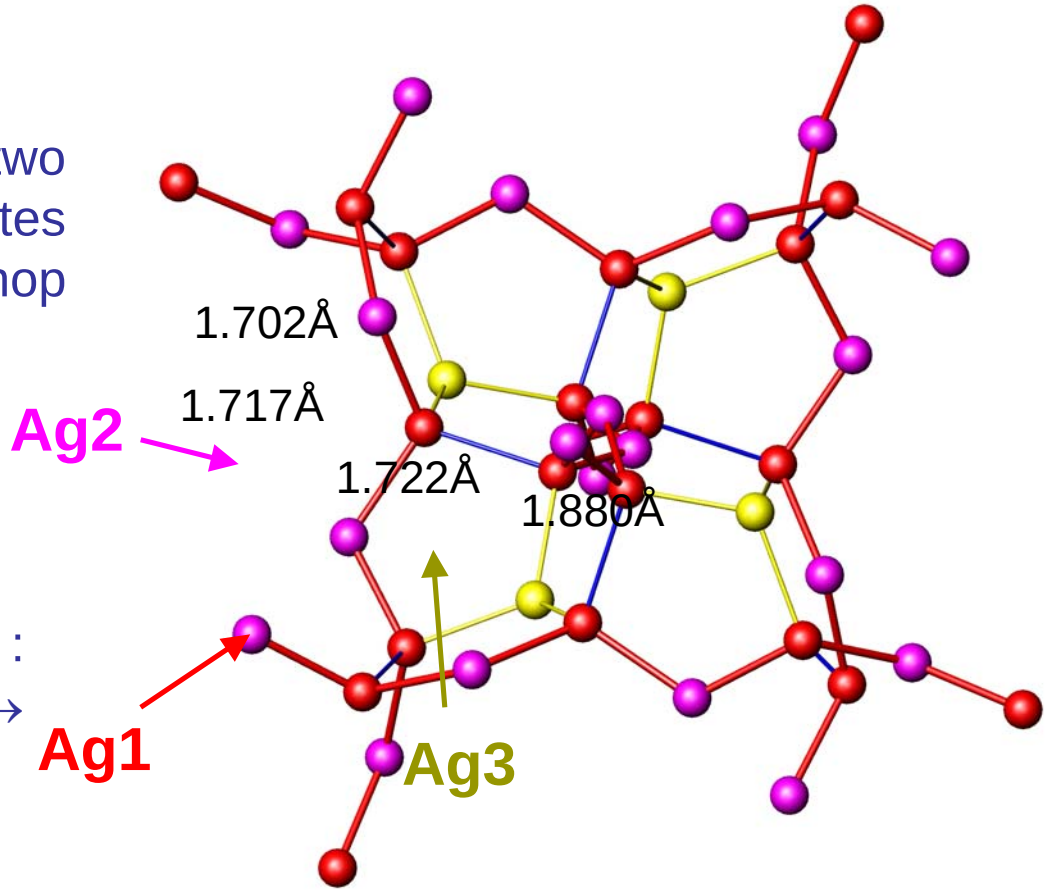
- conduction of Ag^+ occurs along one-dimensional channels.

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

Ag_4RbI_5 : Diffusion between channels

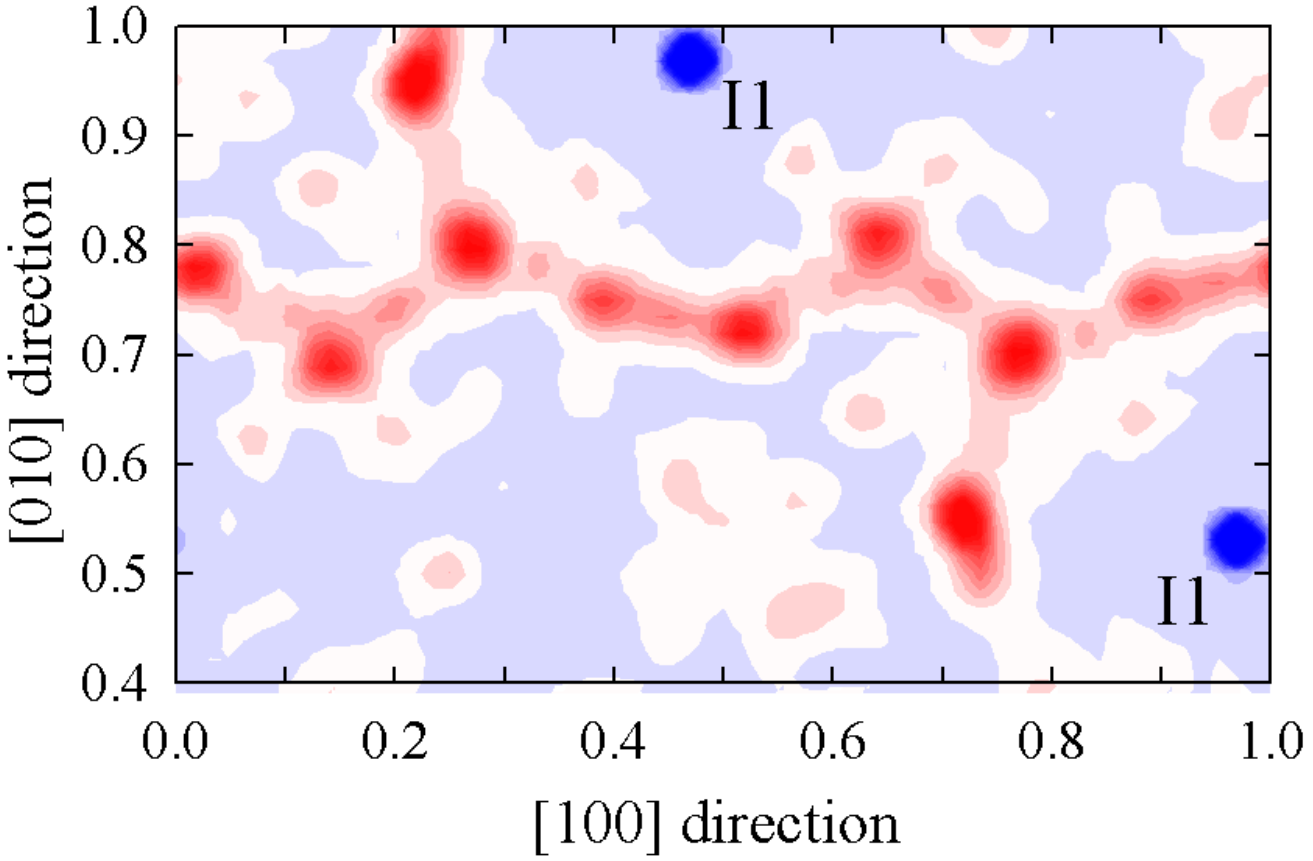
There are two plausible routes for Ag^+ to hop between channels.

