

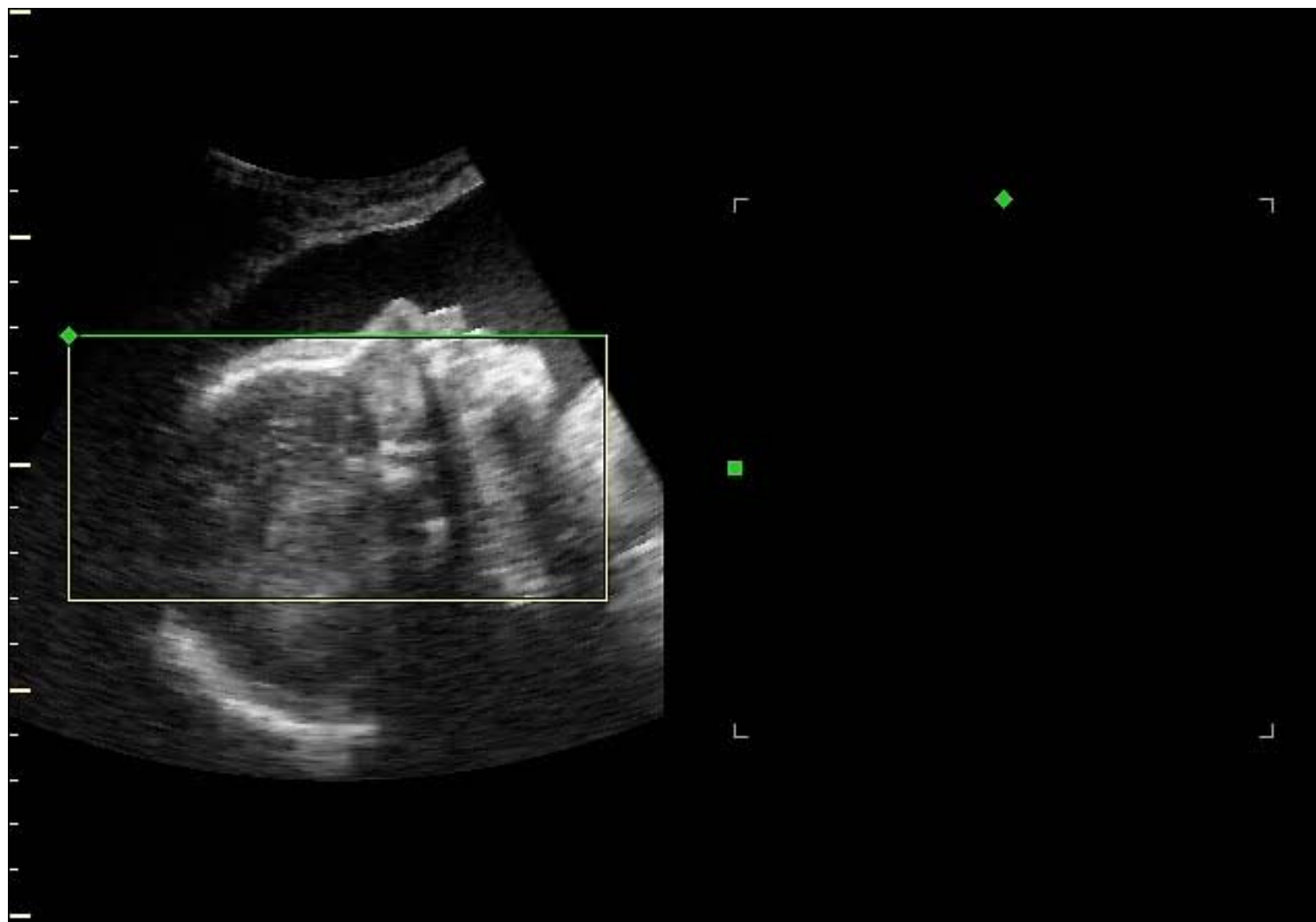


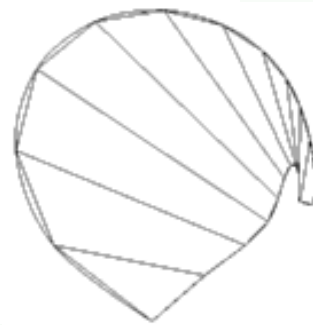
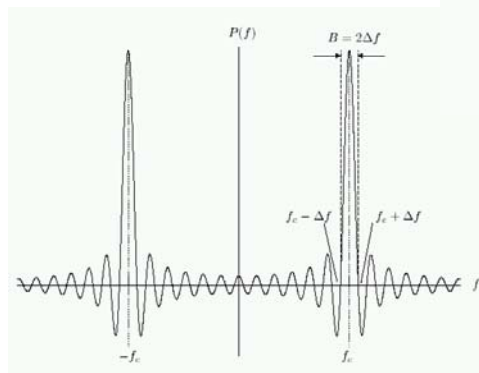
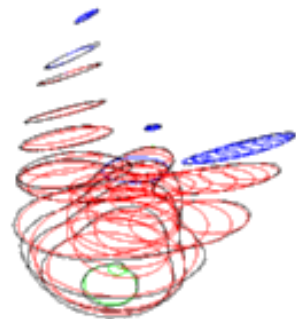
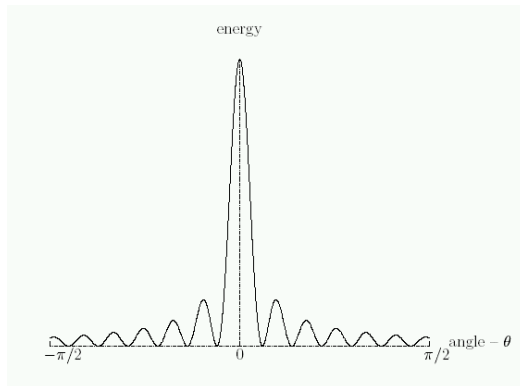
Neutron Scattering Data Analysis

Robert McGreevy

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

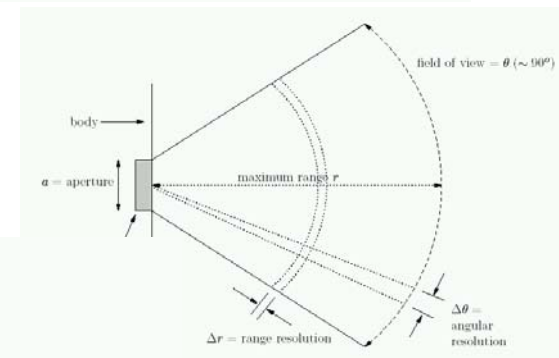






$$S(t) = \text{Re} \int_{-a/2}^{a/2} e^{-i2\pi f_c (t-r(y)/c)} dy$$

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

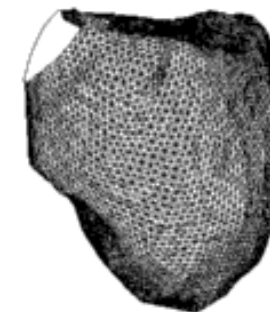


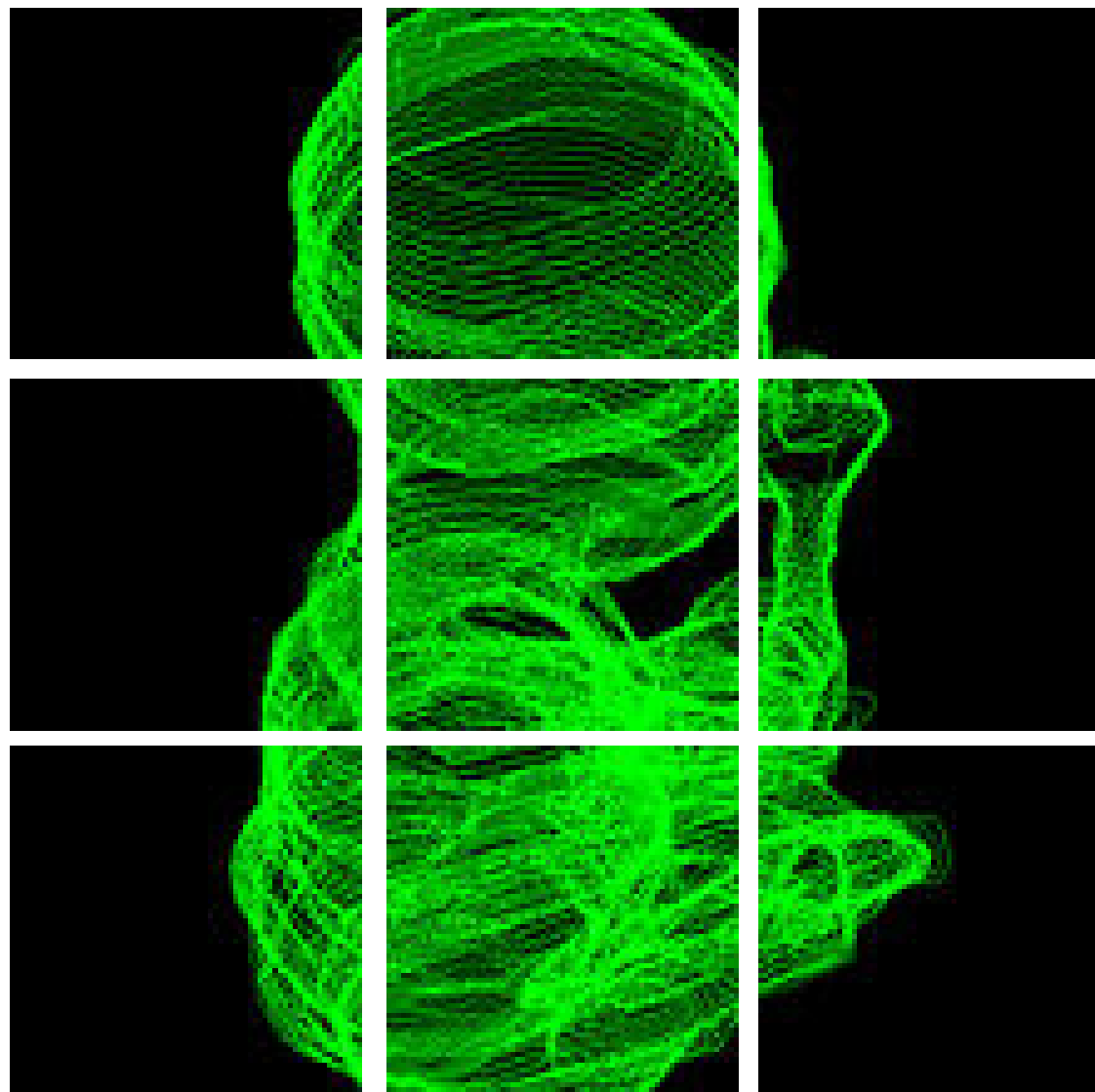
$$= \frac{a}{N} \sum_{n=0}^{N-1} e^{i2\pi f_c a [n+(1-N)/2](\sin \theta - \sin \theta_0)/(Nc)}$$

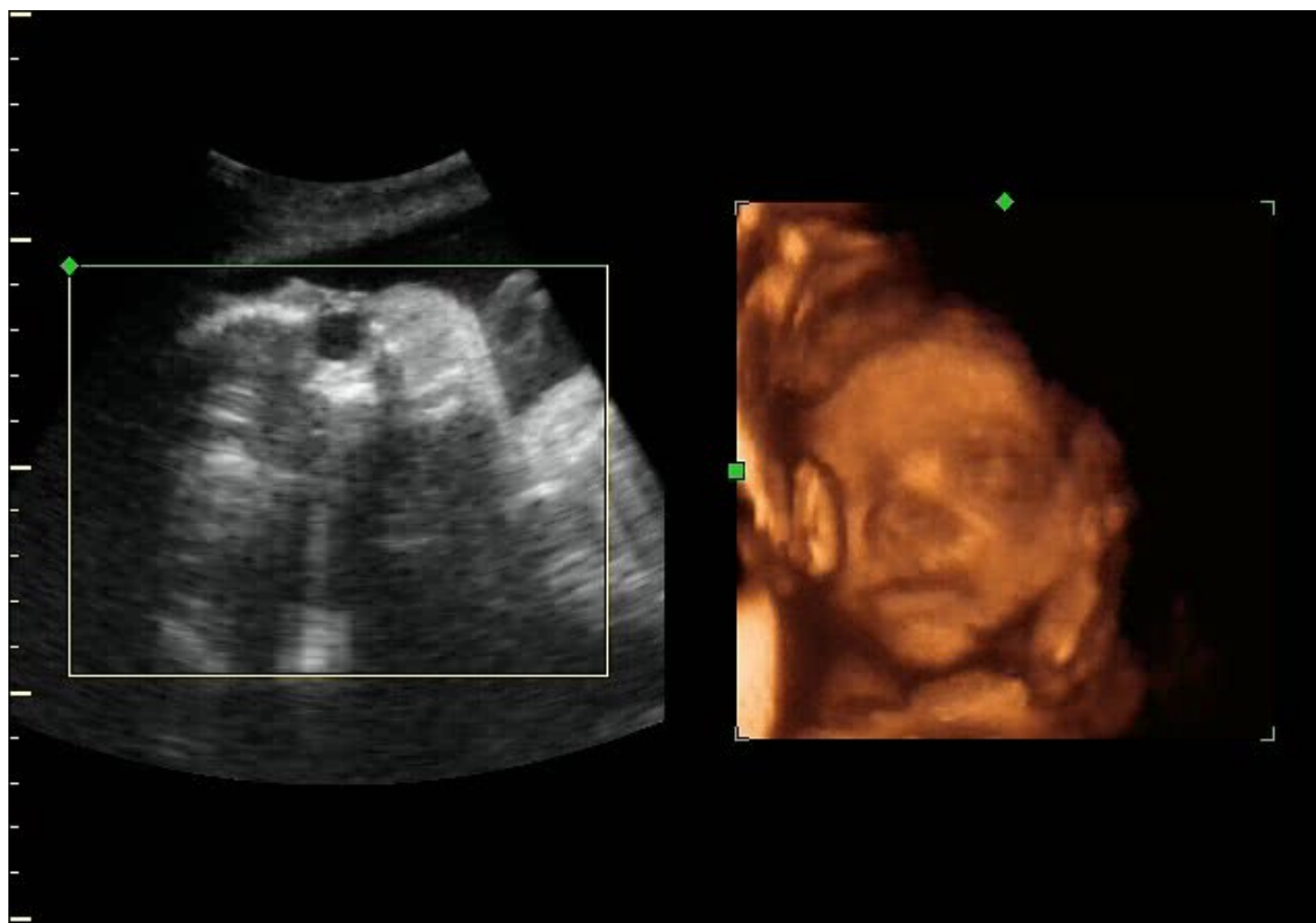
$$= \frac{a}{N} e^{i2\pi f_c a (1-N)(\sin \theta - \sin \theta_0)/(2Nc)} \sum_{n=0}^{N-1} e^{i2\pi f_c n a (\sin \theta - \sin \theta_0)/(Nc)}$$

$$= \frac{a}{N} e^{i2\pi f_c a (1-N)(\sin \theta - \sin \theta_0)/(2Nc)} \sum_{n=0}^{N-1} e^{ikn}$$

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





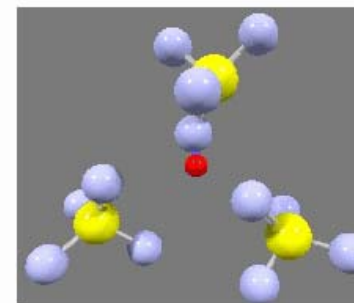
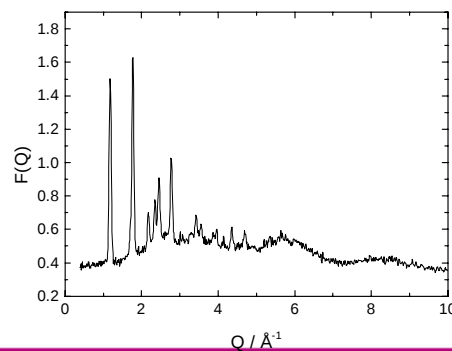


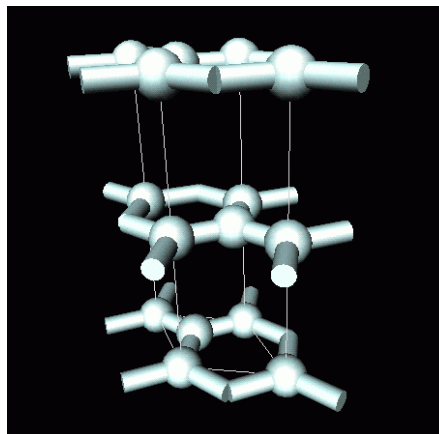
Neutron Scattering Data Analysis

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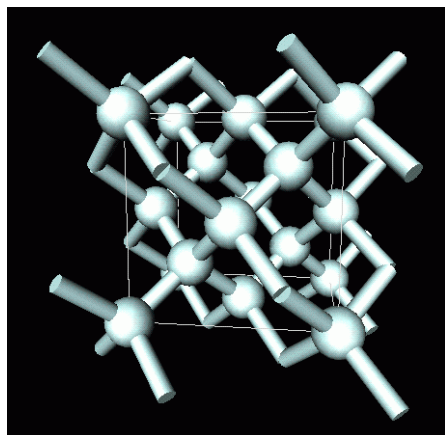
*ISIS Facility,
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From here to there