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



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

Ag_4RbI_5 : Maximum entropy Fourier map



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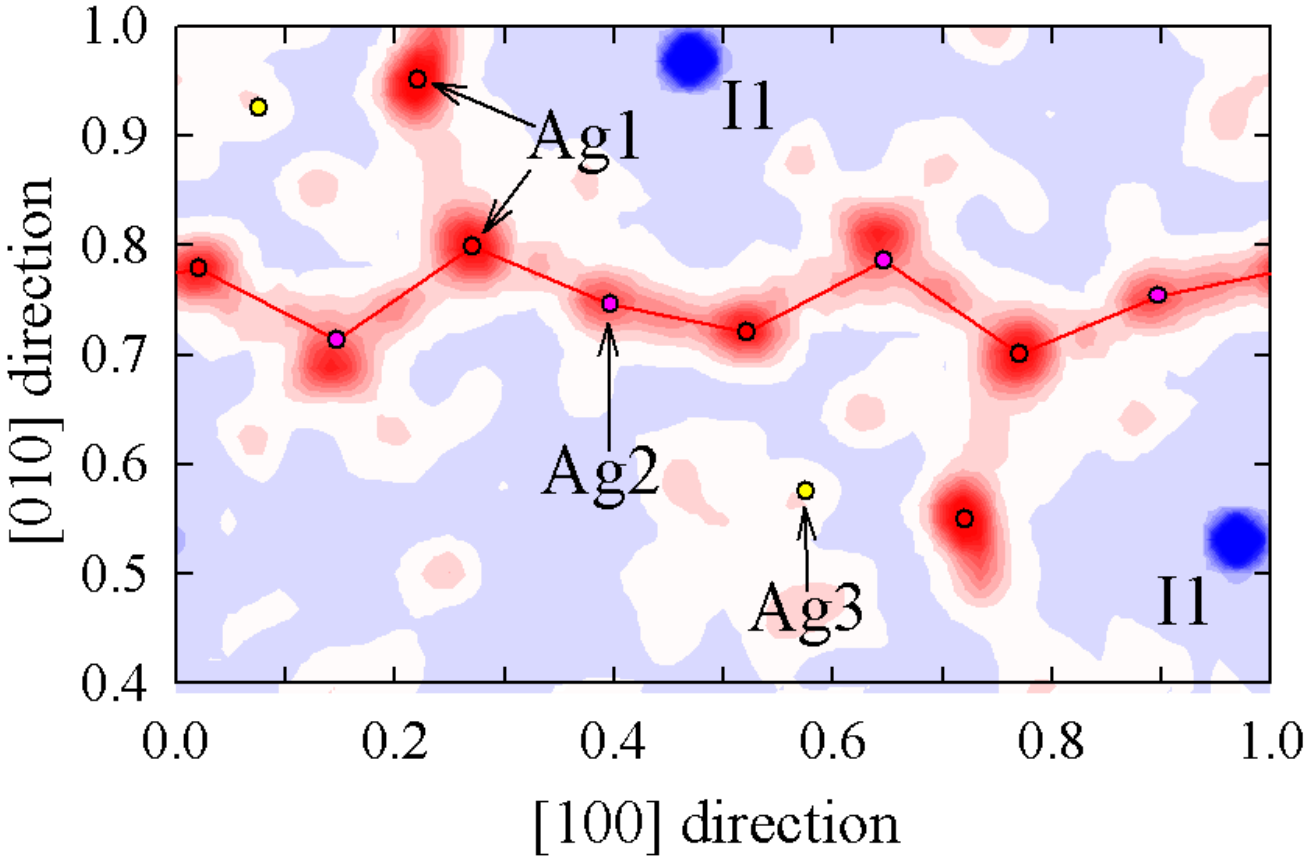
Ag_4RbI_5 : Maximum entropy Fourier map



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

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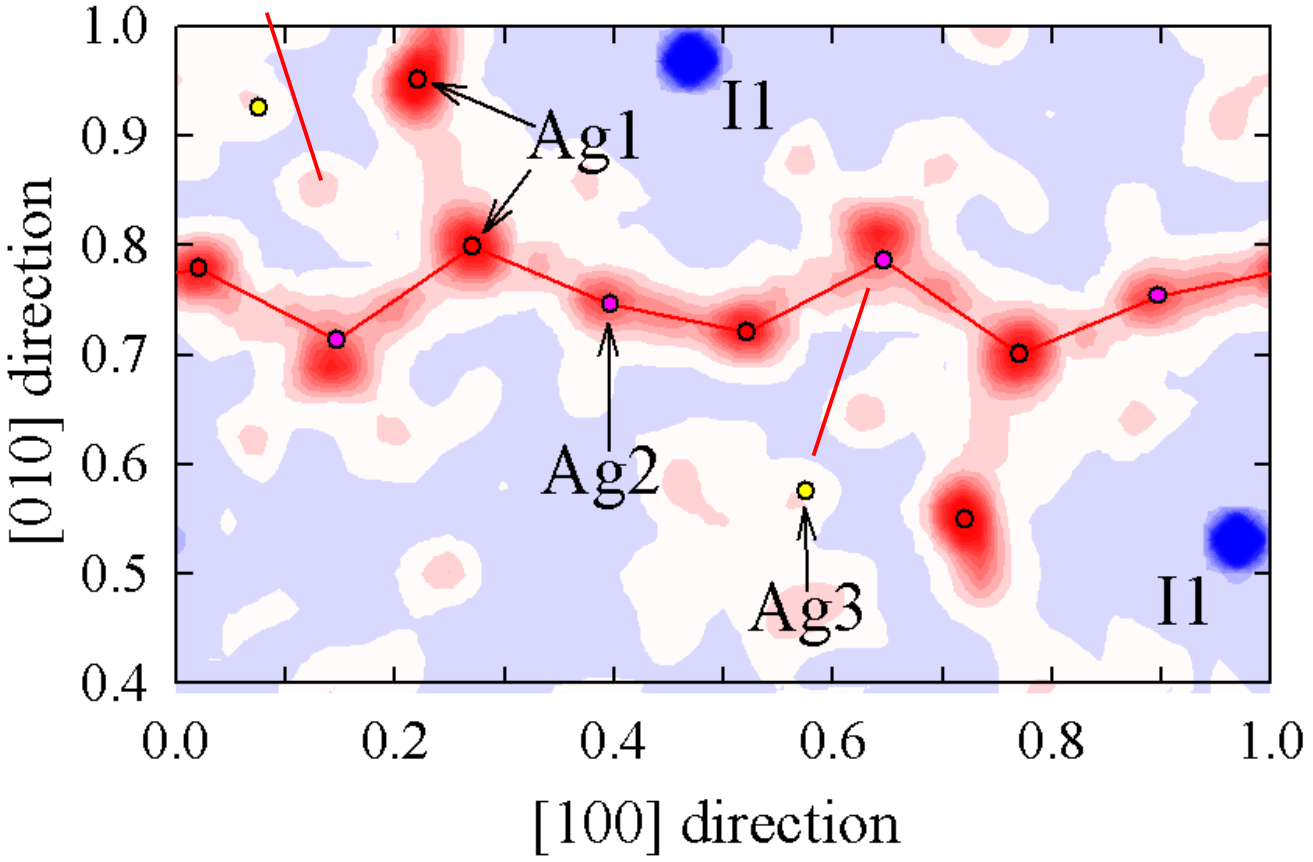
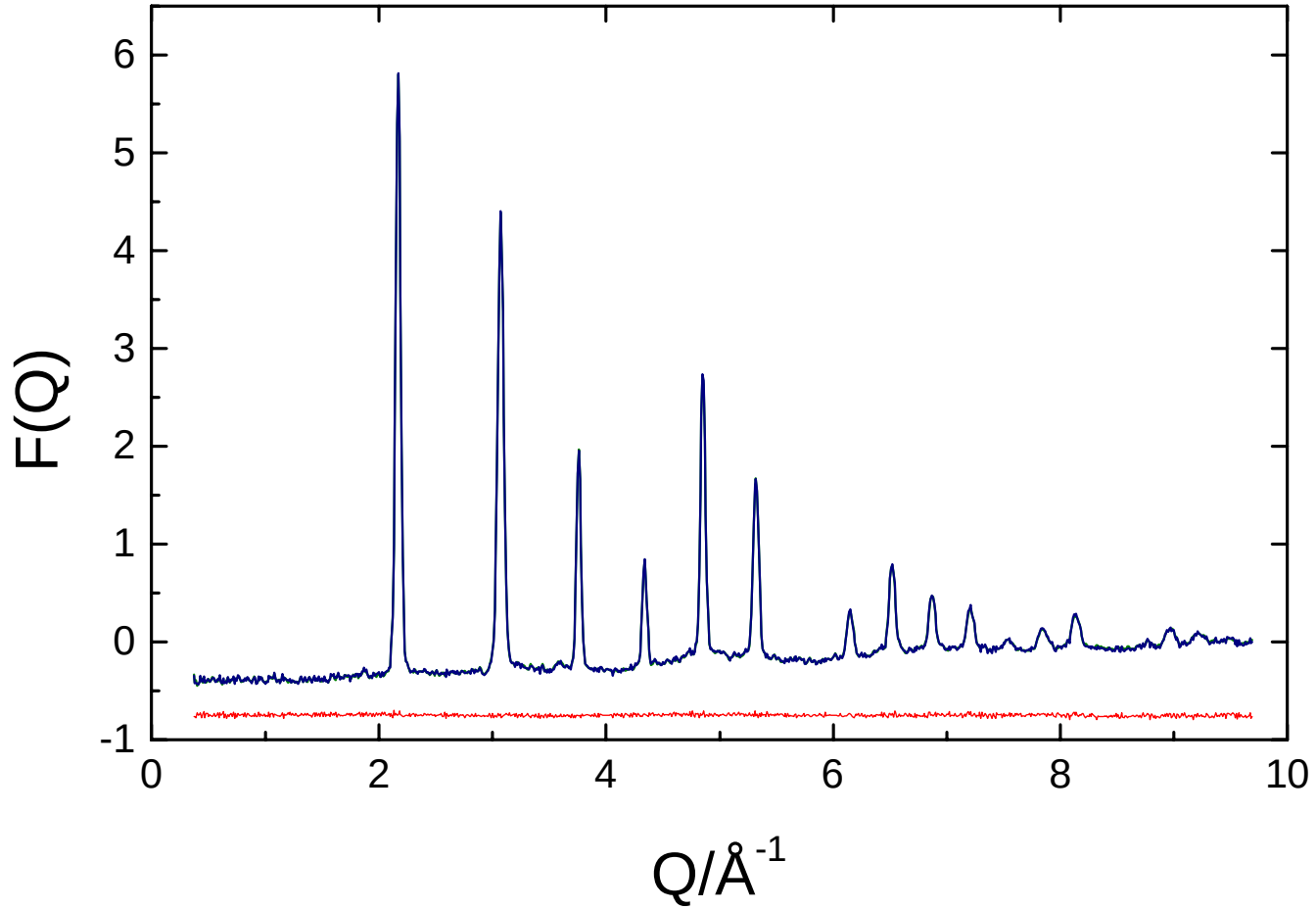
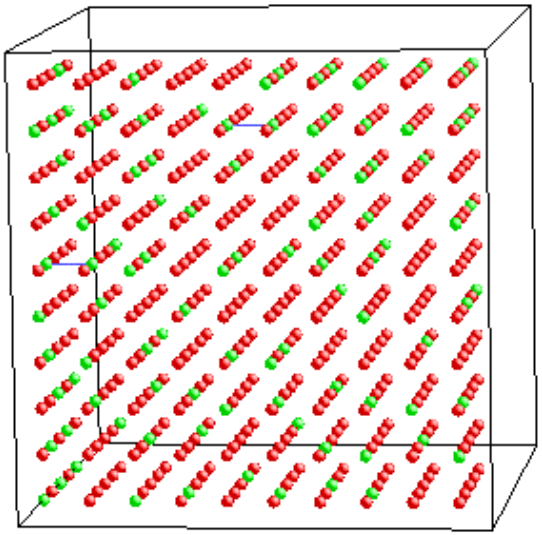
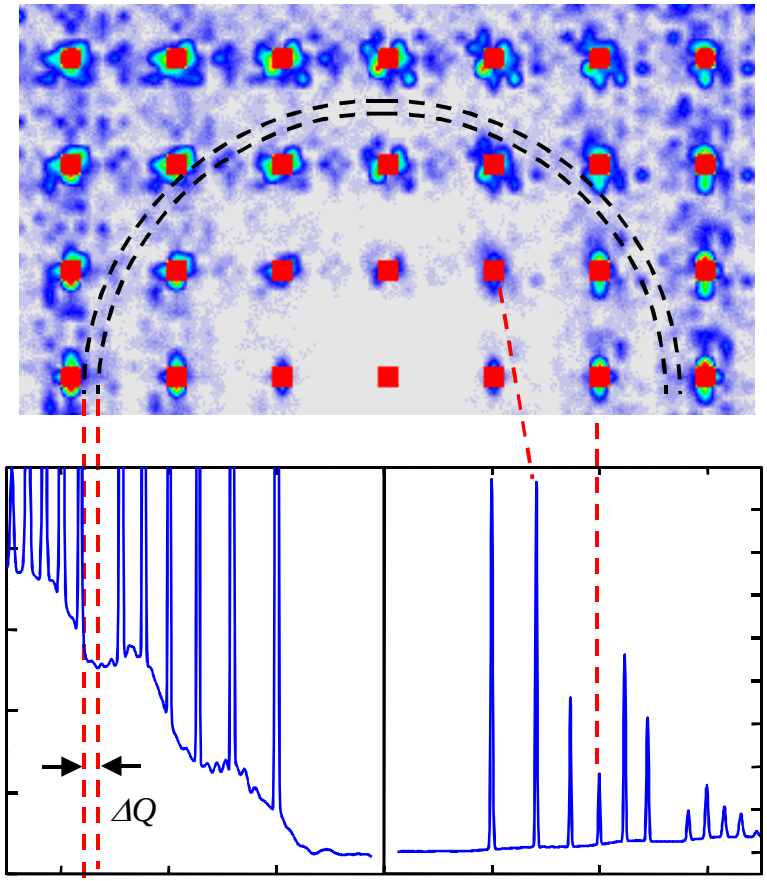
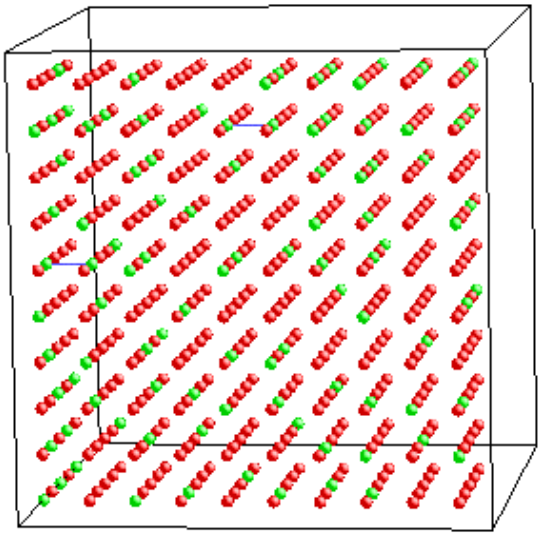