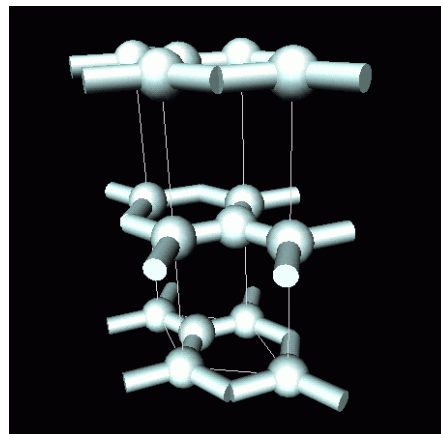




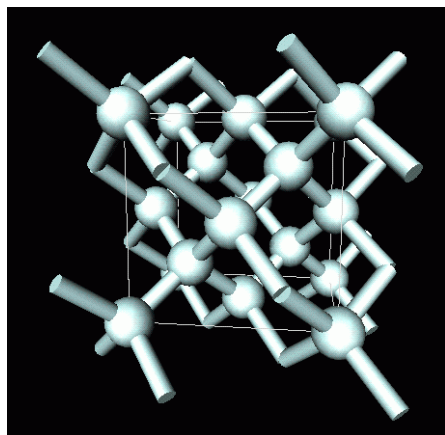
Graphite



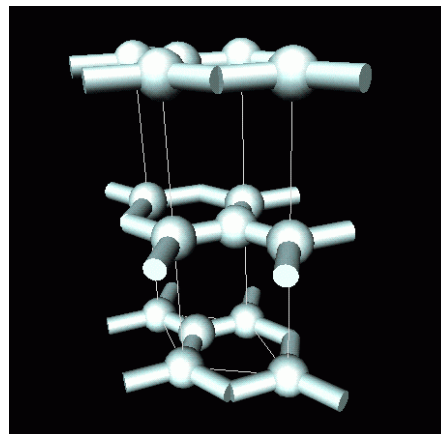
Diamond



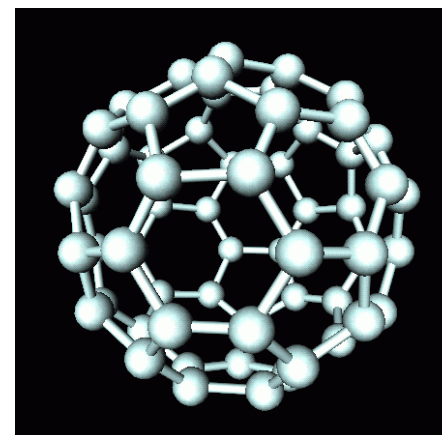
Graphite



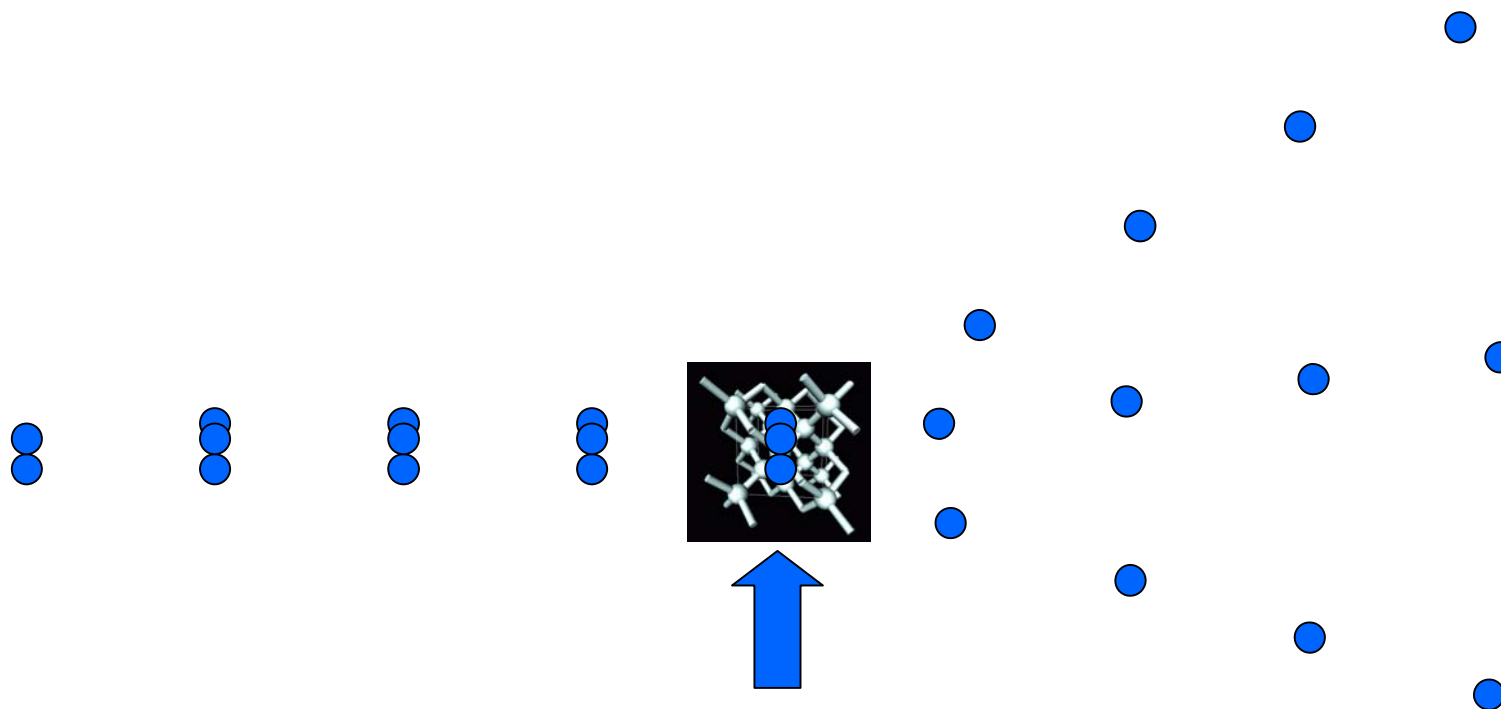
Diamond



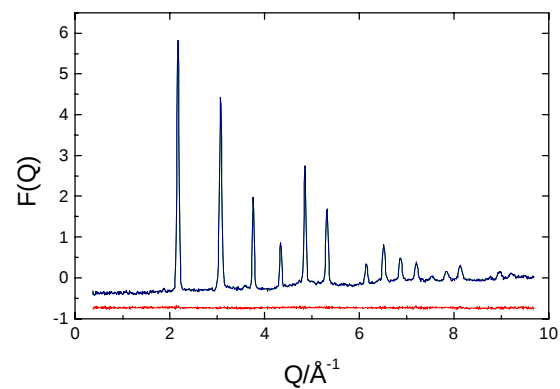
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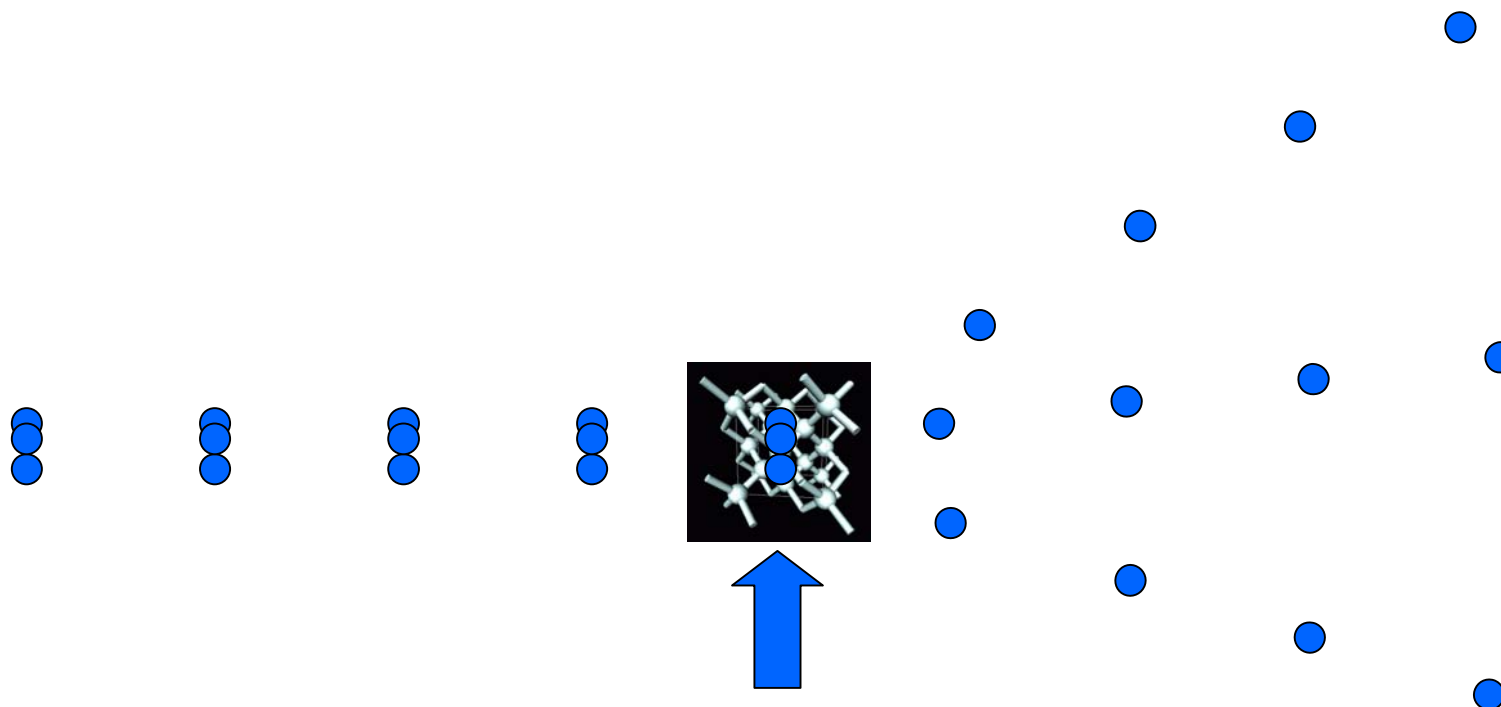


Fullerene

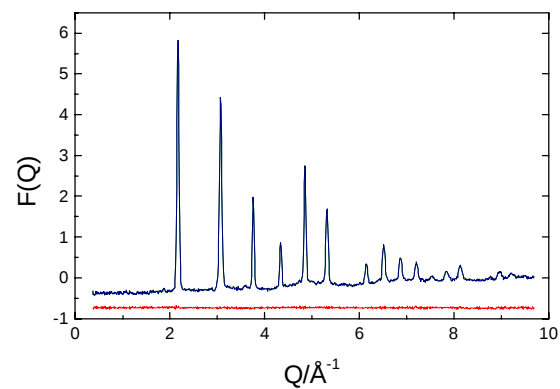


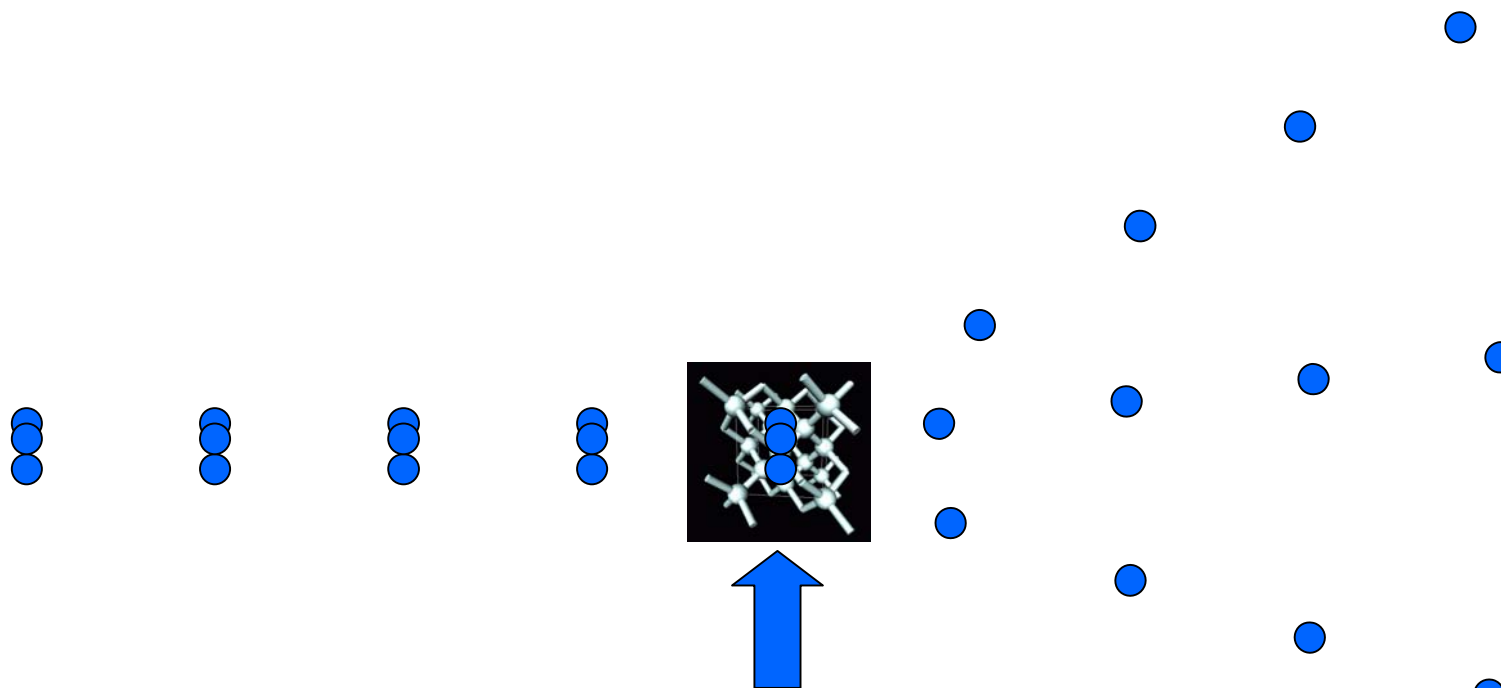
Neutron
Diffraction



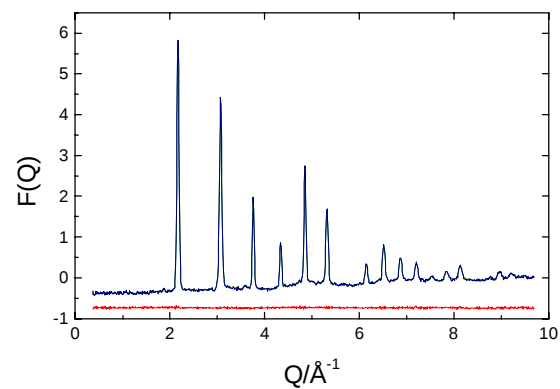


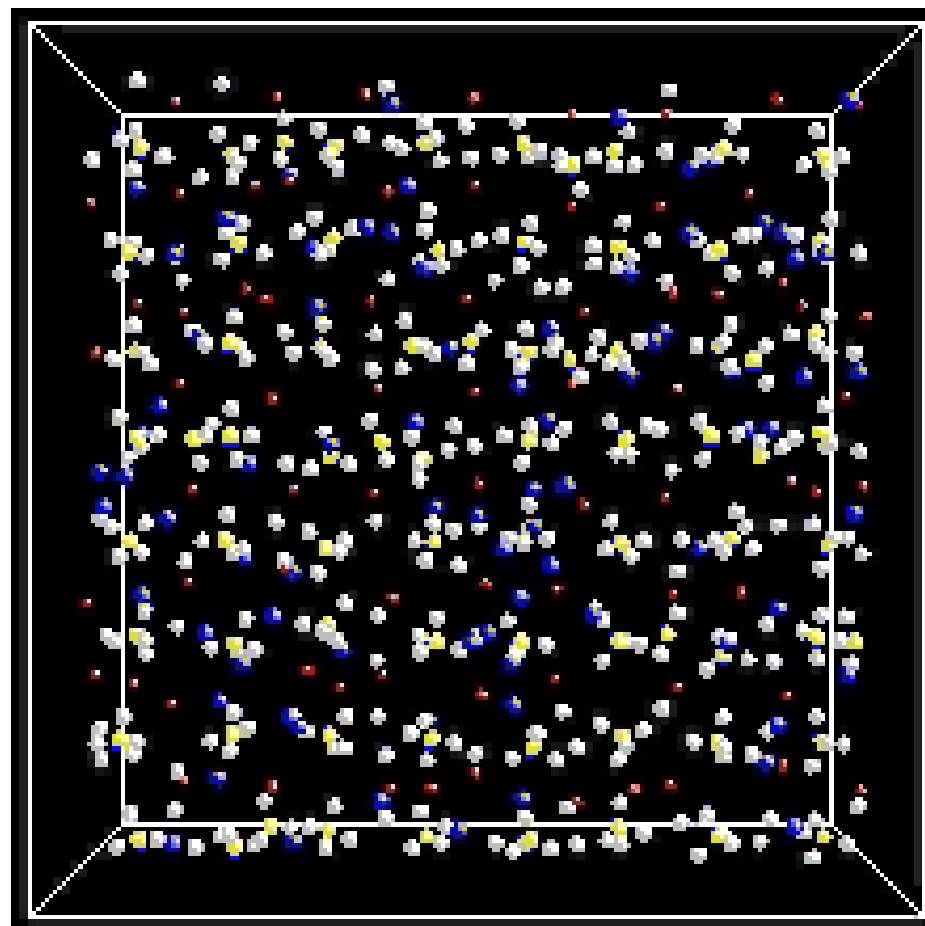
Neutron
Diffraction



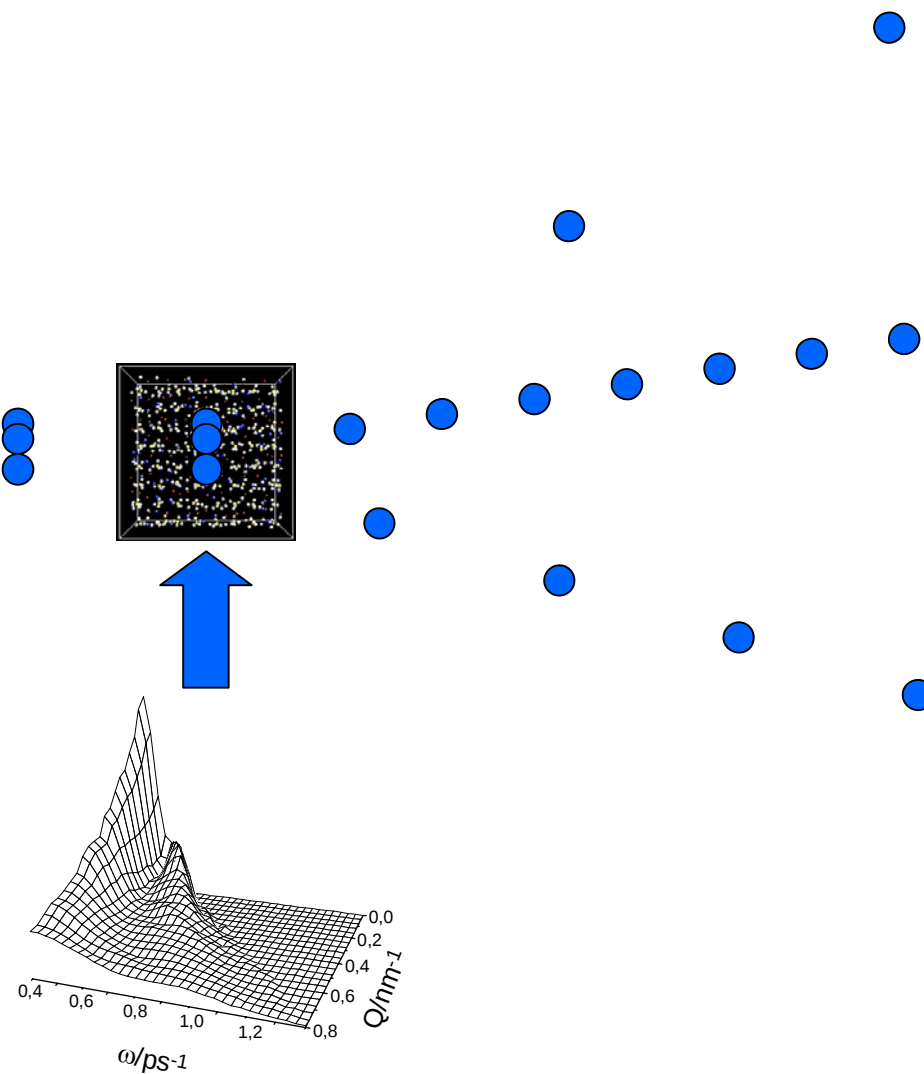


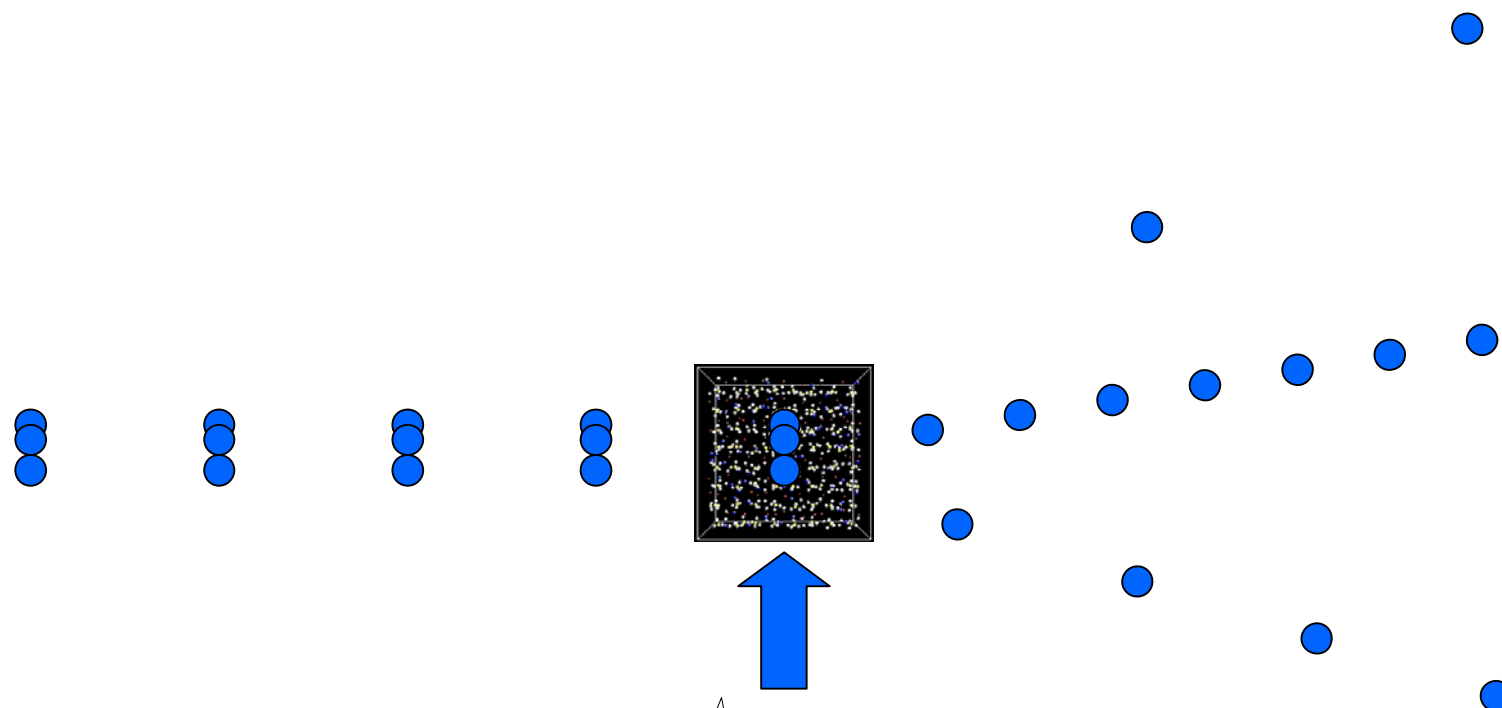
Neutron
Diffraction



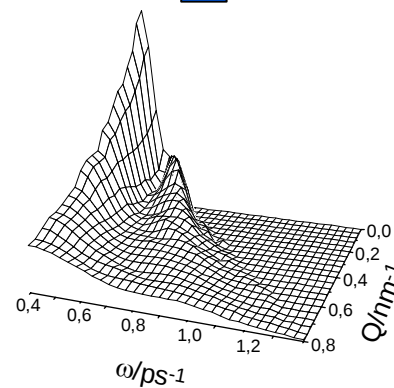


Inelastic Neutron Scattering

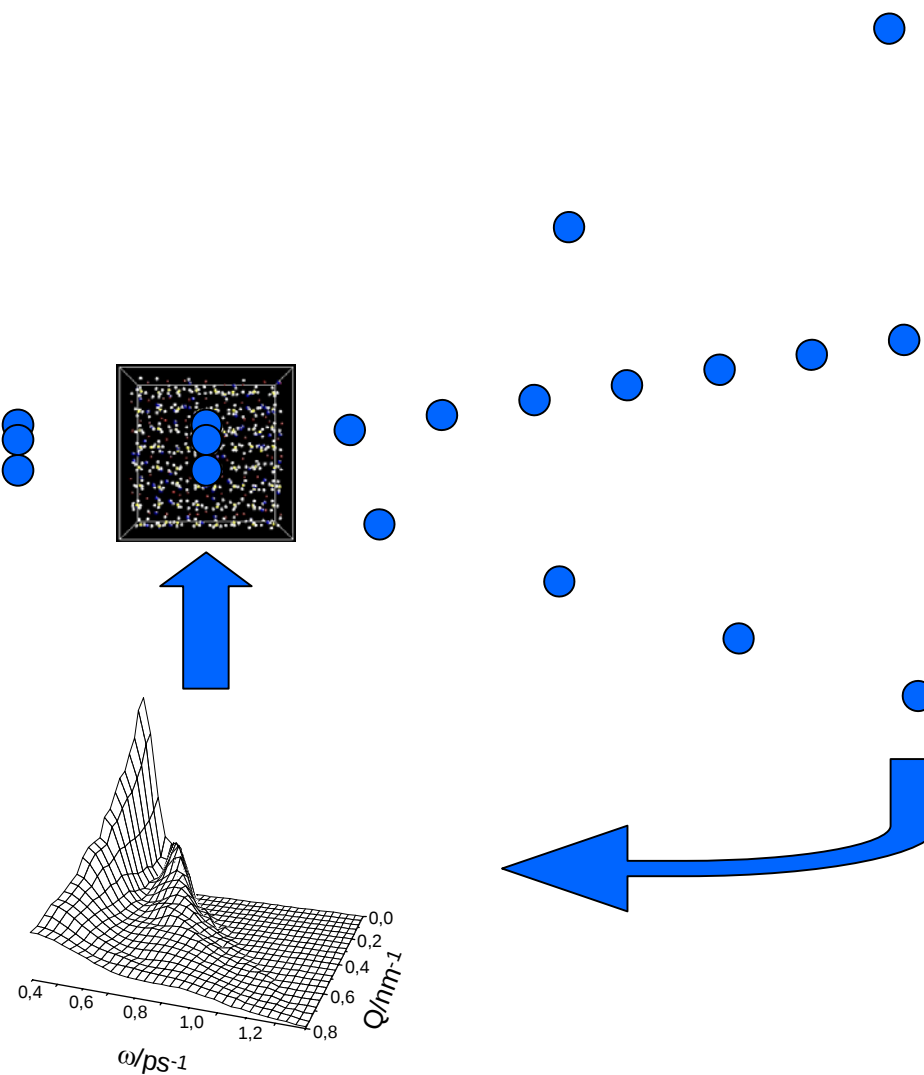




Inelastic
Neutron
Scattering



Inelastic Neutron Scattering



The Nobel Prize in Physics 1994



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



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 wave 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 in metallic hydrides, or 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.



Diagram illustrating the neutron diffraction technique, showing the incident neutron beam, the sample, and the diffracted beams.

Neutrons see more than X-rays

X-rays are scattered by electrons, so they can't see light elements. Neutrons, however, are scattered by nuclei, so they can see all elements, even light ones like hydrogen.



Neutrons show where atoms are

When the neutrons collide with atoms in the sample material, they change direction (are scattered) - elastic scattering.

Atoms in a crystalline sample

Crystals that scatter neutrons in a regular way (are crystalline) produce a regular pattern of scattered neutrons.

Detectors record the directions of the neutrons and a diffraction pattern is obtained. The pattern shows the positions of the atoms relative to one another.



Diagram illustrating the neutron diffraction technique, showing the incident neutron beam, the sample, and the diffracted beams.

Neutrons reveal inner stresses

Neutrons can be used to study the internal stresses in materials. This is because neutrons are scattered by the nuclei of atoms, and the scattering is affected by the internal stresses.

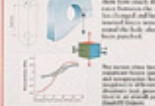


Diagram illustrating the neutron diffraction technique, showing the incident neutron beam, the sample, and the diffracted beams.

Neutrons show what atoms remember

Neutrons can be used to study the magnetic properties of materials. This is because neutrons are scattered by the magnetic moments of atoms, and the scattering is affected by the magnetic properties.

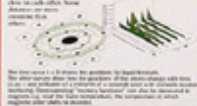


Diagram illustrating the neutron diffraction technique, showing the incident neutron beam, the sample, and the diffracted beams.

Neutrons behave as particles and as waves

Neutrons reveal structure and dynamics

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

Research reactor

Neutron beam

Sample

Diffracted neutrons

Detectors

Changes in the strength of the magnetic moments are first detected in an analysis of the pattern.

When the neutrons penetrate the sample they start to scatter (diffract) in the atoms. If the neutrons scatter at different angles, it means they are interacting with different parts of the sample.

Crystal that starts to form a new phase (a new structure) will scatter neutrons in a different way.

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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.

Reuben N. Bruckshaus, McMaster University, Hamilton, Ontario, Canada, winner one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.



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

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

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KUNGLIGA VETENSKAPSAKADEMIEN THE ROYAL SWEDISH ACADEMY OF SCIENCES

Further reading

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

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

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

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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.

Neutrons show where atoms are

When the neutrons collide with atoms in the sample material, they change direction and are scattered – elastic scattering.

Crystals that scatter neutrons in a regular way are called neutron crystals.

Detectors record the directions of the neutrons and a diffraction pattern is obtained. The pattern shows the positions of the atoms relative to one another.

Neutrons show what atoms do

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

Research reactor

3-axis spectrometer with sensitive crystals and electronic circuitry

Atoms in a crystalline lattice

When the neutrons penetrate the sample they start or cancel oscillations in the atoms. If the neutrons create phonons or magnons they themselves lose the energy these atoms absorb – inelastic scattering.

Changes in the strength of the oscillations are first analysed in an analyser crystal, and the neutrons then counted in a detector.

Neutrons see more than X-rays

X-rays are scattered by electron clouds, by nuclei and by magnetic forces. Neutrons, by contrast, interact with nuclei and with magnetic forces. Neutrons can see through most materials, and they can see through the walls of the container. Neutrons can see through the walls of the container.

Neutrons reveal inner stresses

A bulk has been produced in a material used in the past. The atoms are now in a regular arrangement. The atoms are now in a regular arrangement. The atoms are now in a regular arrangement.

Neutrons show what atoms remember

At their earlier position where they were randomly in motion, they now move in a regular way. The atoms are now in a regular arrangement. The atoms are now in a regular arrangement.

How it started

Bruckshaus and Shull made their pioneering contributions at the first nuclear reactor in the USA and Canada back in the 1940s and 1950s. It was then that the neutrons became available for scientific research.

Some in conclusion

The history of neutrons has been one of some working in the many scientific research centres throughout the world. Now and then advanced neutron scattering facilities have been built and more are planned in Europe, the USA and Asia. In these regions, the neutrons are used to study the structure of new materials, superconductors, materials, membranes, on surfaces of metals for catalysis without cleaning, virus structures and the interaction between the neutrons and the atomic properties of polymers.

Further reading

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

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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.

Neutrons show where atoms are

When the neutrons collide with atoms in the sample material, they change direction - elastic scattering.

Crystals that sort and for which neutrons have a certain wavelength "spring" regular unscattered neutrons.

Research reactor

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

Neutrons show what atoms do

3-axis spectrometer with sensitive crystals and sensitive neutron.

Atoms in a crystalline lattice.

When the neutrons penetrate the sample they start or cancel oscillations in the atoms. If the neutrons create phonons or magnons they themselves lose the energy these atoms absorb.

Changes in the strength of the oscillations are first analysed in an analyser crystal.

Neutrons see more than X-rays

X-rays are scattered by electron clouds by nuclei and by light elements. Neutrons, however, are scattered by nuclei and by light elements. Neutrons can see through most materials and can penetrate deep into the sample.

Neutrons reveal inner stresses

A bulk has been produced in an industrial metal part.

When the part is put under stress, the atoms in the lattice are pushed apart. This causes the lattice to expand and the neutrons to scatter.

Neutrons show what atoms remember

When the neutrons enter the sample, they are scattered by the atoms. The neutrons then pass through the sample and are detected by a detector.

How it started

Bruckshaus and Shull made their pioneering contributions at the first nuclear reactor in the USA and Canada back in the 1940s and 1950s. It was then that the neutrons became available for scientific research.

Some in conclusion

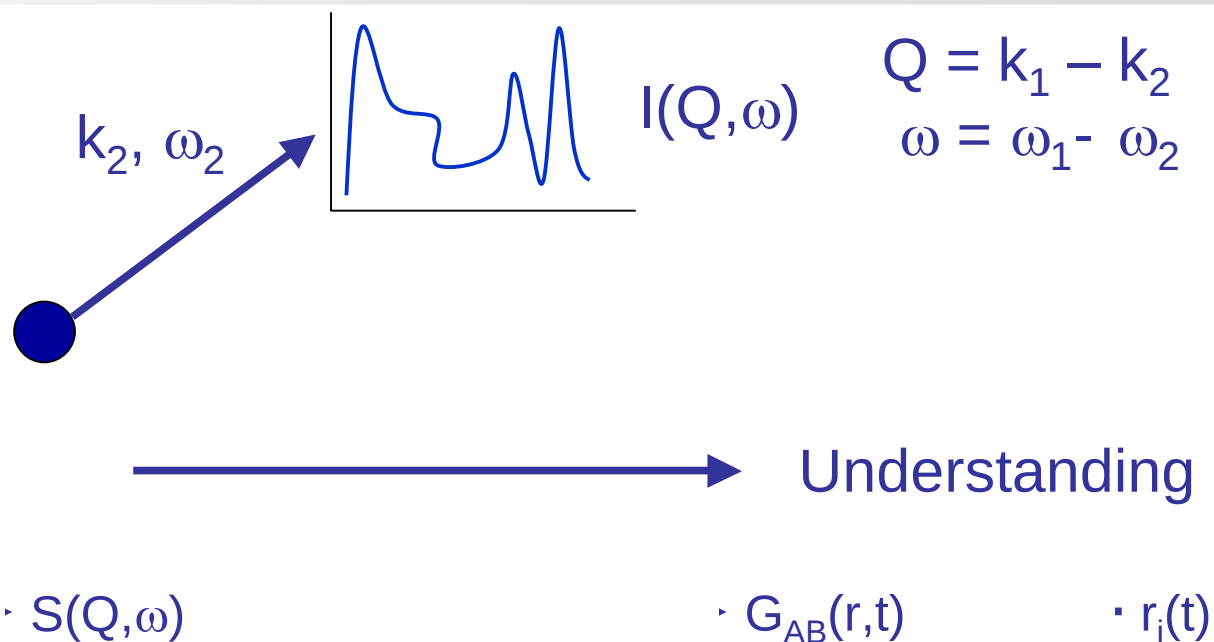
The neutron is a very useful tool in the study of condensed matter. Neutrons are scattered by nuclei and by light elements. Neutrons can see through most materials and can penetrate deep into the sample.

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

No they don't!



Constant b

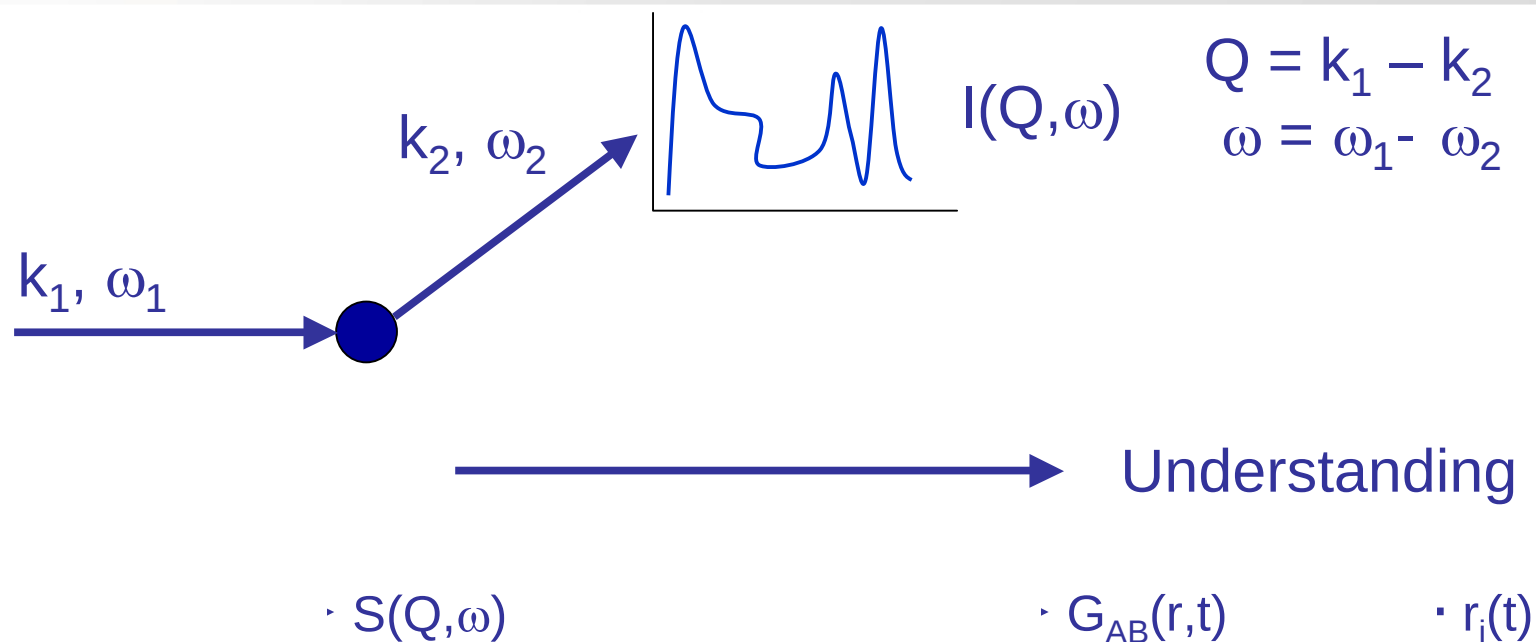
Isotopic
substitution

Wide (Q, ω)
range

Under defined
Poorly conditioned

Truncation

Phase problem



Constant b

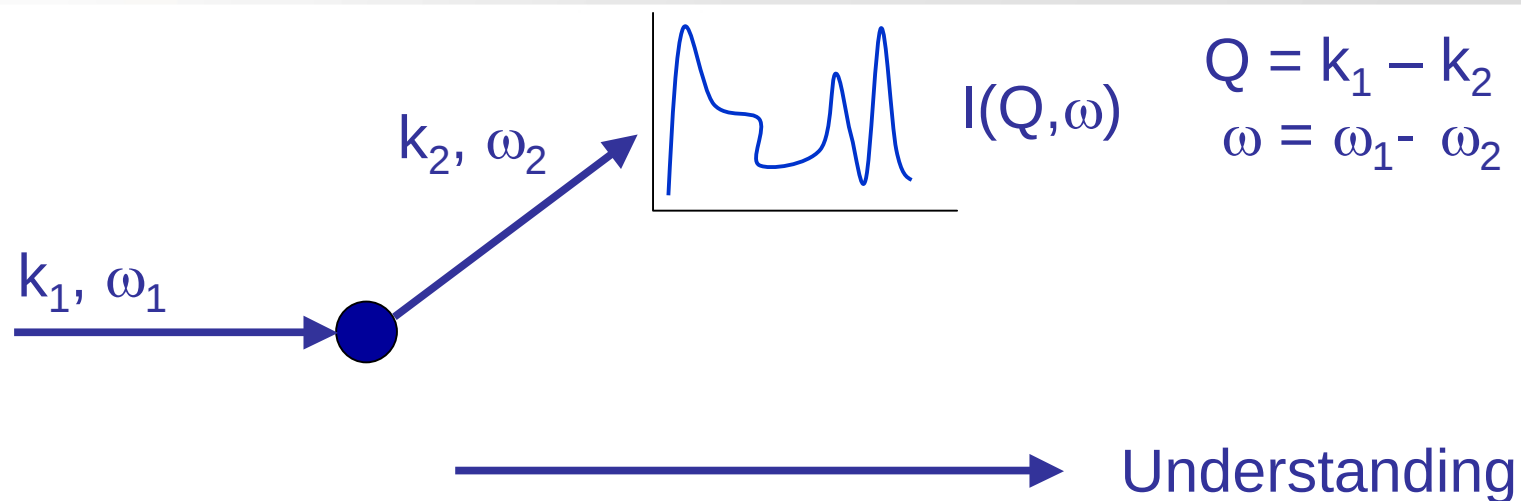
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Phase problem



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

Constant b

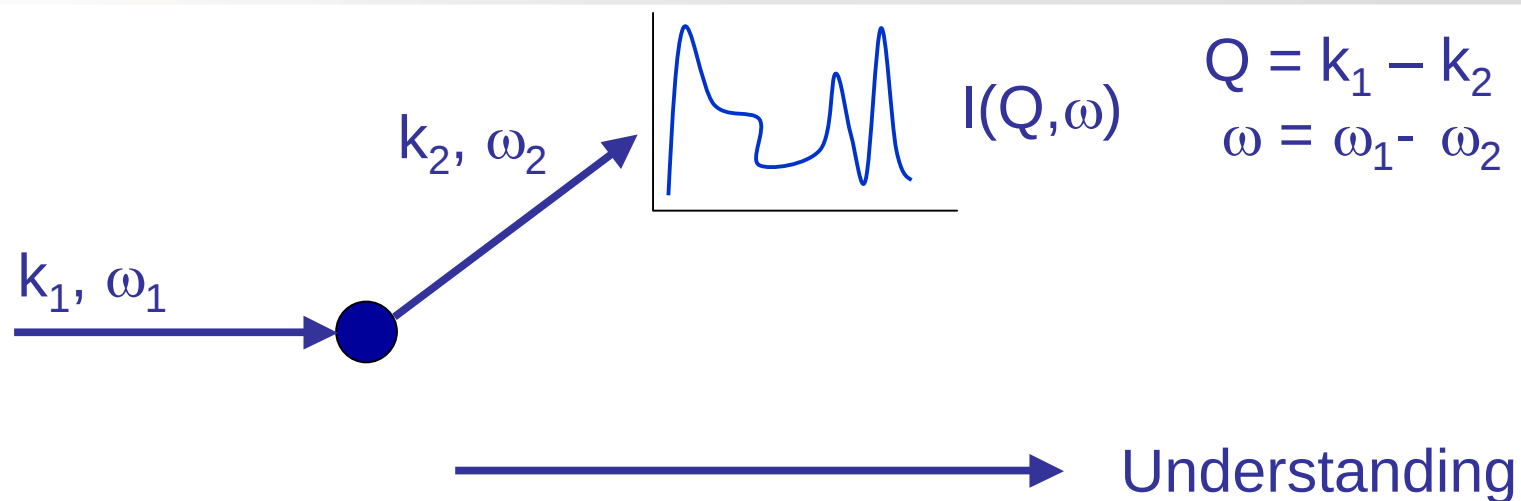
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Phase problem



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

Corrections

Constant b

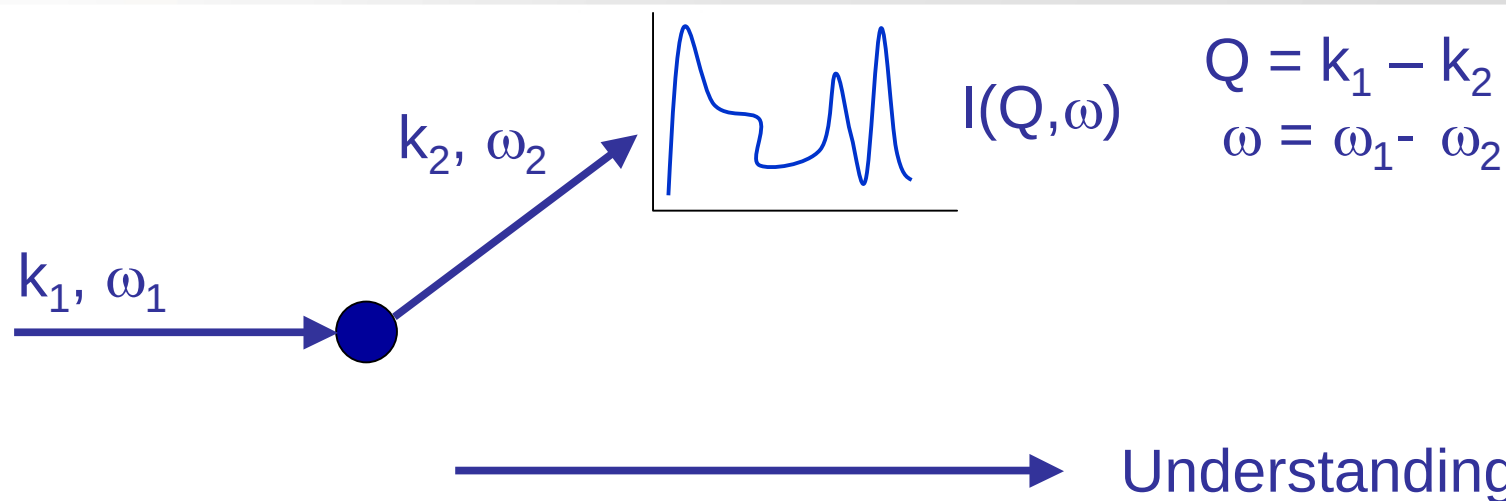
Isotopic
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Truncation

Phase problem



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

Corrections

Constant b

Separation

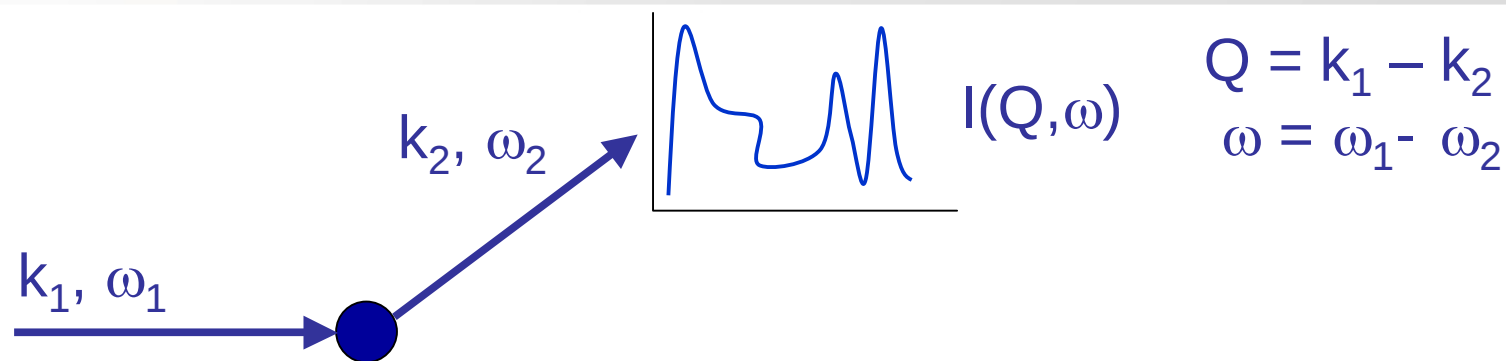
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→ Understanding

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

Corrections

Constant b

Separation

Isotopic
substitution

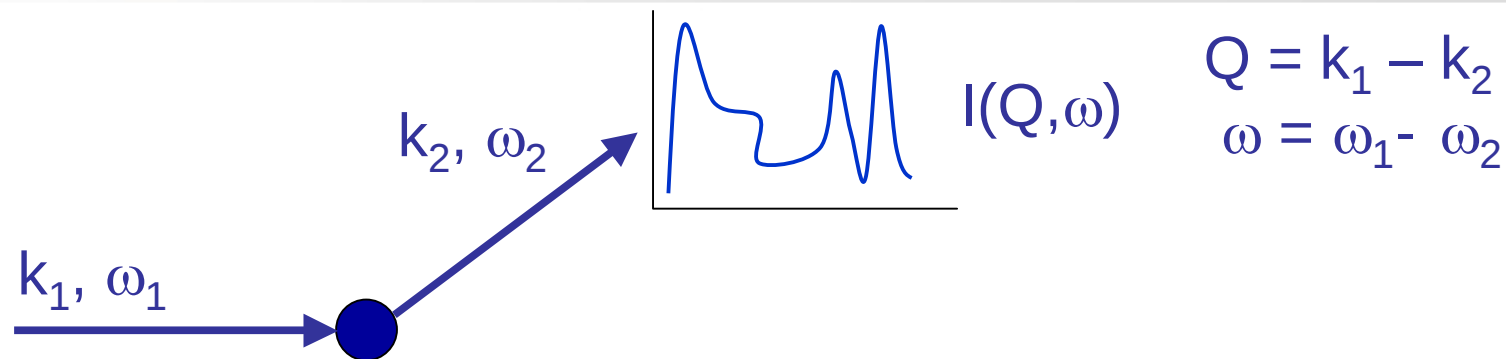
Transform

Wide (Q, ω)
range

Under defined
Poorly conditioned

Truncation

Phase problem



Understanding

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

Corrections

Constant b

Separation

Isotopic substitution

Transform

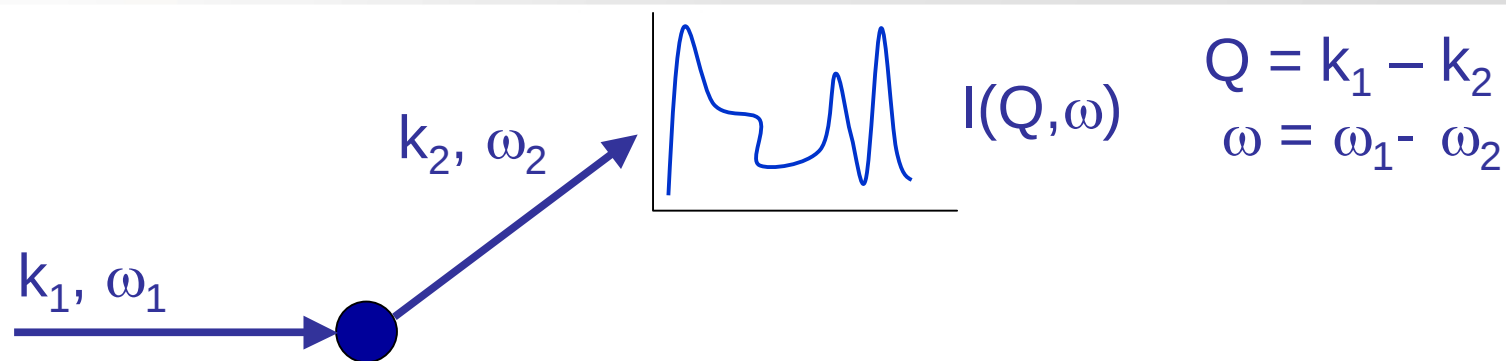
Wide (Q, ω) range

?