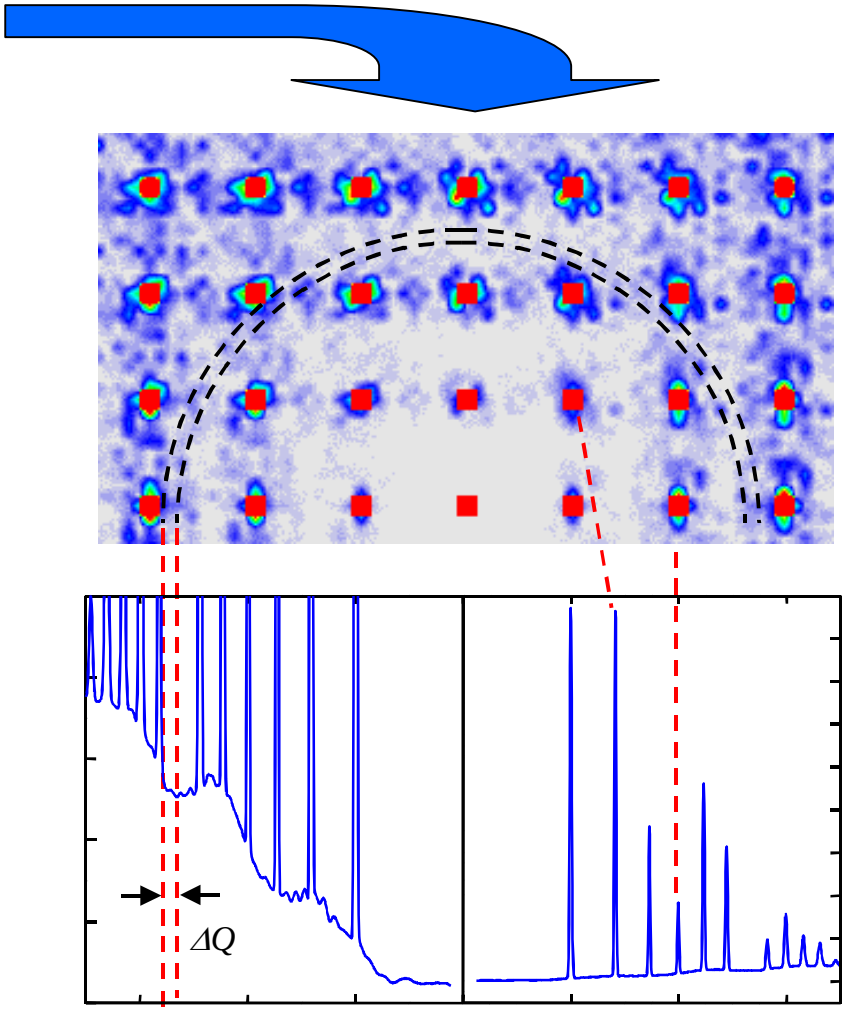
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