Under defined
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Truncation

Phase problem



Measurement $\longrightarrow$ Understanding

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

Corrections

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Separation

Isotopic
substitution

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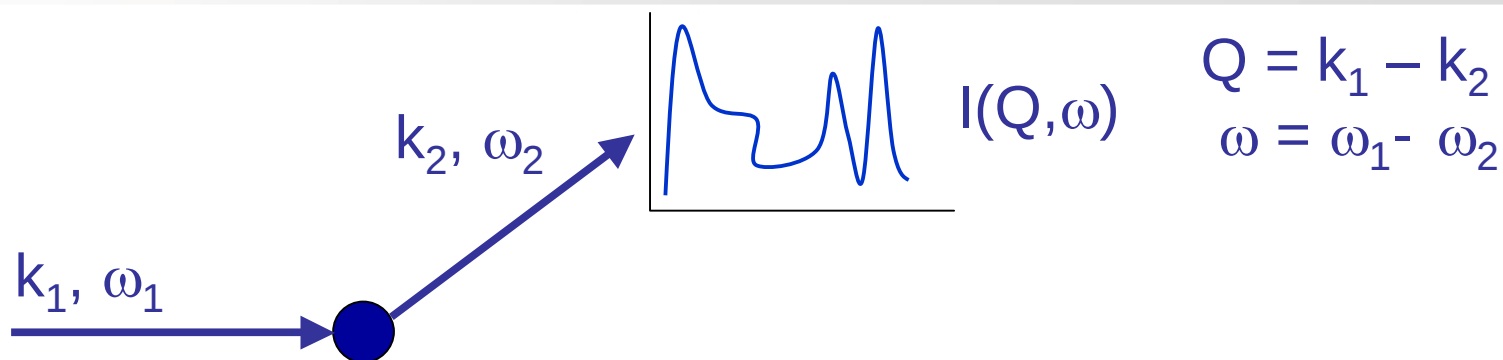
Wide (Q, ω)
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Measurement $\longrightarrow$ Understanding

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Corrections

Constant b

Weak probe

Separation

Isotopic substitution

Under defined
Poorly conditioned

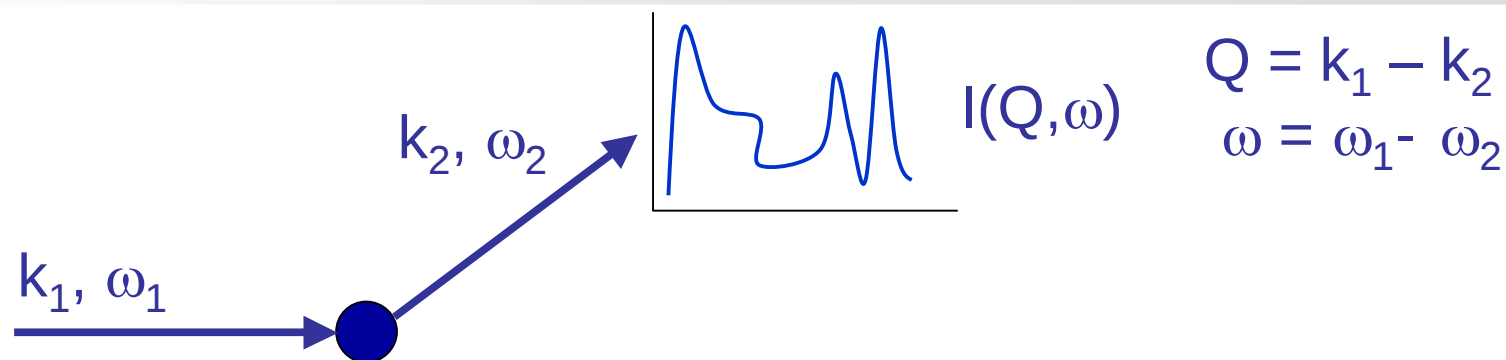
Transform

Wide (Q, ω)
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Truncation

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Corrections

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Errors

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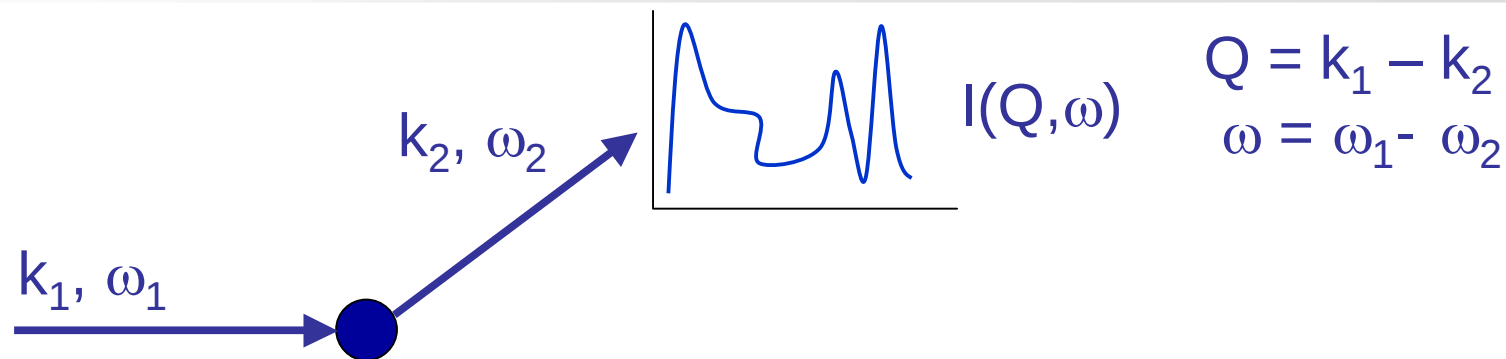
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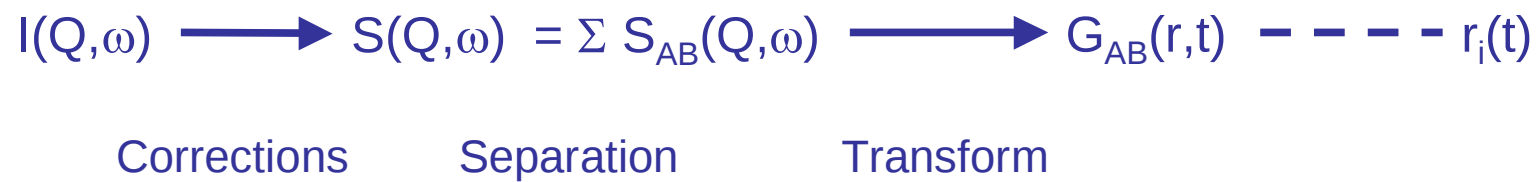
SO ...

Neutron scattering data analysis

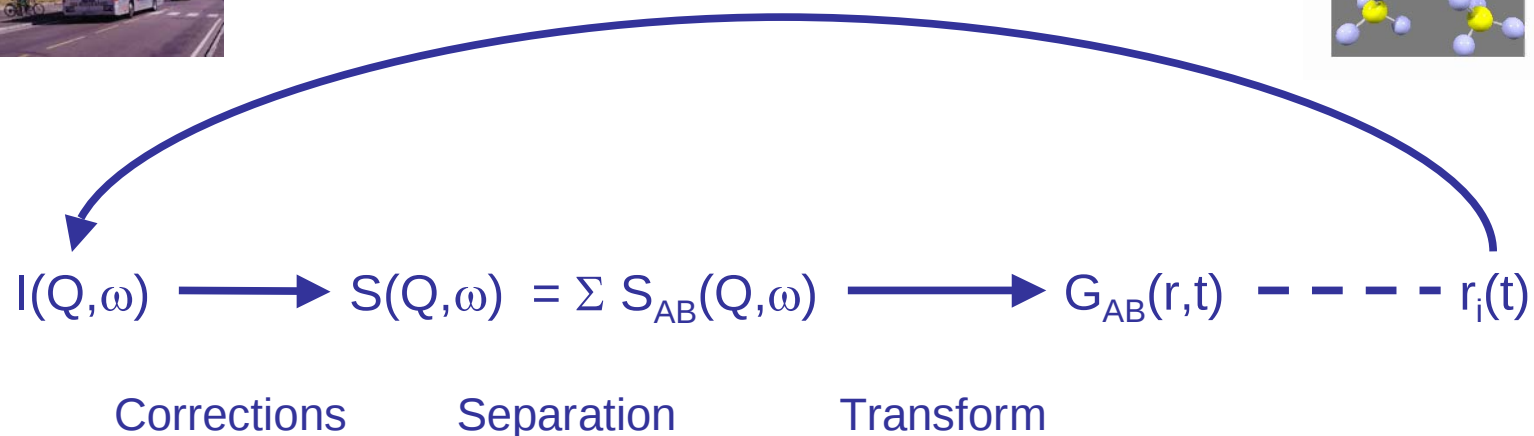
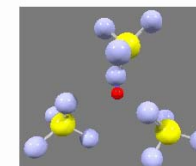
is an

INVERSE

problem



Errors
Under defined
Poorly conditioned
Truncation
Phase problem



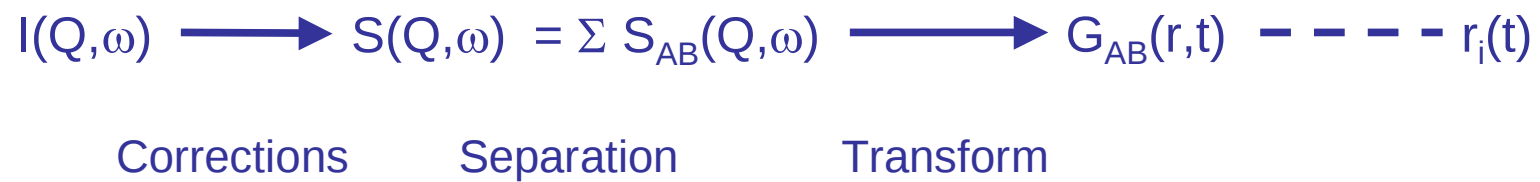
Errors Under defined
Poorly conditioned Truncation Phase problem

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

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

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

$$\begin{aligned} I(\theta) \propto F(\mathbf{Q}) &= \int_{-\infty}^{\infty} S(\mathbf{Q}, \omega) d\omega = S(\mathbf{Q}, t = 0) = \int e^{i\mathbf{Q} \cdot \mathbf{r}} G(\mathbf{r}, t = 0) d\mathbf{r} \\ &= \frac{1}{N} \sum_{j, j'} \langle e^{-i\mathbf{Q} \cdot (\mathbf{R}_j(0) - \mathbf{R}_{j'}(0))} \rangle = \frac{1}{N} \left| \sum_j e^{-i\mathbf{Q} \cdot \mathbf{R}_j(0)} \right|^2 \end{aligned}$$



Errors
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Poorly conditioned
Truncation
Phase problem