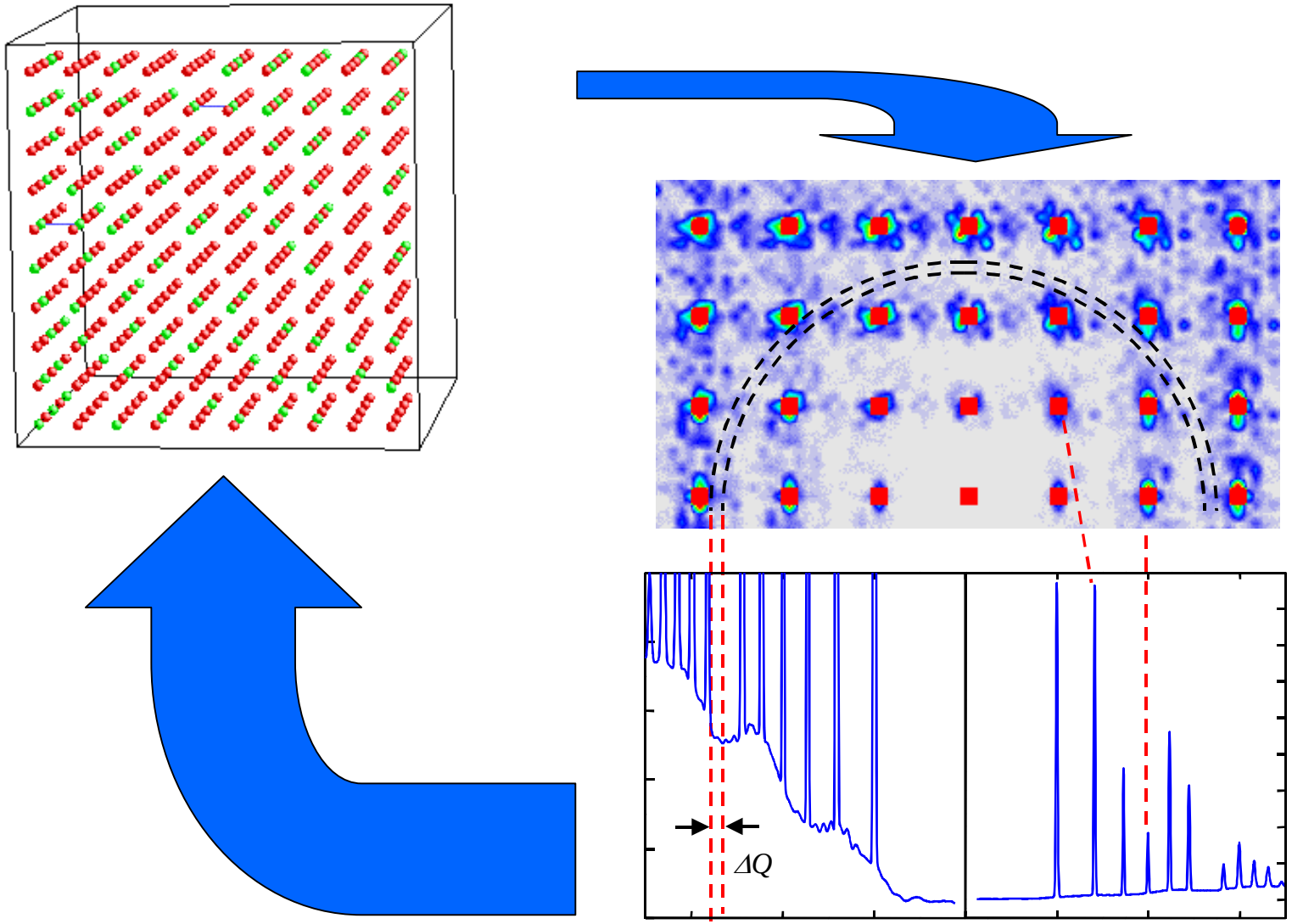

F(Q)
Q/Å-1
6
5
4
3
2
1
0
-1
0
2
4
6
8
10

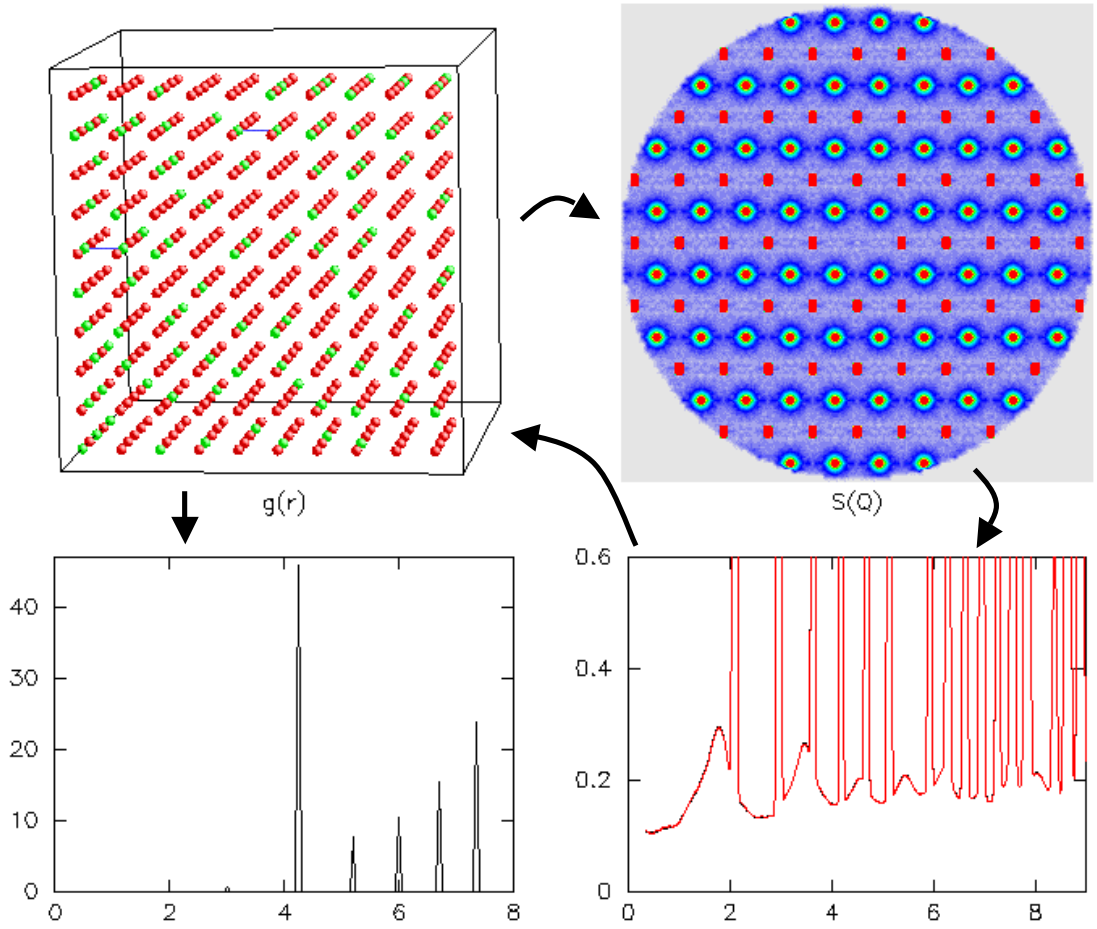


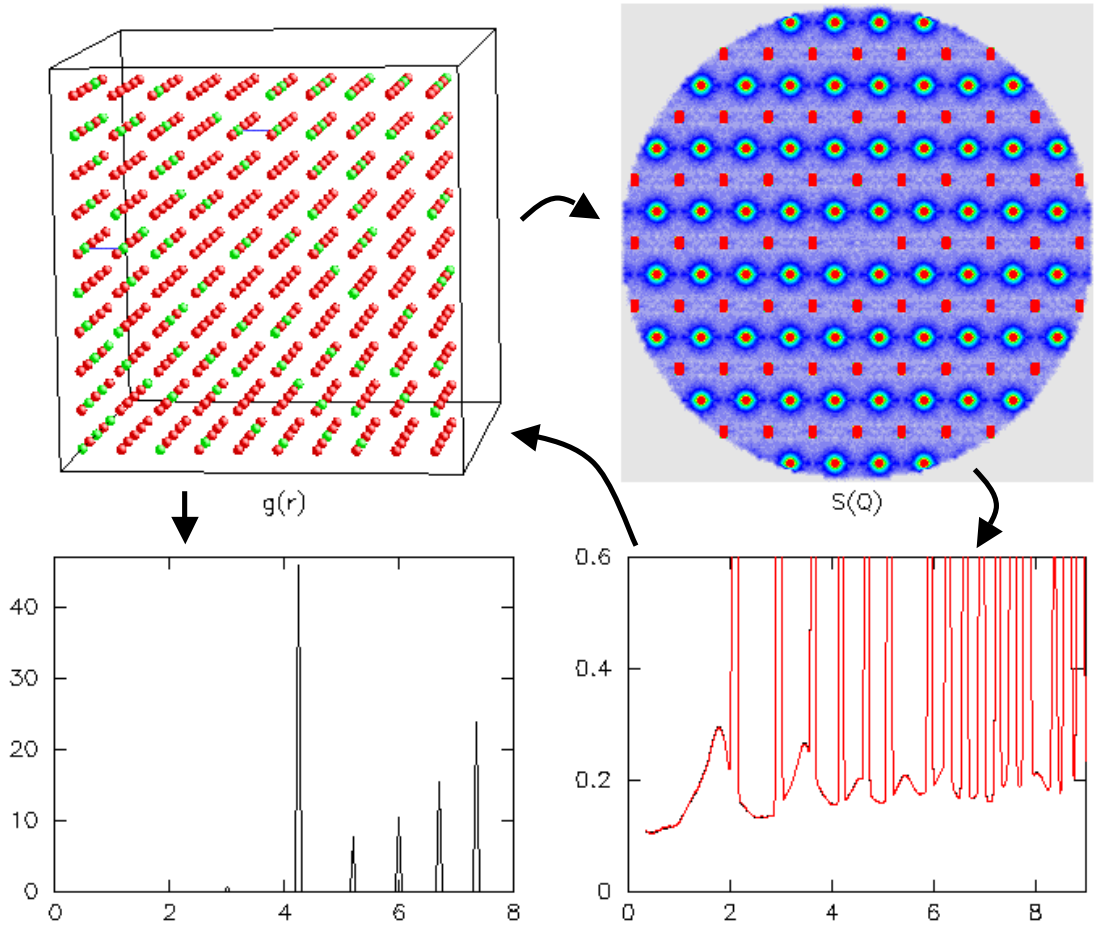

ΔQ

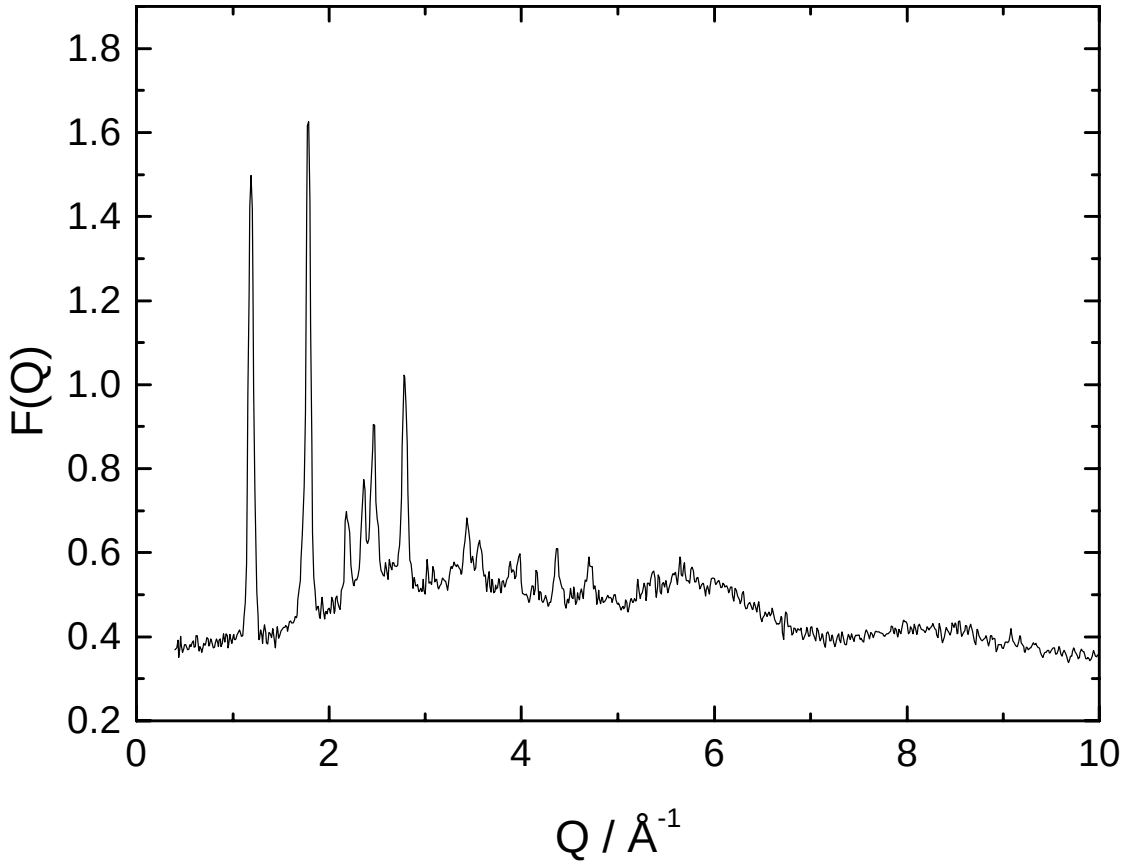



ΔQ

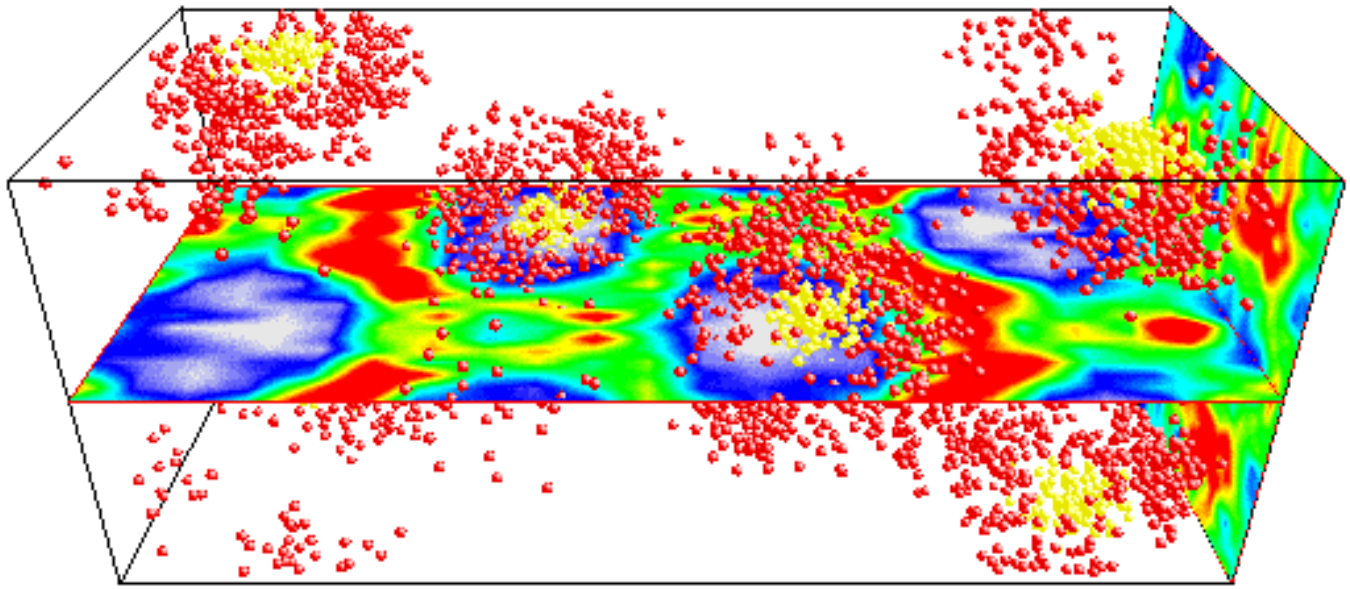

ΔQ


g(r)
S(Q)
40
30
20
10
0
0
2
4
6
8
0.6
0.4
0.2
0
0
2
4
6
8


g(r)
S(Q)
40
30
20
10
0
0
2
4
6
8
0.6
0.4
0.2
0
0
2
4
6
8

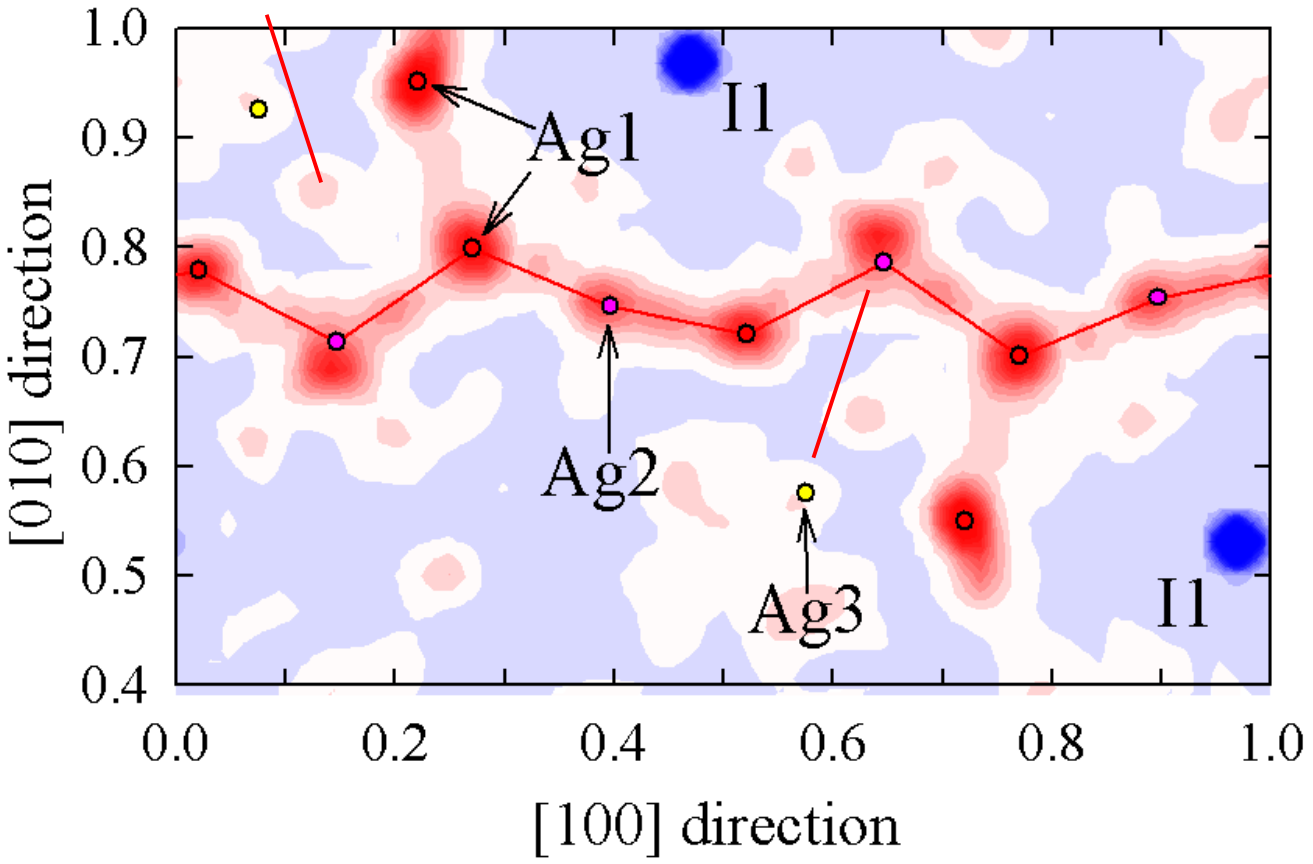


$CsDSO_4$