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

Corrections

Separation

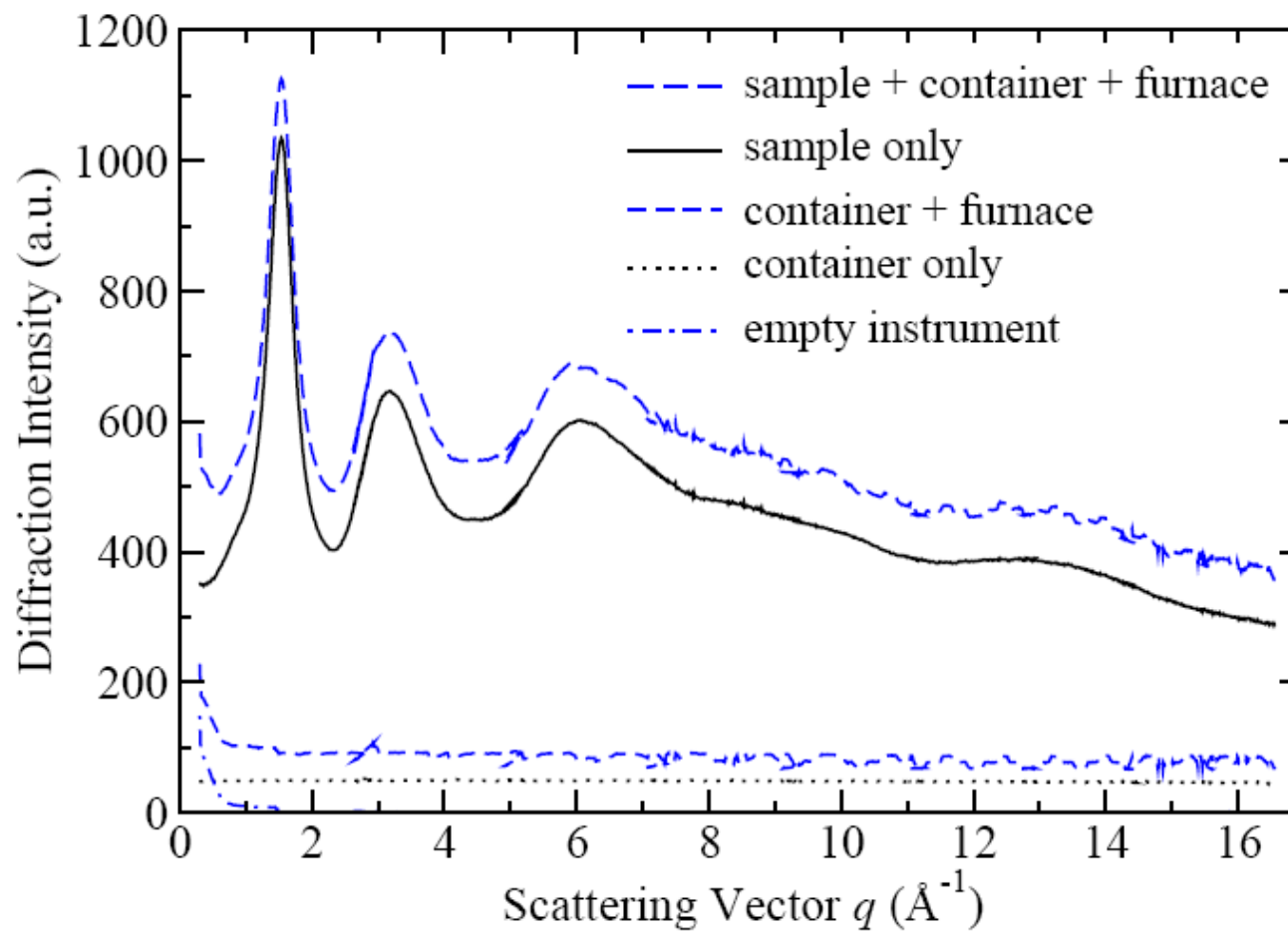
Transform

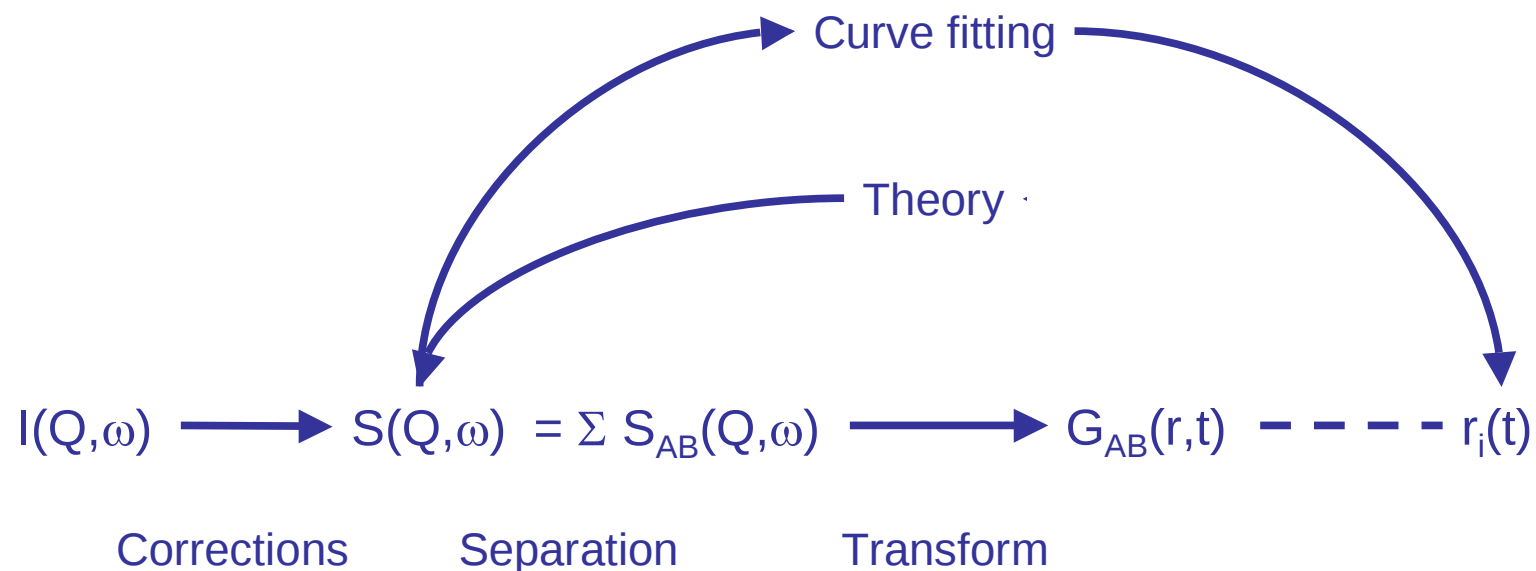
Errors

Under defined
Poorly conditioned

Truncation

Phase problem



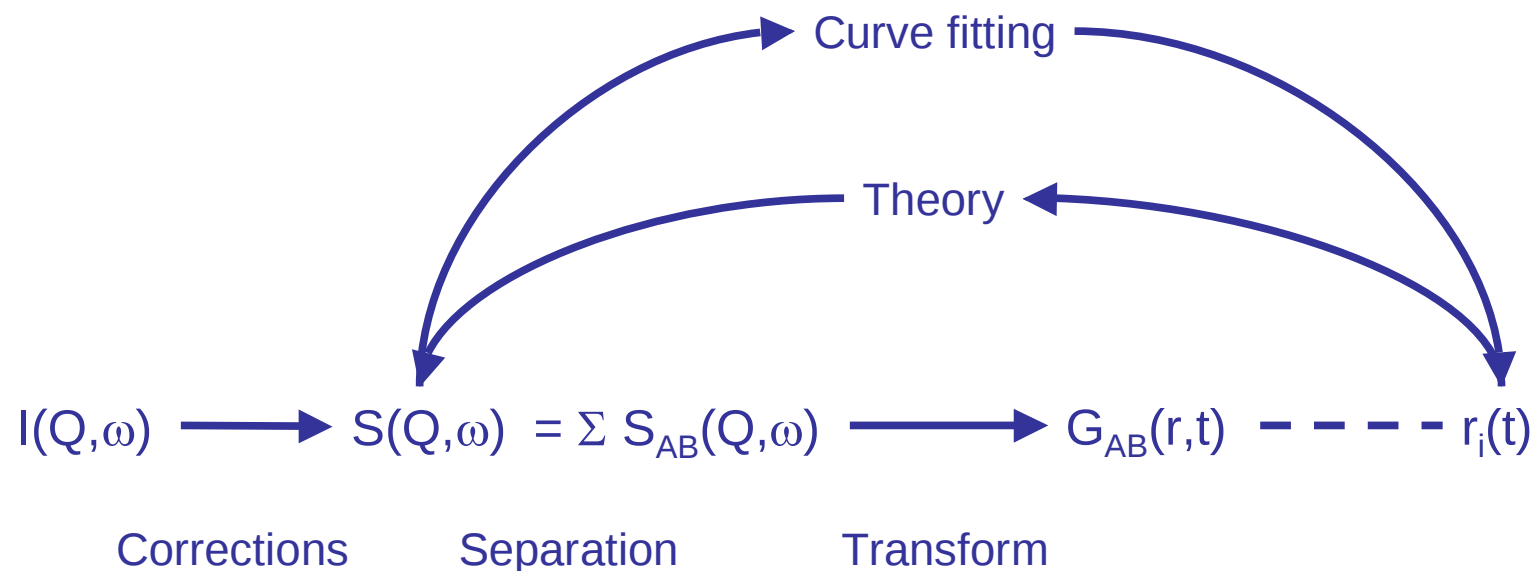


Errors

Under defined
Poorly conditioned

Truncation

Phase problem

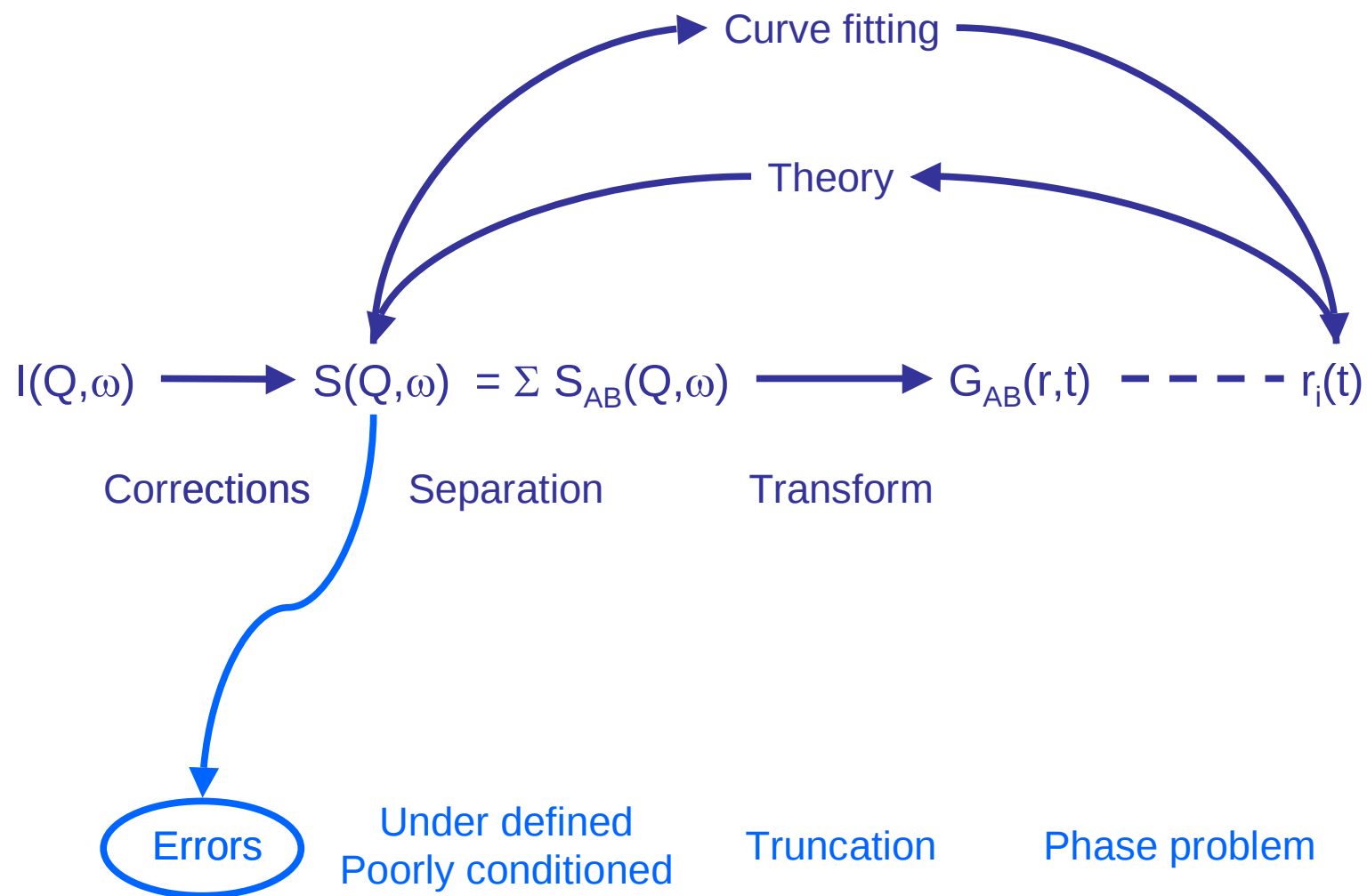


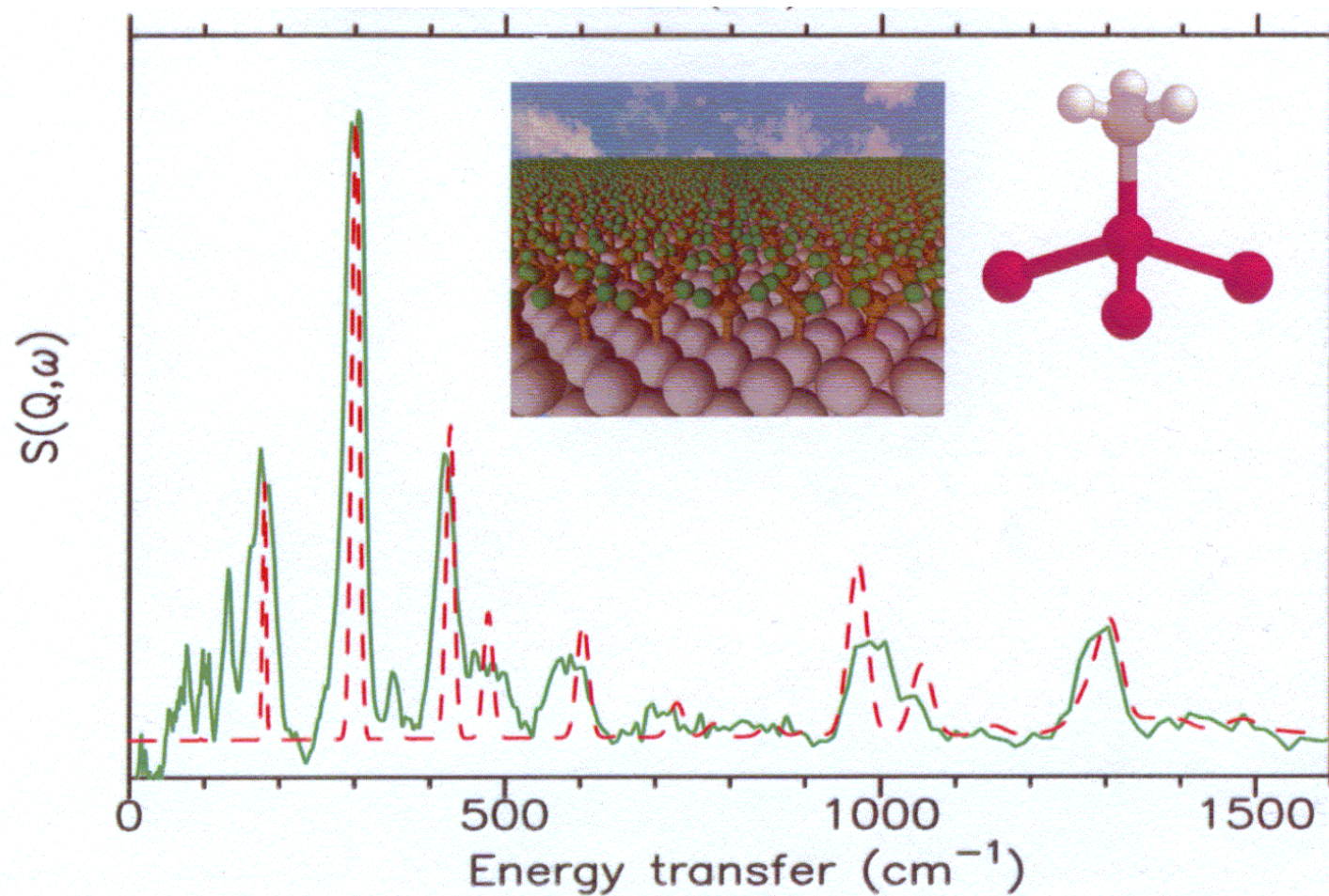
Errors

Under defined
Poorly conditioned

Truncation

Phase problem





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

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

What is N ?

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

What is N ?

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

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 ...

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

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

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

If we assume no knowledge of N then

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

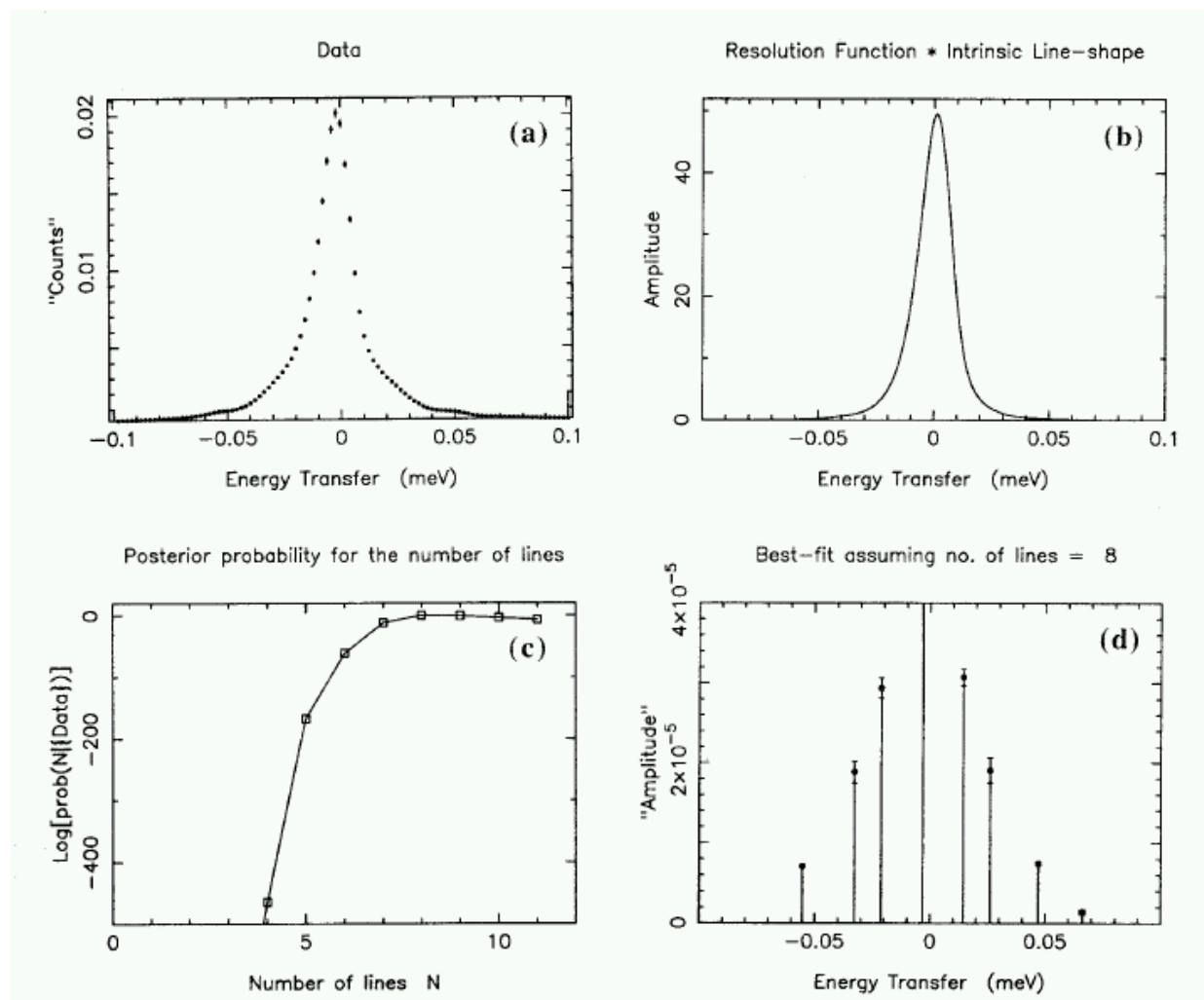
so

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

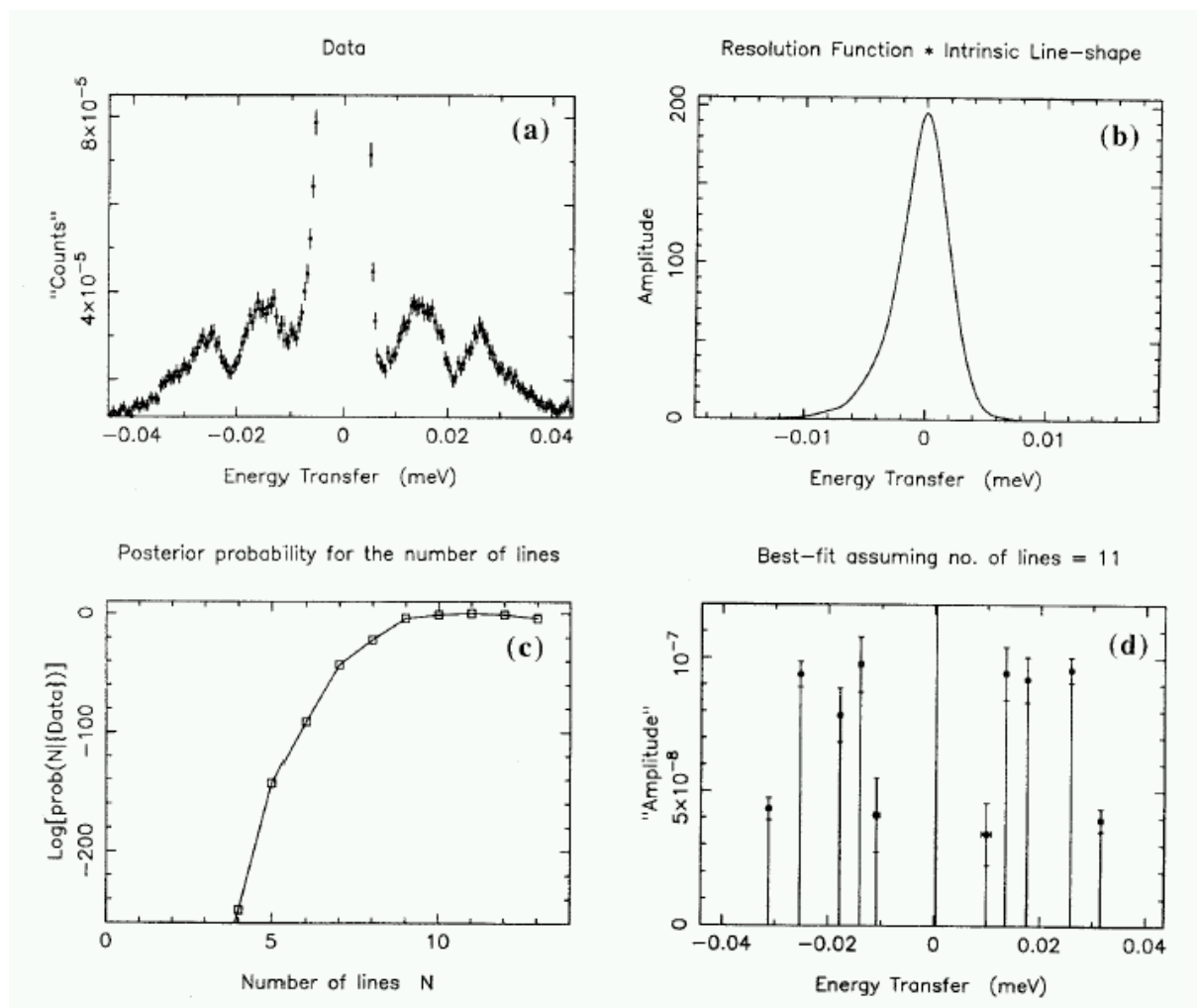
so calculate the integral above and then maximise

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

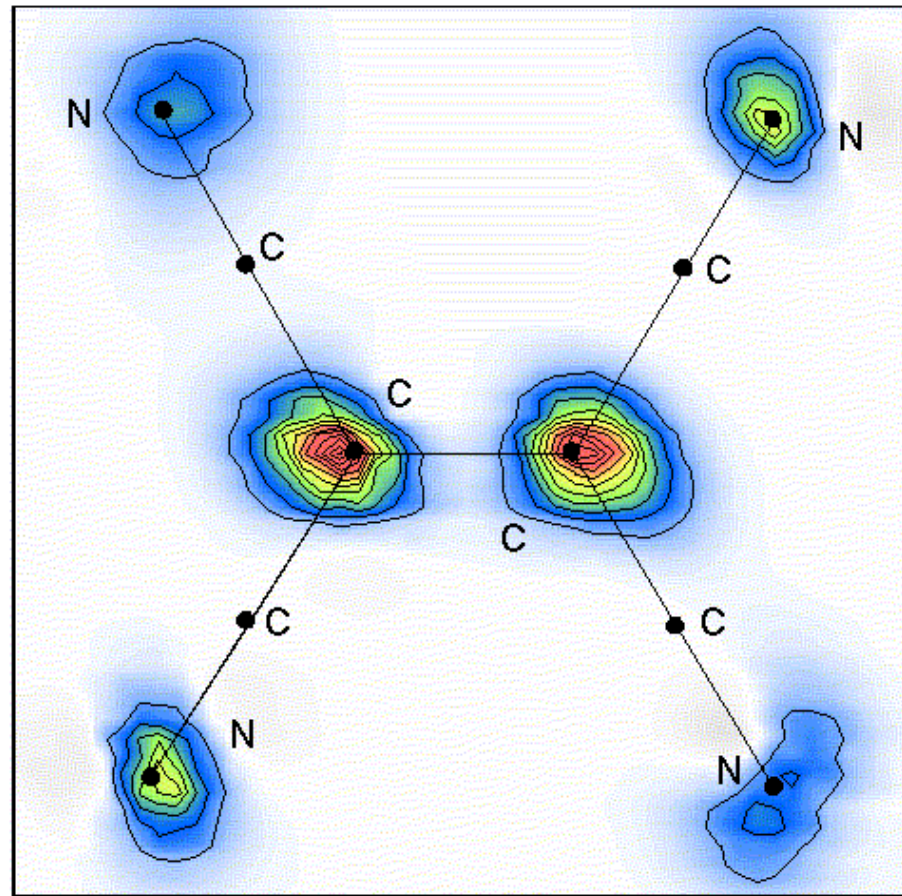
D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992



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

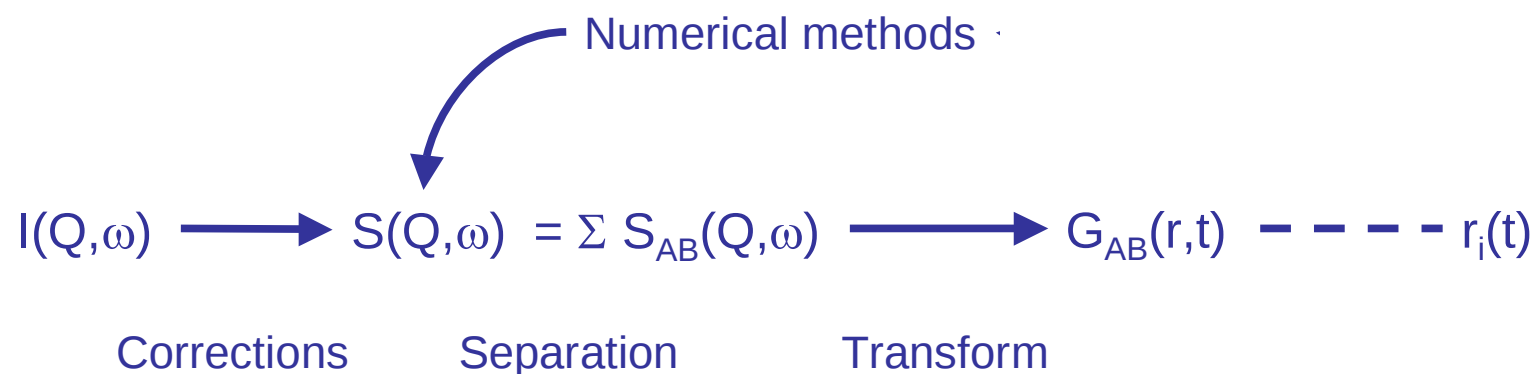


D S Sivia and C J Carlile J. Chem. Phys. **96** 171 1992

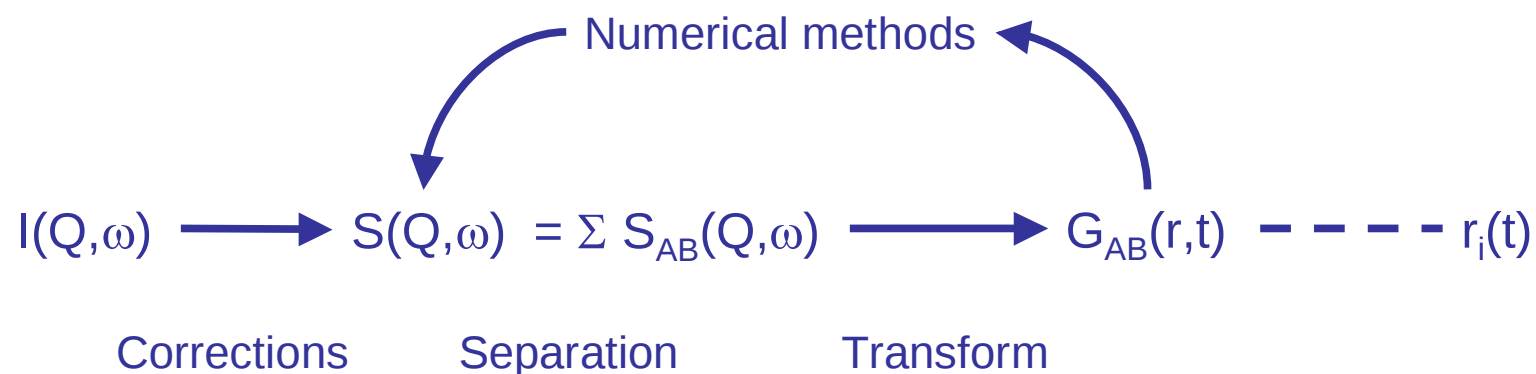


What not to do

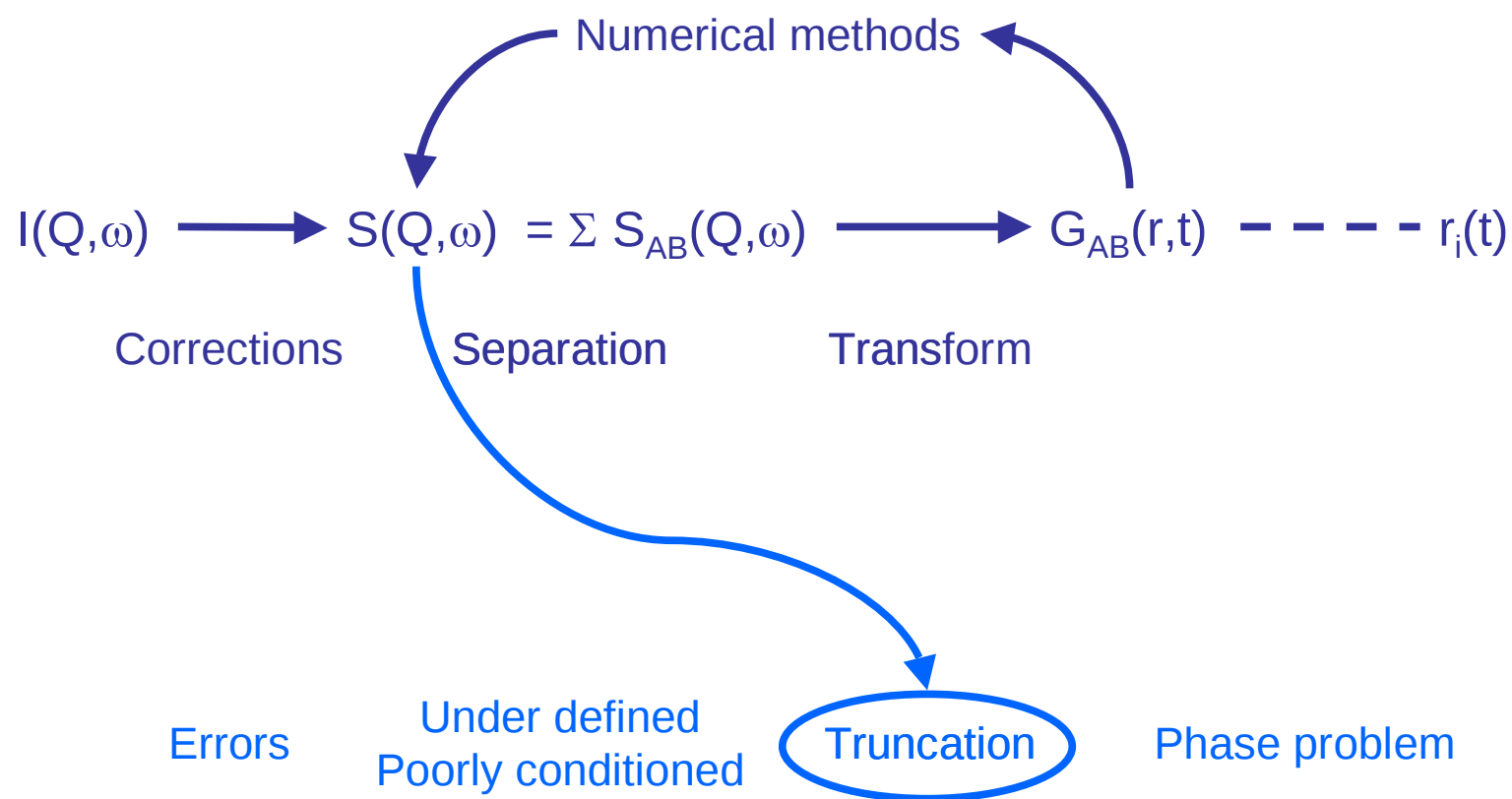
Choose the prior to get the answer you want

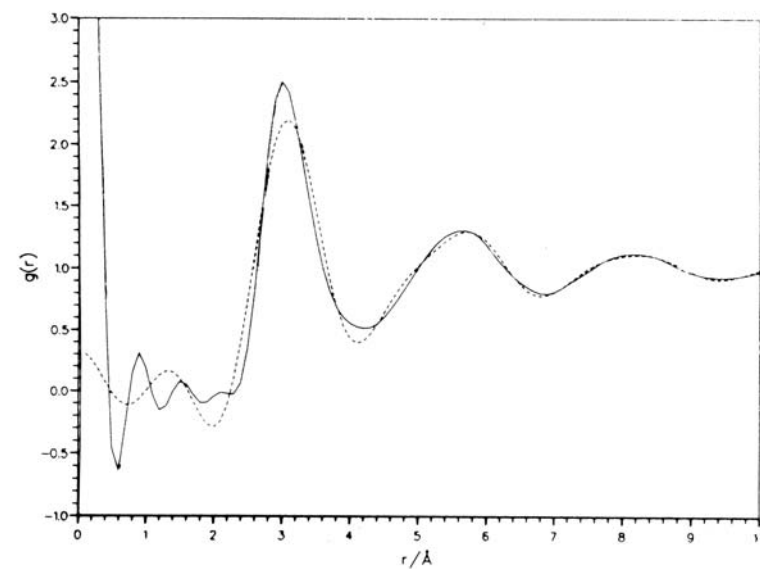
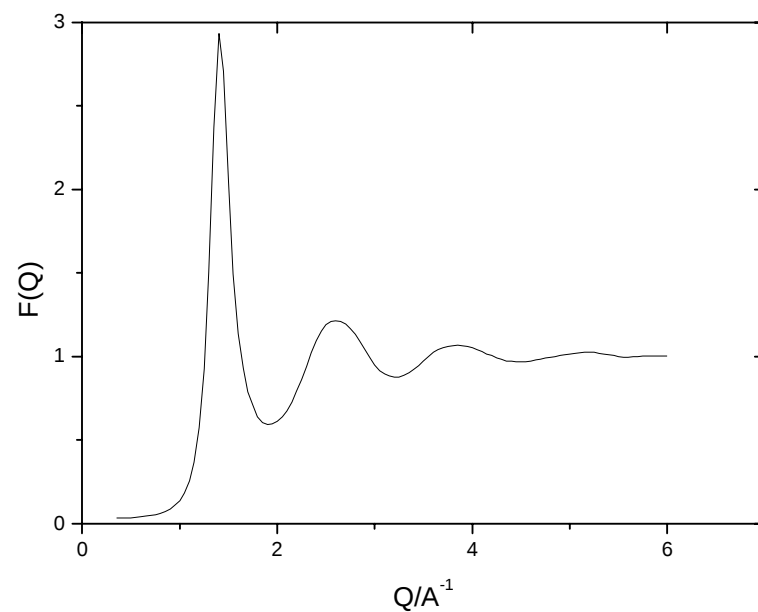


Errors Under defined Truncation Phase problem
 Poorly conditioned



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.)

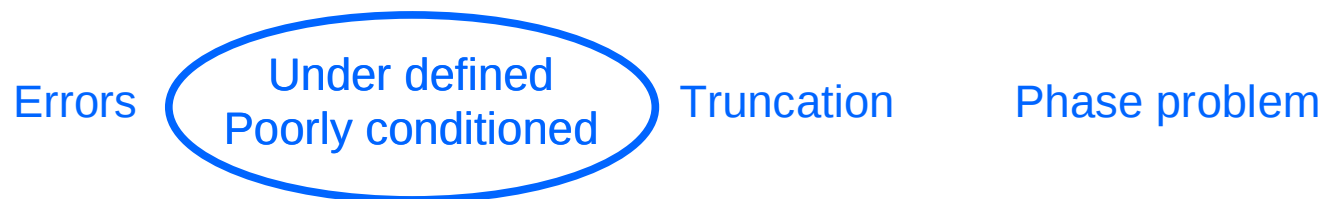
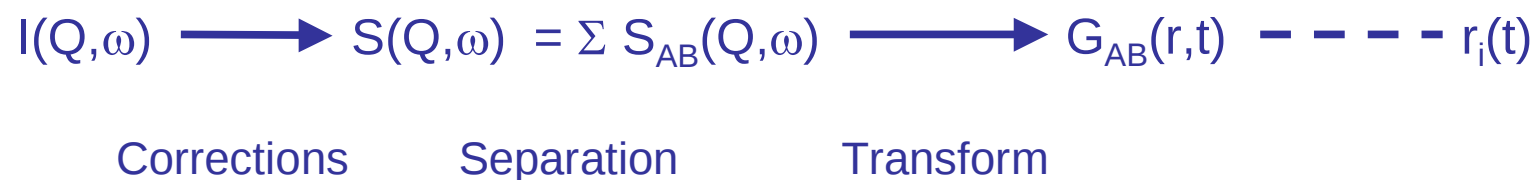
$$H' = \sum w(r) d''(r)$$

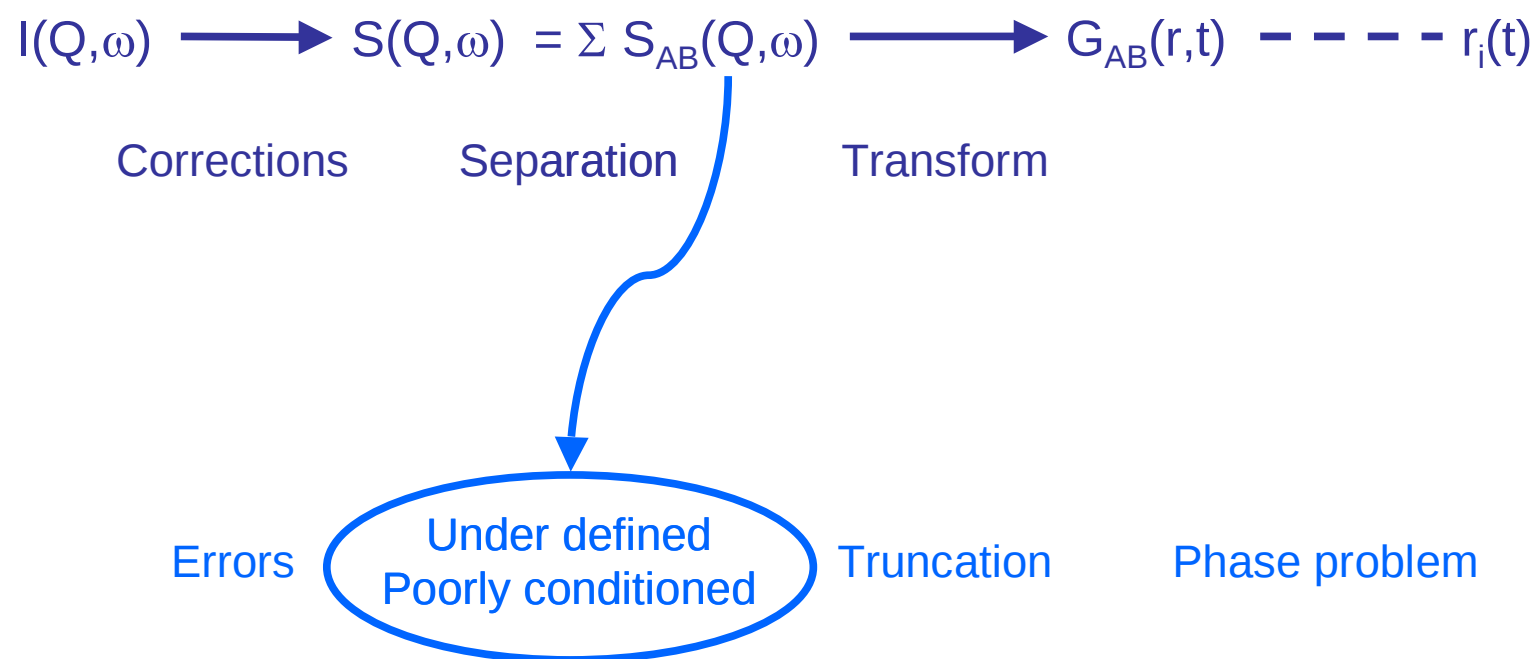
$$d(r) = n(r) - p(r)$$

‘Least noisy’

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

‘Shortest line’





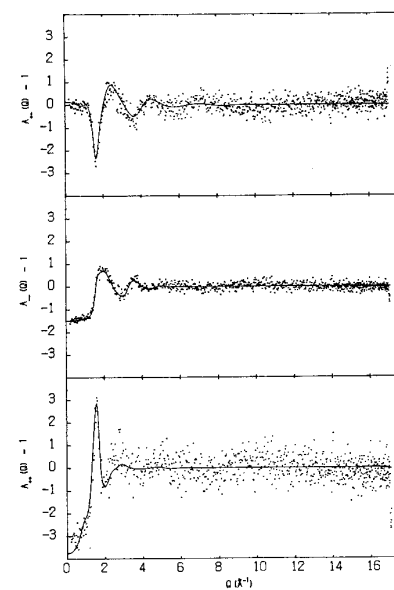
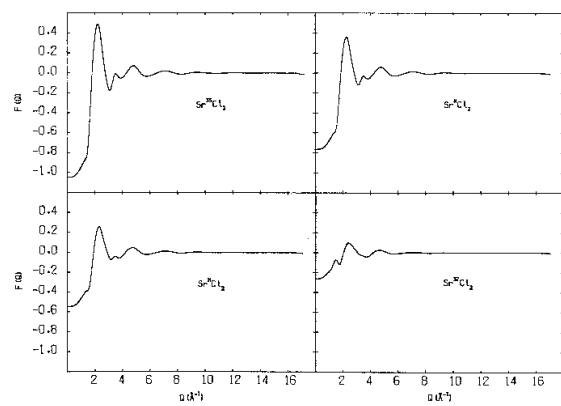
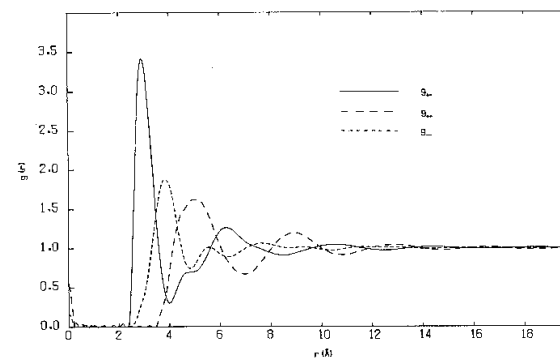
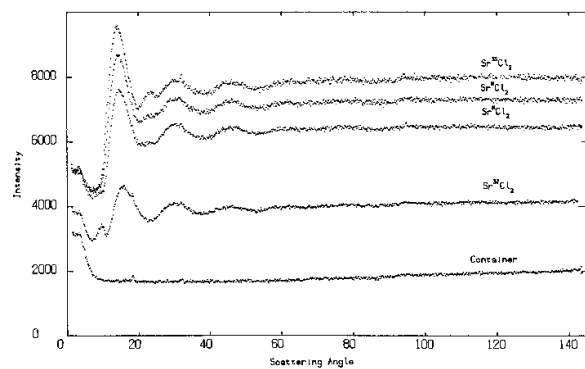
$$F^{(k)}(Q) = \sum_{\alpha} \sum_{\beta} c_{\alpha\beta}^{(k)} (A_{\alpha\beta}(Q) - 1)$$

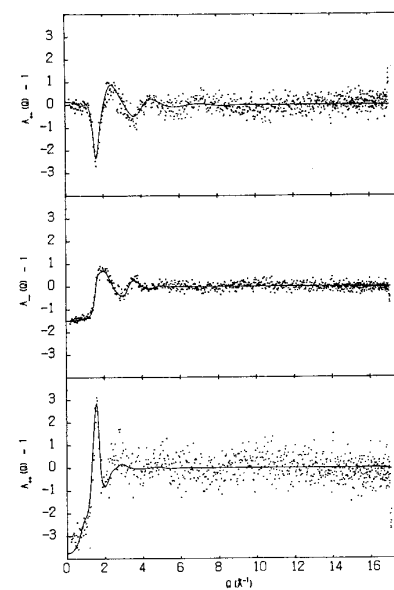
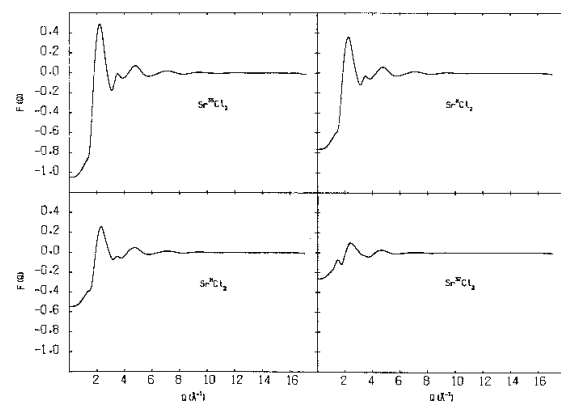
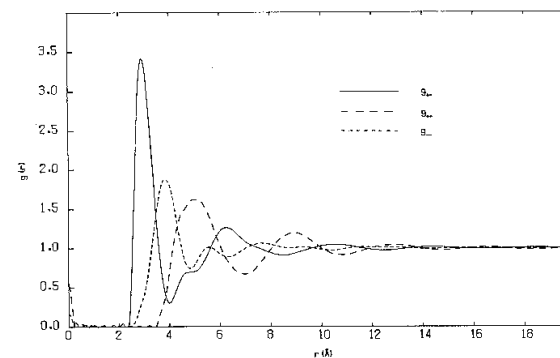
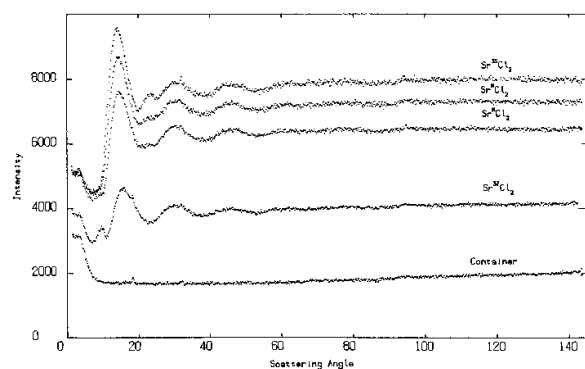
$$\vec{F} = \mathbf{C} \vec{A} \quad \vec{A} = \mathbf{C}^{-1} \vec{F}$$

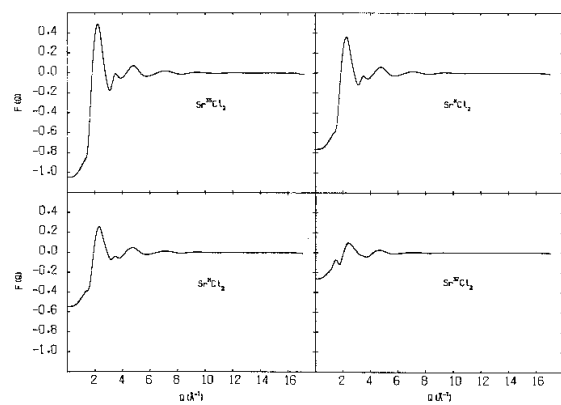
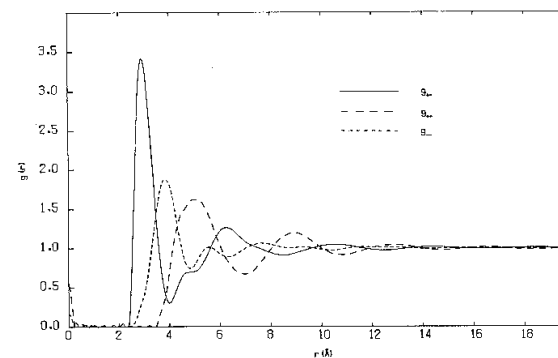
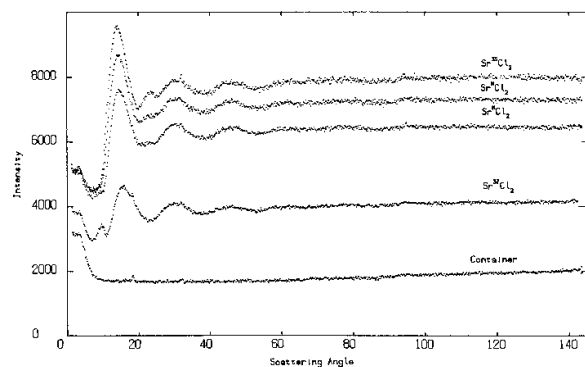
Make a set of measurements with varying coefficients $c_{\alpha\beta}^{(k)}$
(isotopic substitution, anomalous scattering, EXAFS) and solve

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

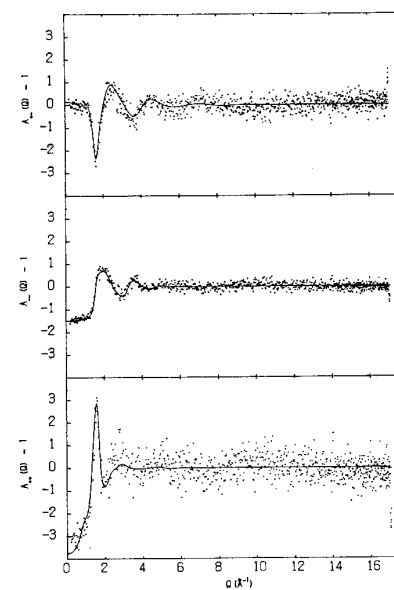
The Turing M conditioning number is a measure of the
conditioning of matrix $\mathbf{C}$

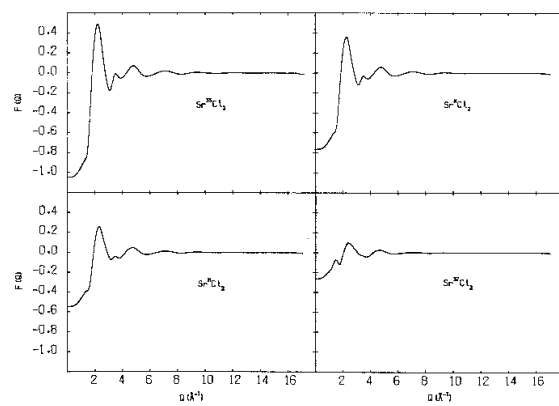
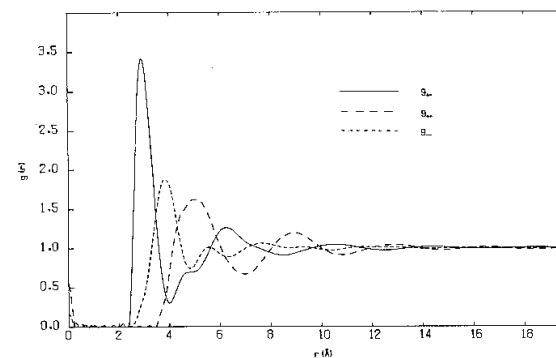
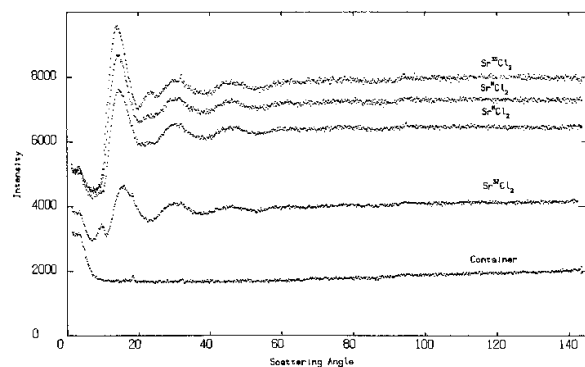