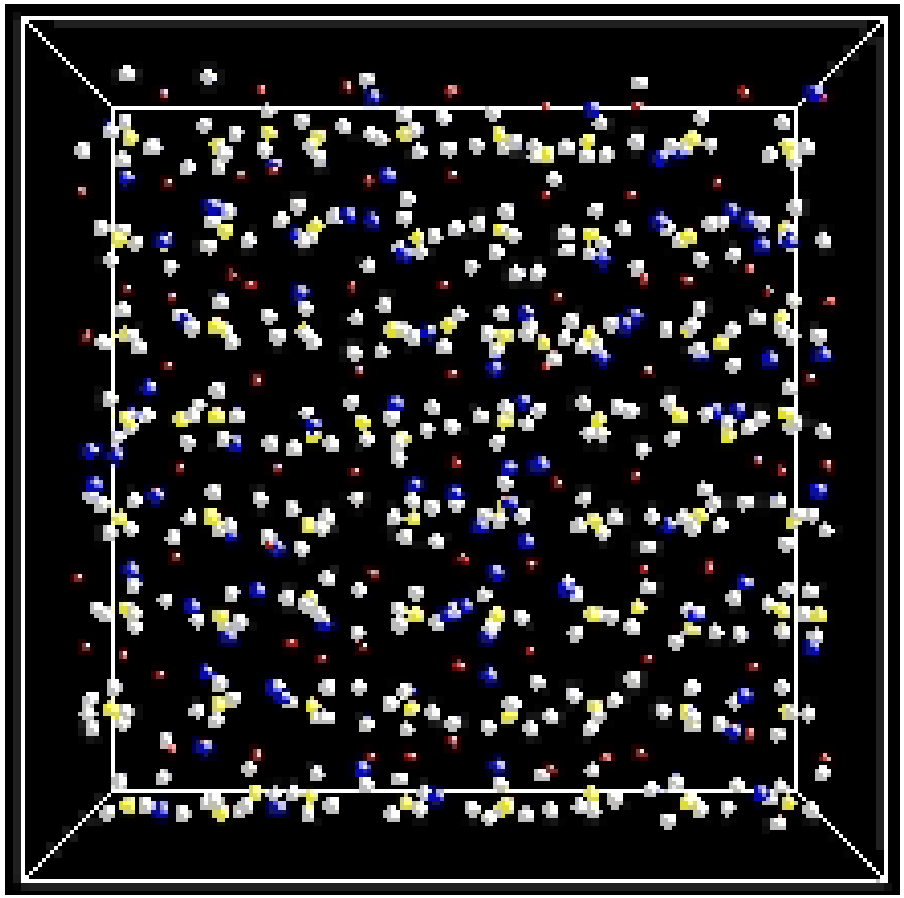


$CsDSO_4$

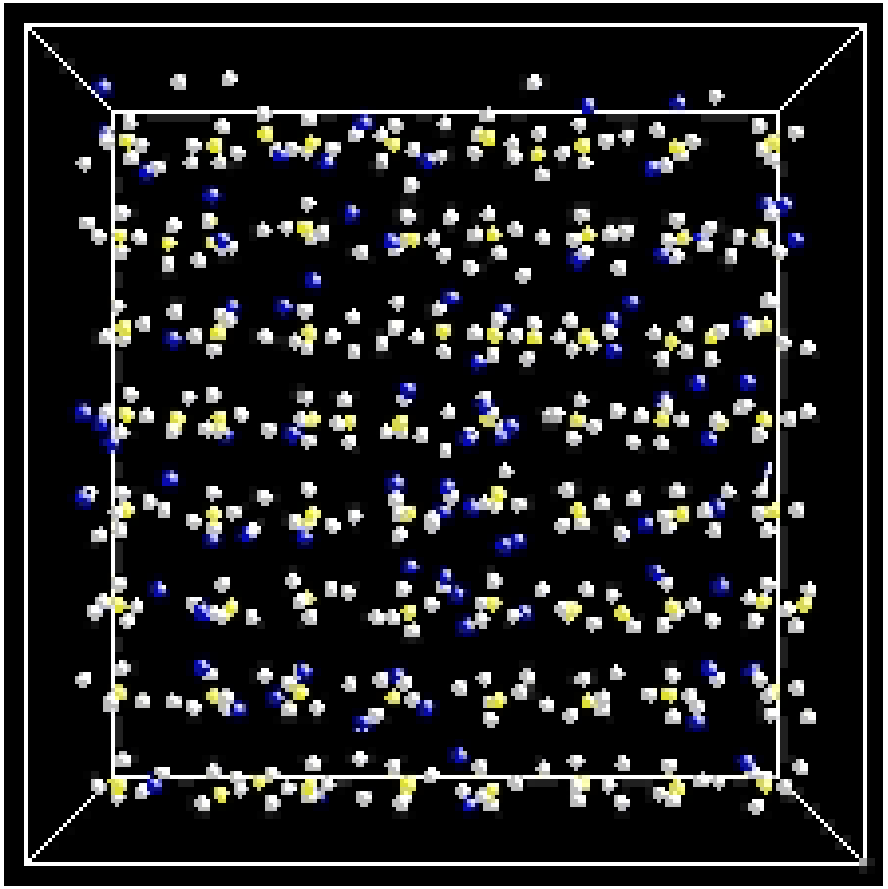
Ag_4RbI_5 : Maximum entropy Fourier map



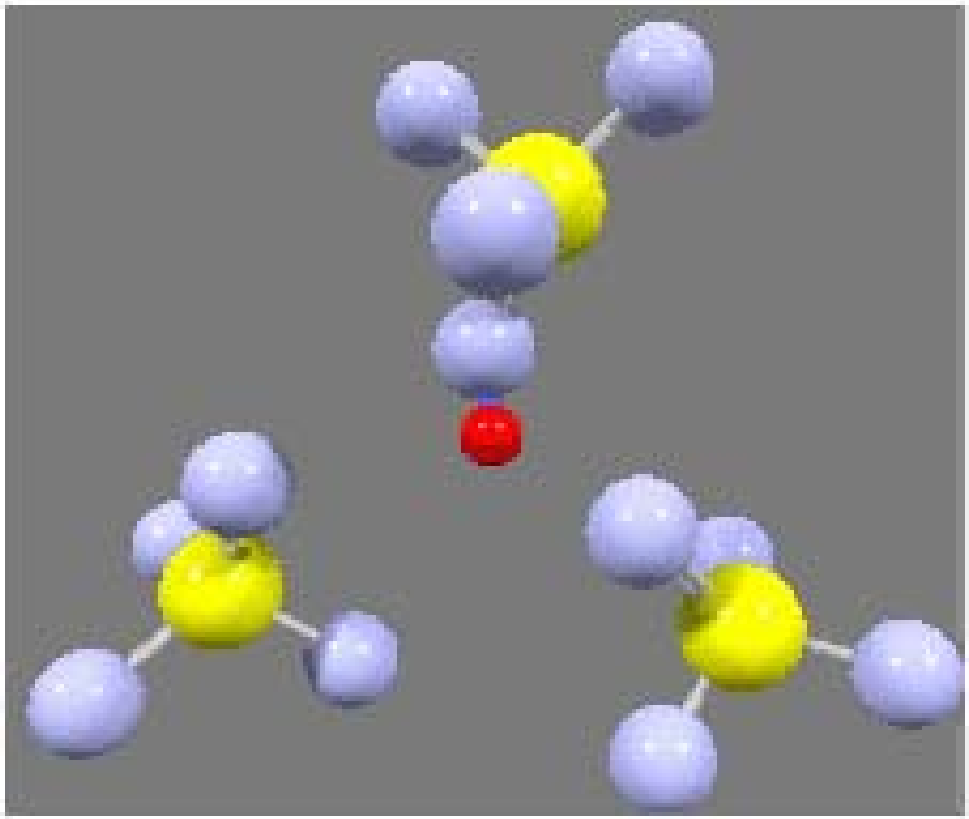
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)