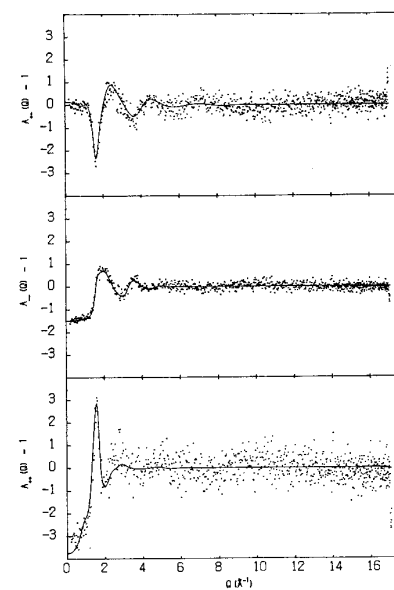


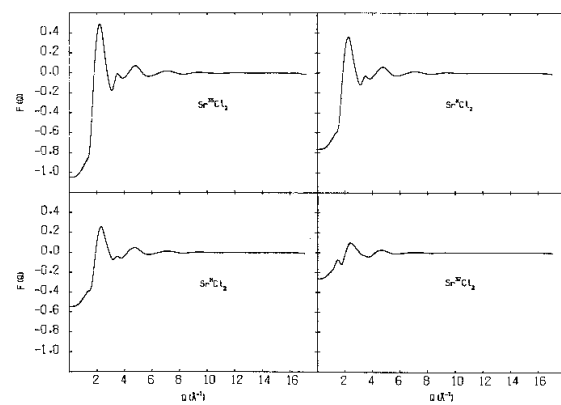
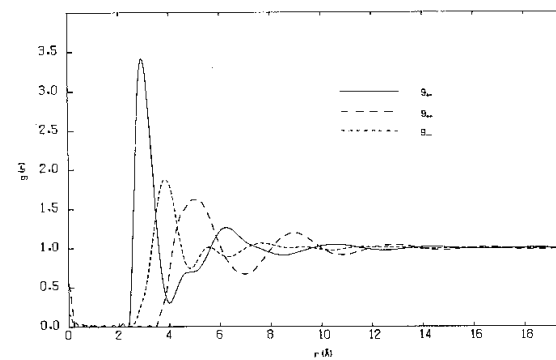
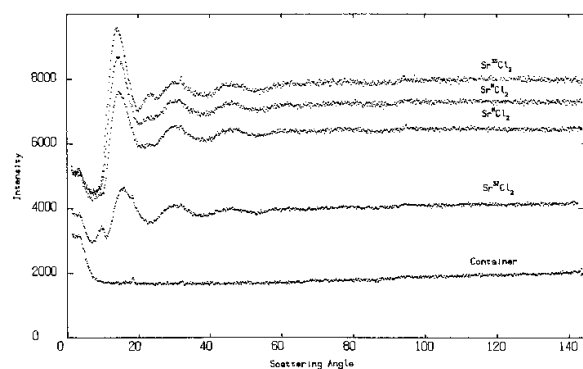
M=35



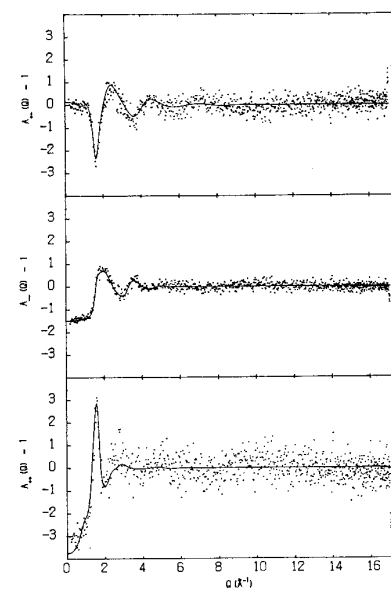


M=35

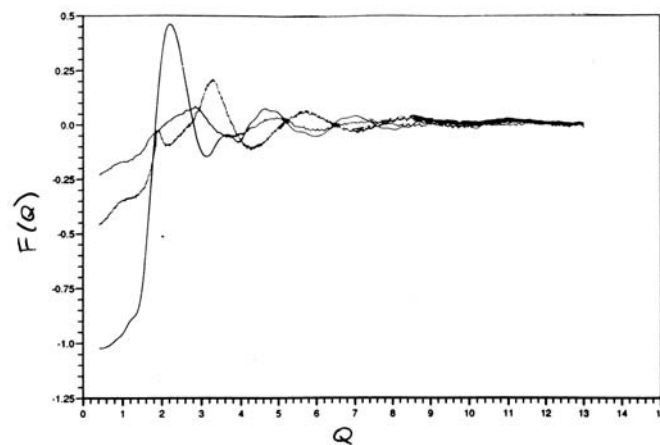




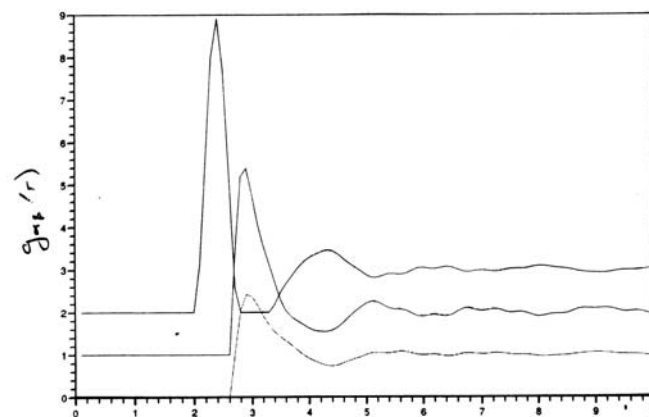
M=35



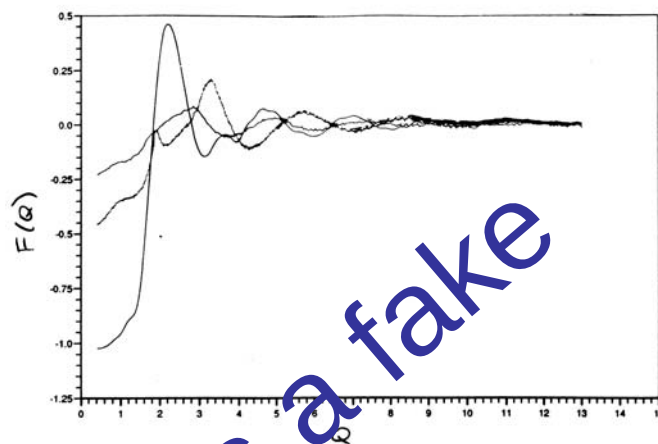
TITLE: QF1,F2,F3
 PLOTTED: 13-AUG-1992 14:03:22 by process Robert
 FILE: qf2.dat



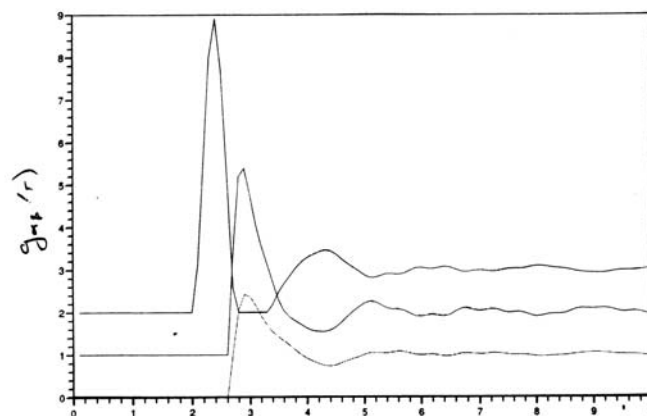
TITLE: $g(r)$
 PLOTTED: 13-AUG-1992 14:04:08 by process Robert
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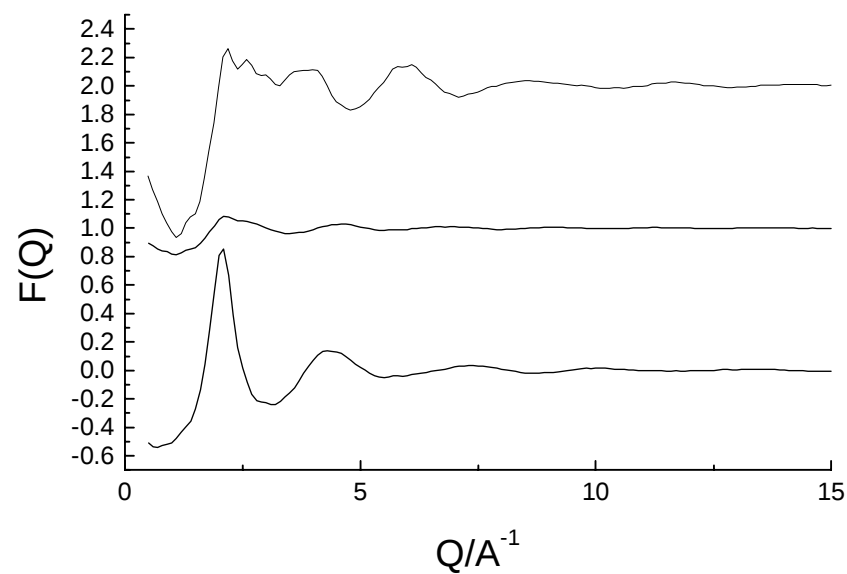


TITLE: QF1,F2,F3
PLOTTED: 13-AUG-1992 14:03:22 by prisma Robert
FILE: qf2.dat

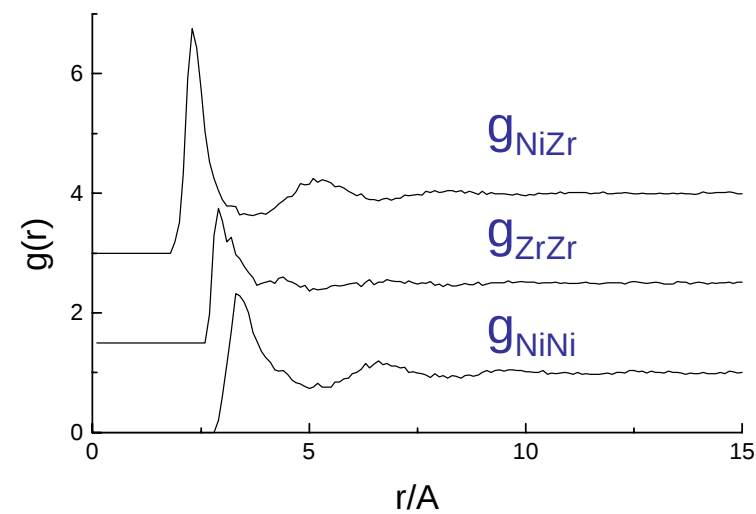


TITLE: $g(r)$
PLOTTED: 13-AUG-1992 14:04:08 by prisma Robert
FILE: qf2.dat




 $^{58}\text{NiZr}$
 $^{(0)}\text{NiZr}$
 $^{62}\text{NiZr}$
 $M=11$

Metallic glass: NiZr


 g_{NiZr}
 g_{ZrZr}
 g_{NiNi}

$^{63}\text{CuZr}$

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

$^{65}\text{CuZr}$

Metallic glass: CuZr

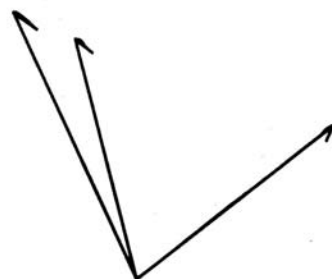
$$c^{(k)} = \begin{pmatrix} c_{11} \\ c_{12} \\ \vdots \\ \vdots \\ c_{nn} \end{pmatrix} \quad \hat{c}^{(k)} = c^{(k)} / \sum c_{\alpha\beta}^2$$

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

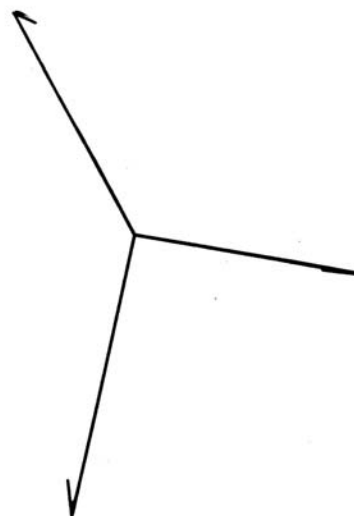
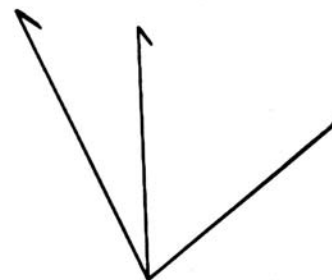
θ_{jk} is a measure of the relative information content
in $F^{(j)}(Q)$ and $F^{(k)}(Q)$

(90° is good!)

NiZr neutron + Ni/Zr EXAFS



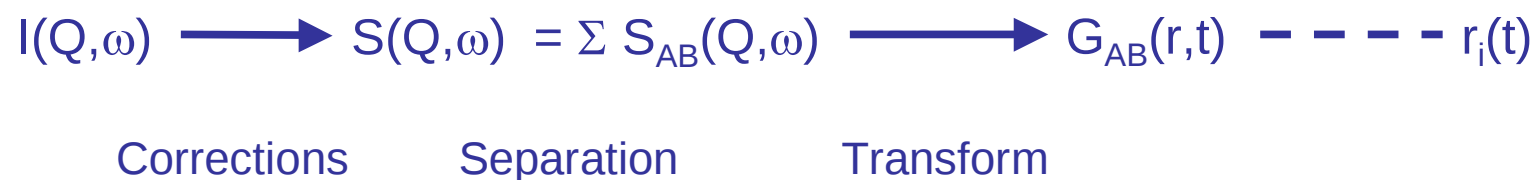
CuZr neutron + Cu/Zr EXAFS



NiZr neutron isotopes



CuZr neutron isotopes

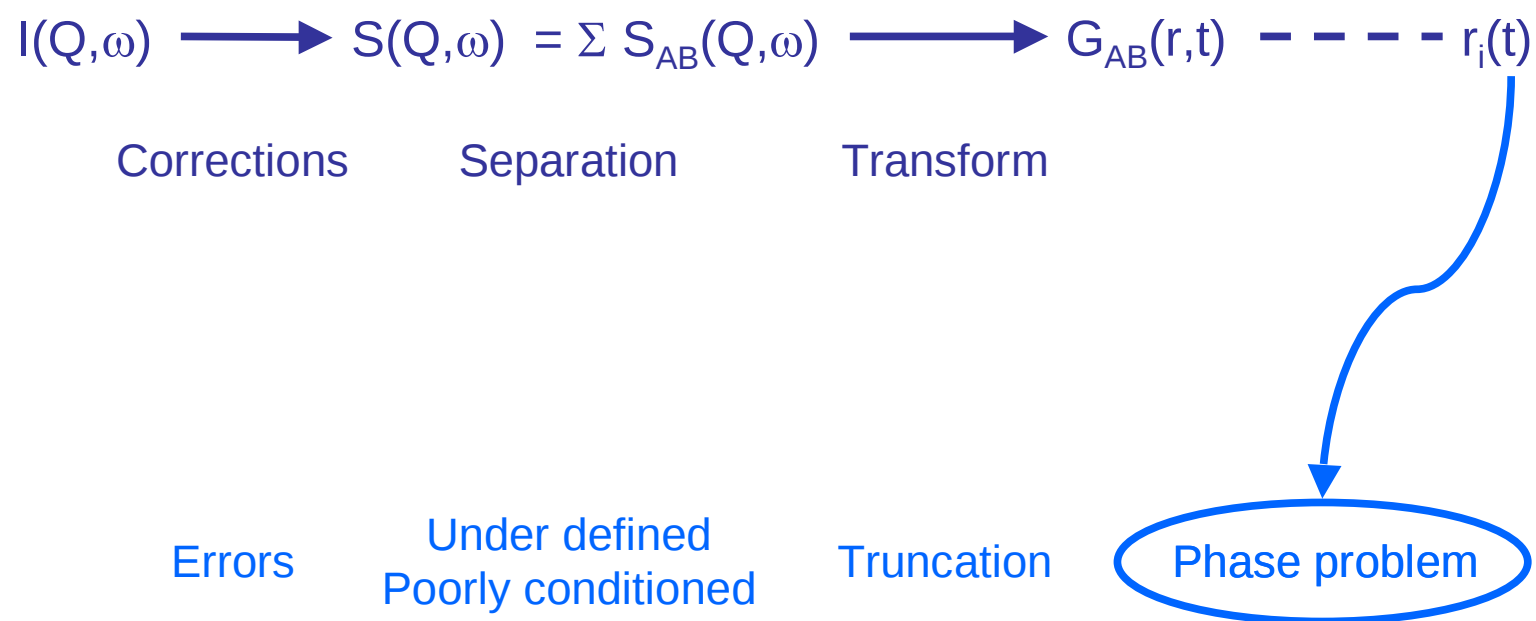


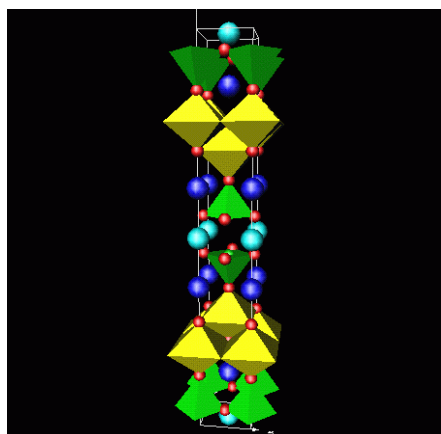
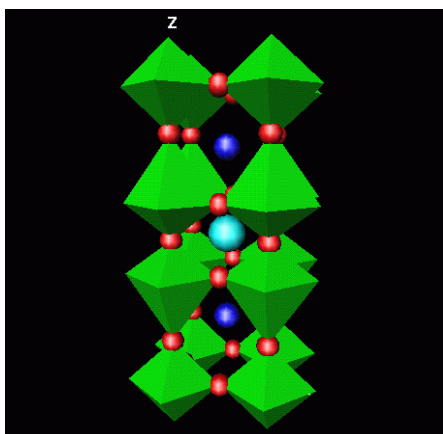
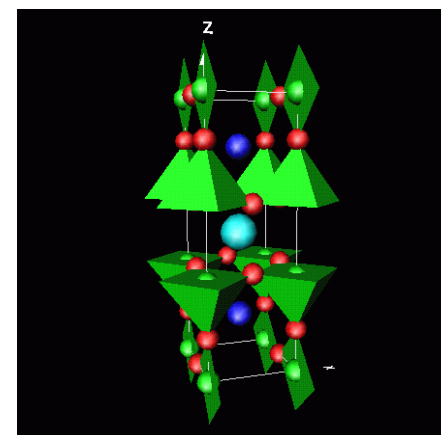
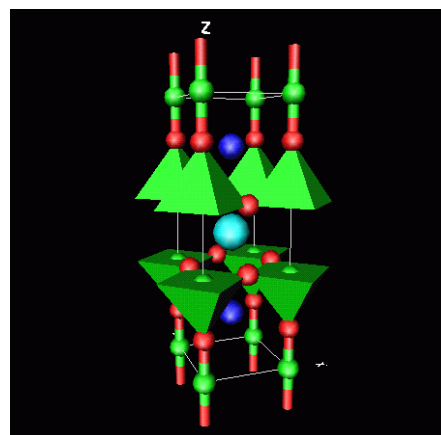
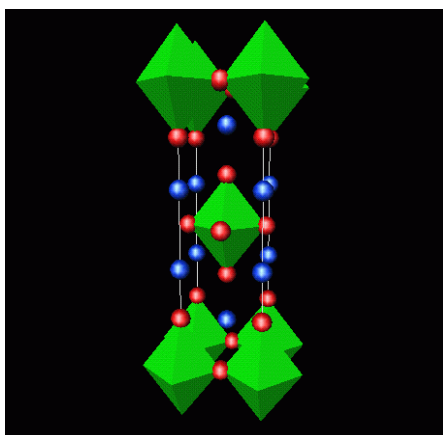
Errors

Under defined
Poorly conditioned

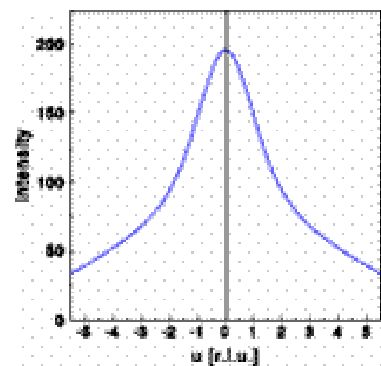
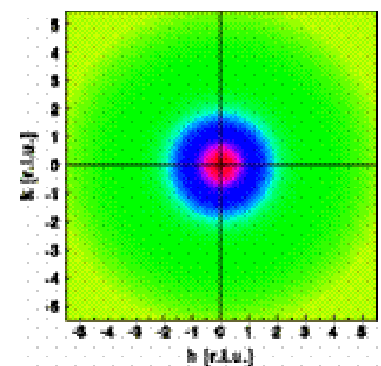
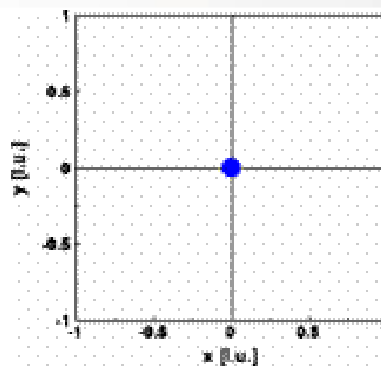
Truncation

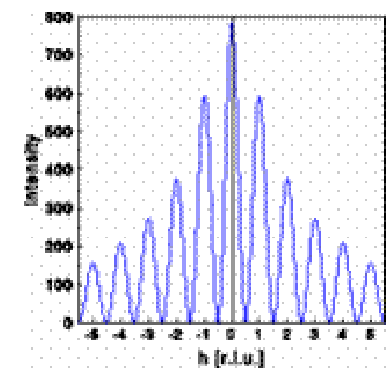
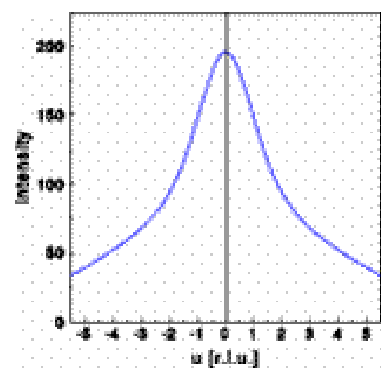
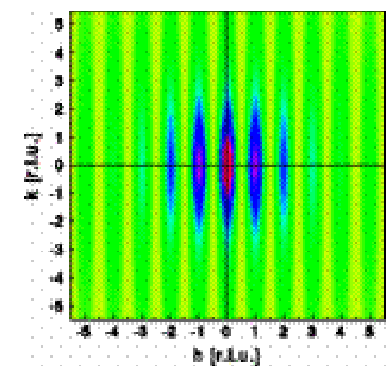
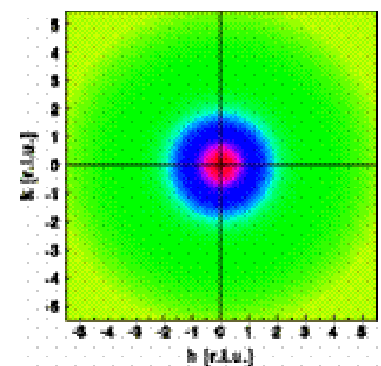
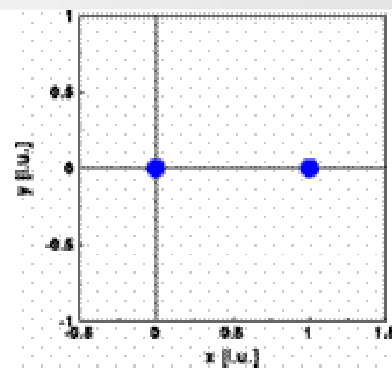
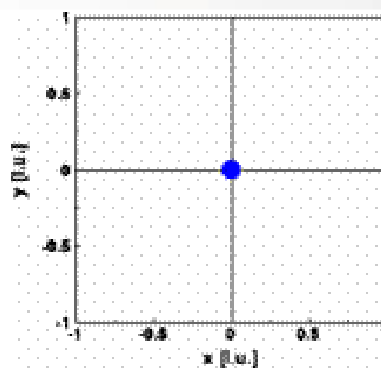
Phase problem