$CsDSO_4$

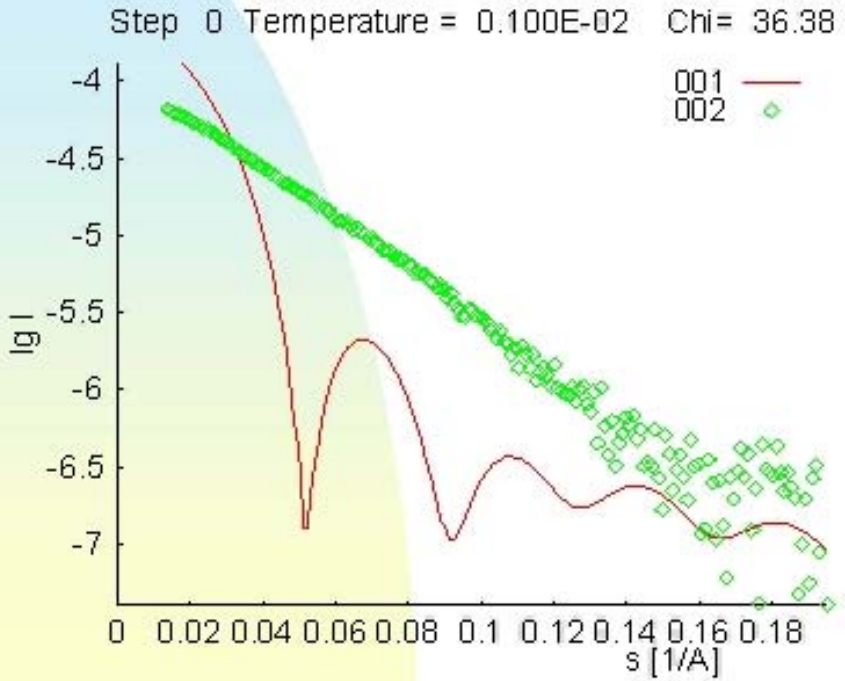


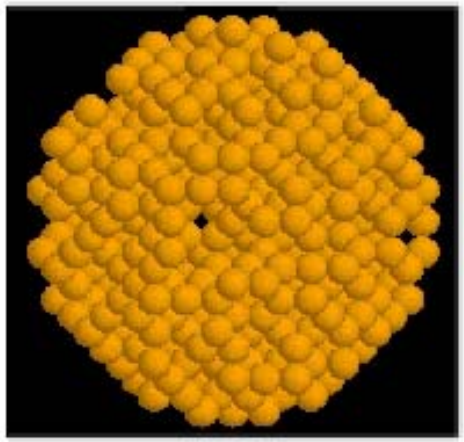
$CsDSO_4$

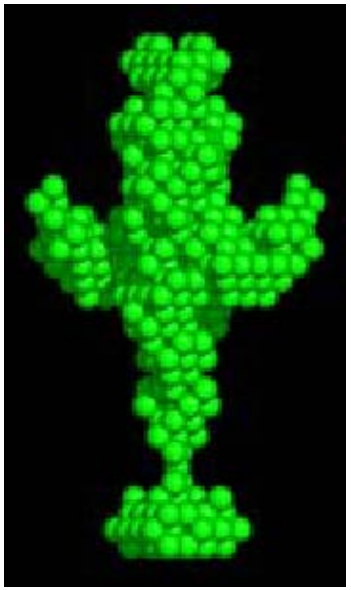


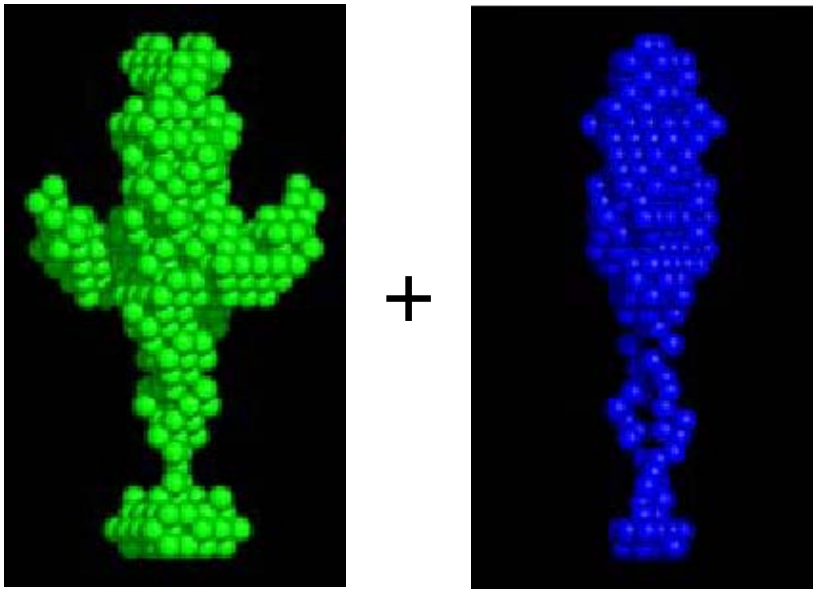
$CsDSO_4$

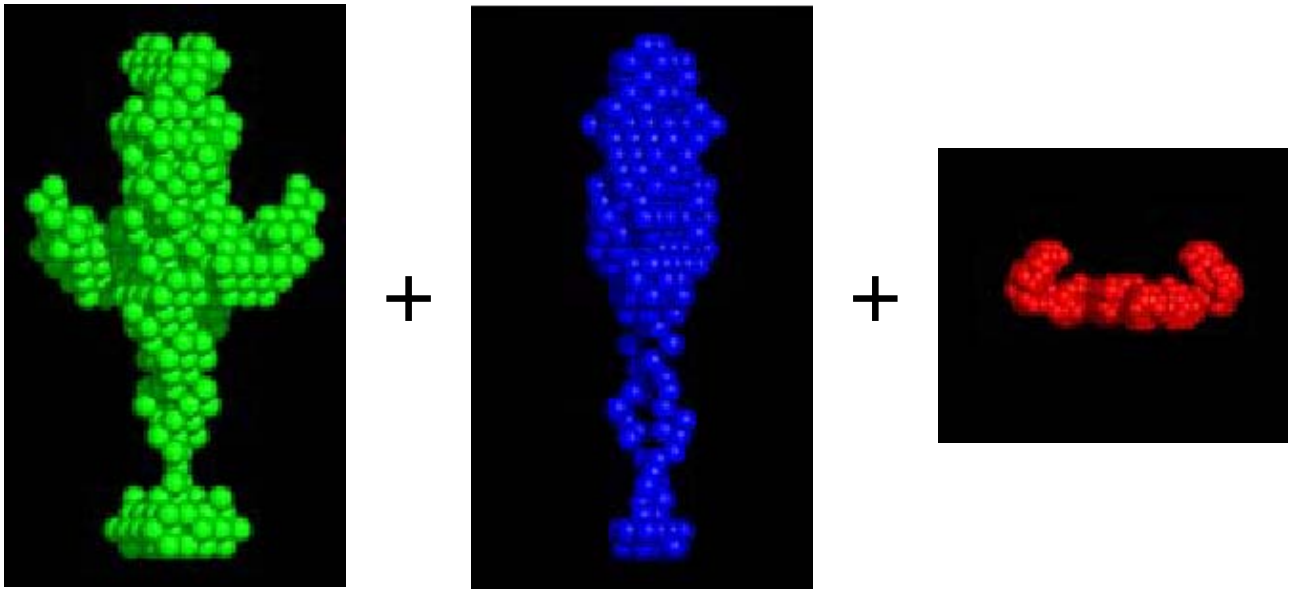
S1 shape reconstruction

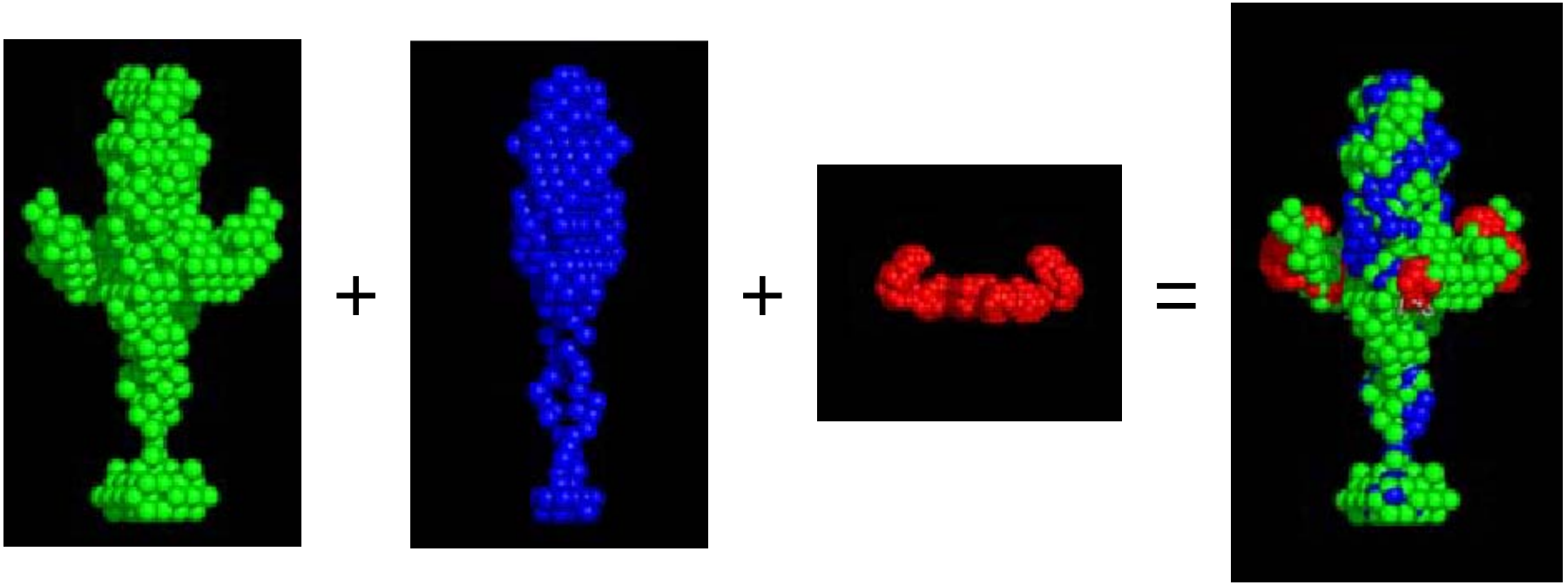












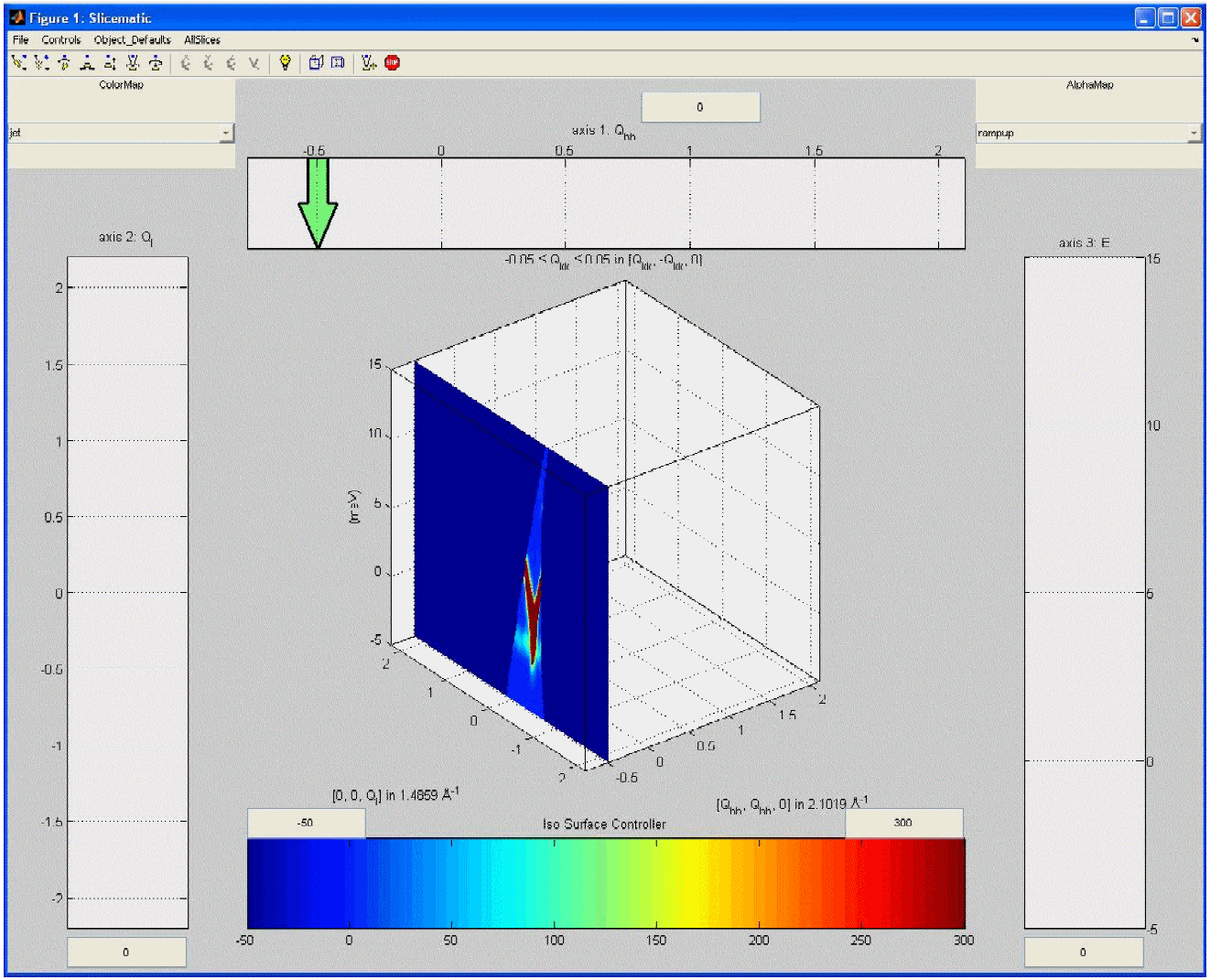


Figure 1: Slicematic
File Controls Object_Defaults AllSlices
ColorMap
jet
AlphaMap
rampup
axis 1: Q_{hh}
axis 2: Q_l
axis 3: E
$-0.05 < Q_{kk} < 0.05$ in $[Q_{kk}, -Q_{kk}, 0]$
[0, 0, Q_l] in 1.4659 $Å^{-1}$
[Q_{hh}, Q_{hh}, 0] in 2.1019 $Å^{-1}$
Iso Surface Controller
-50
300

Neutron Scattering Data Analysis

Robert McGreevy

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

From here …….. to there