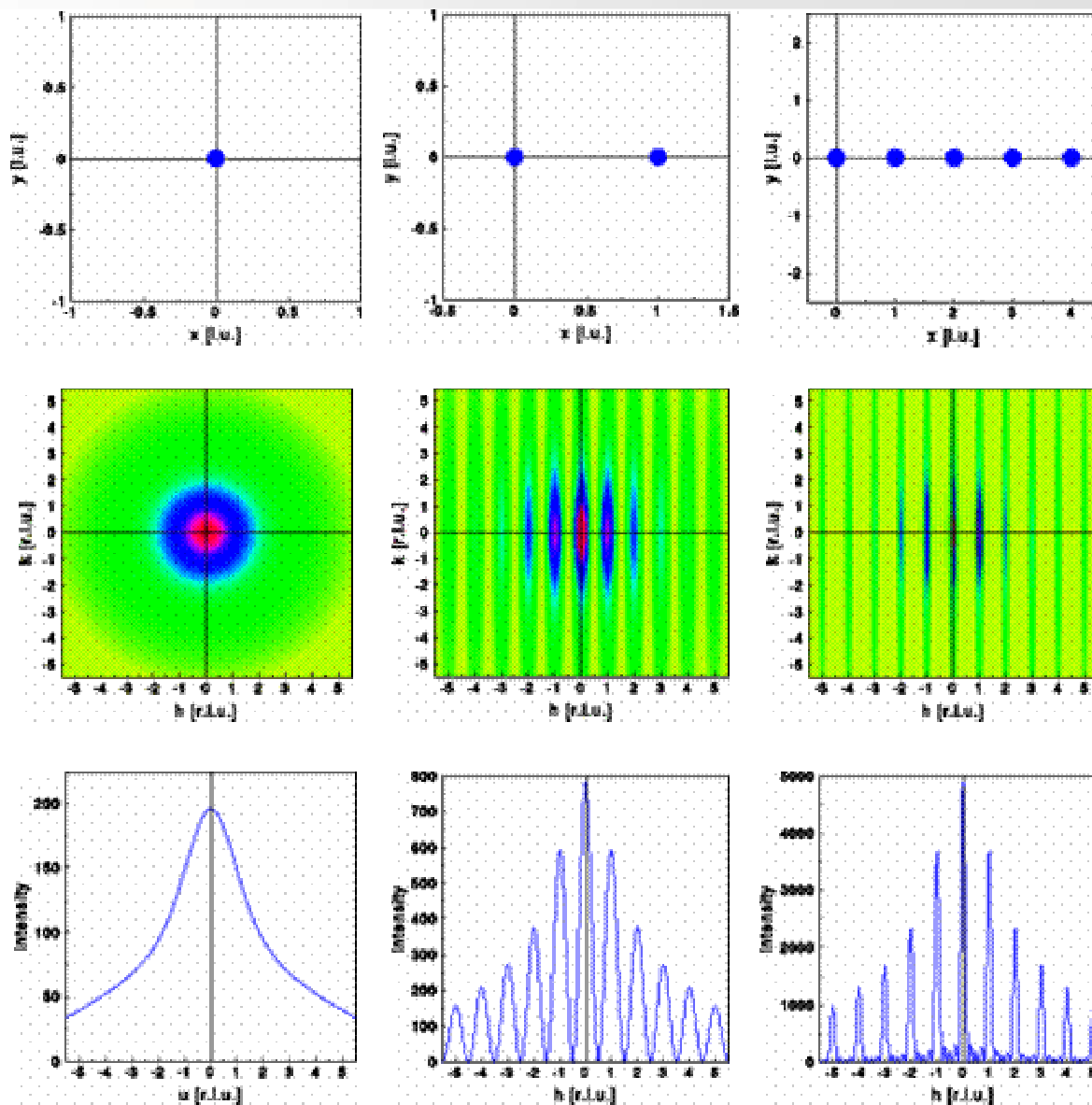


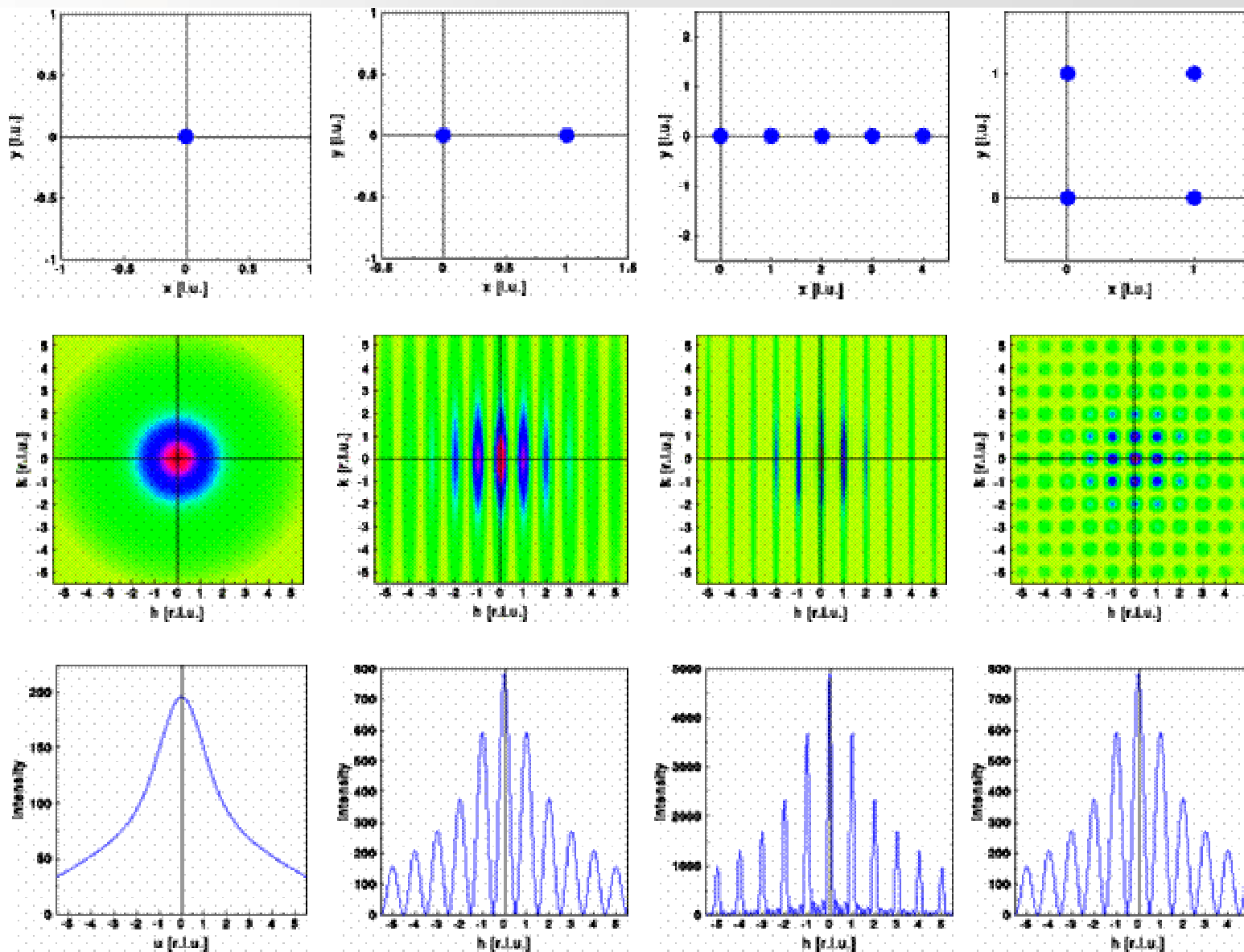


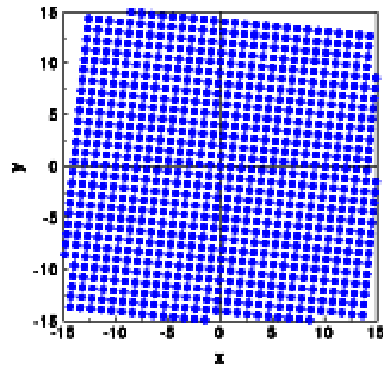
High temperature
superconductors

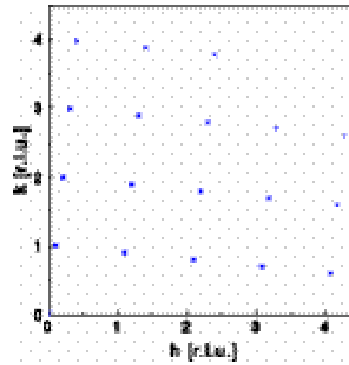
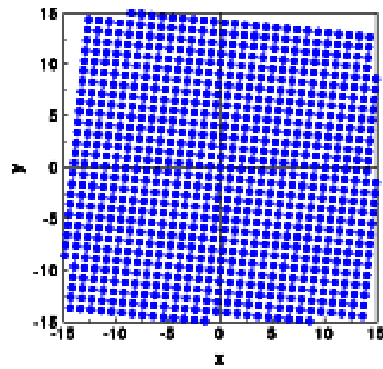


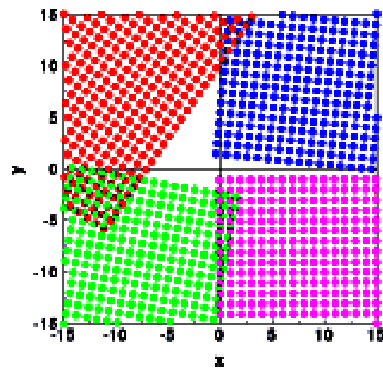
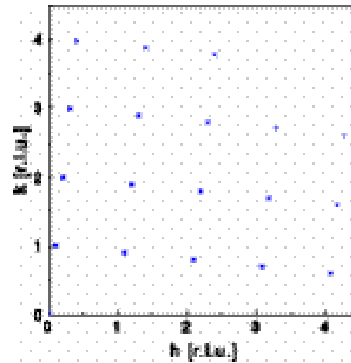
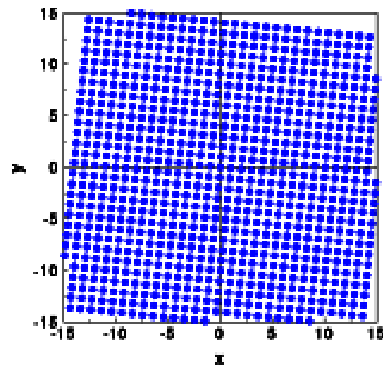


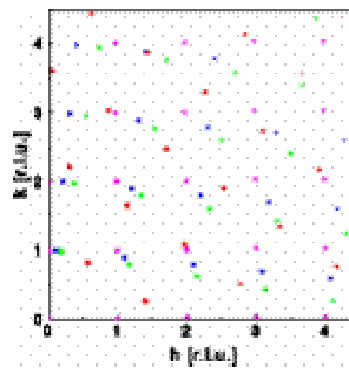
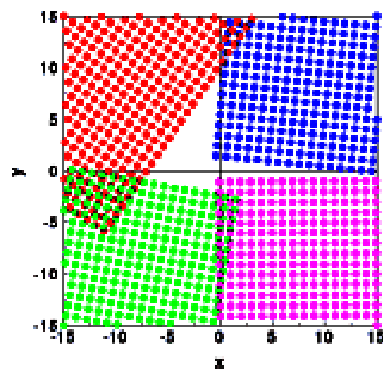
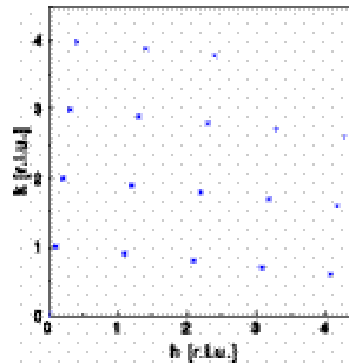
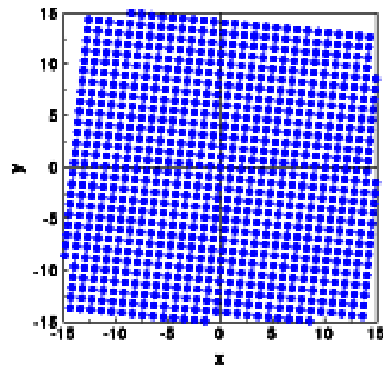


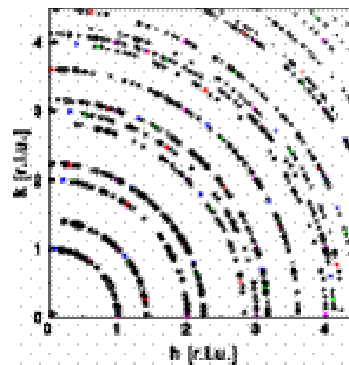
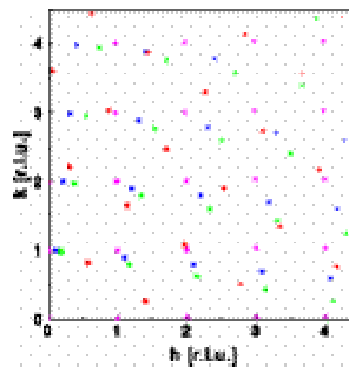
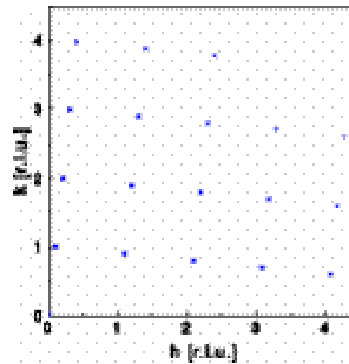
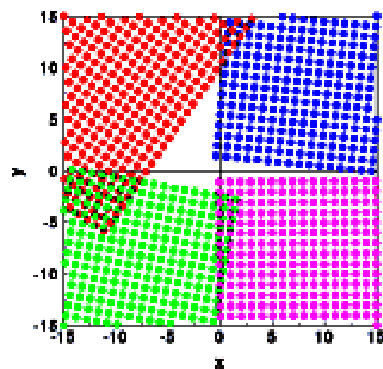
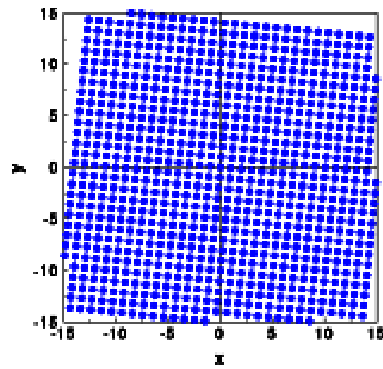


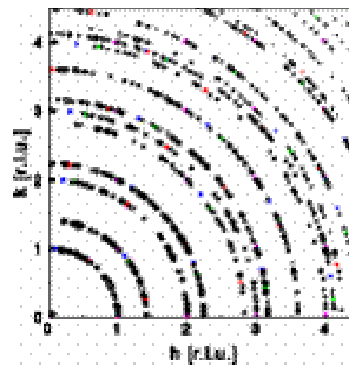
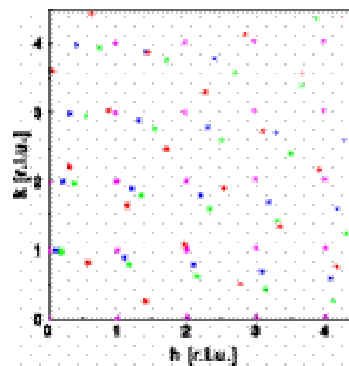
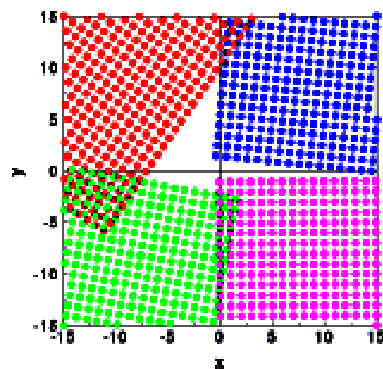
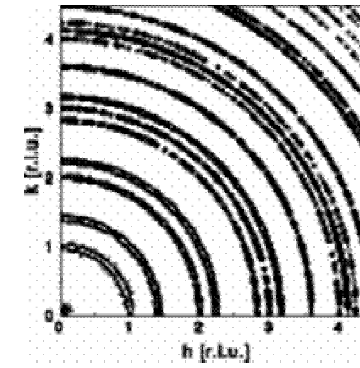
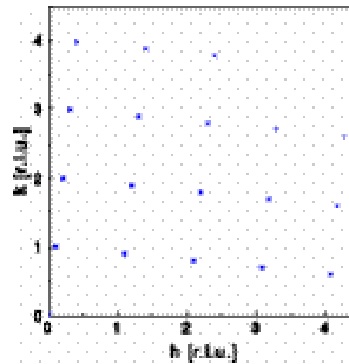
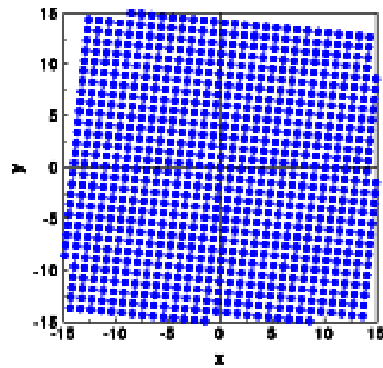


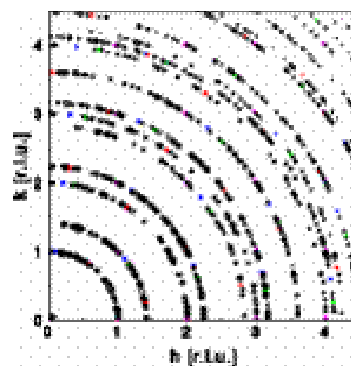
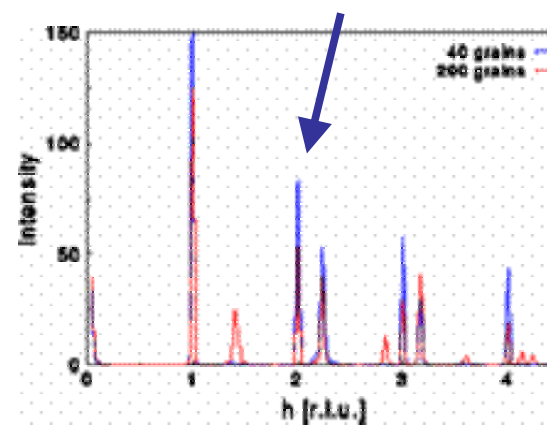
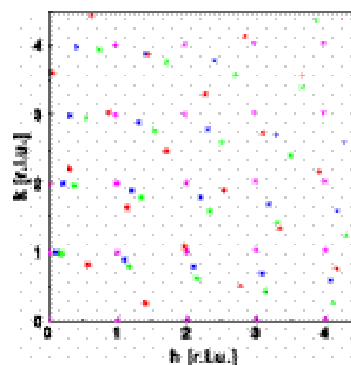
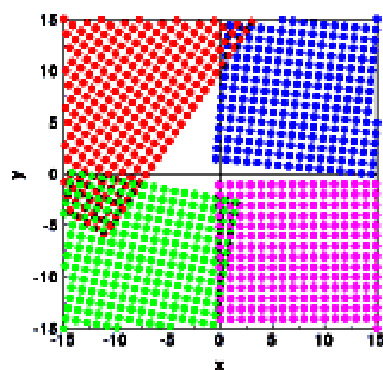
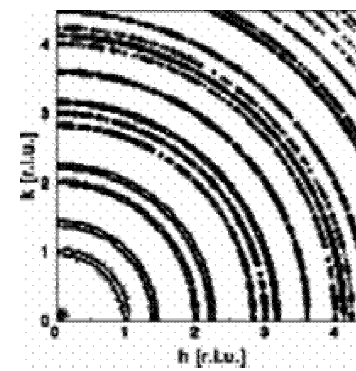
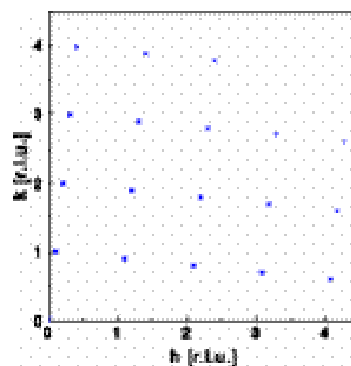
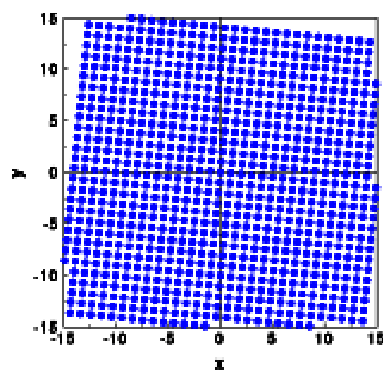


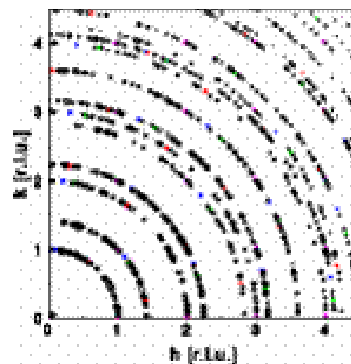
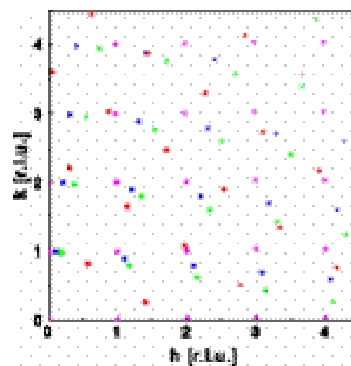
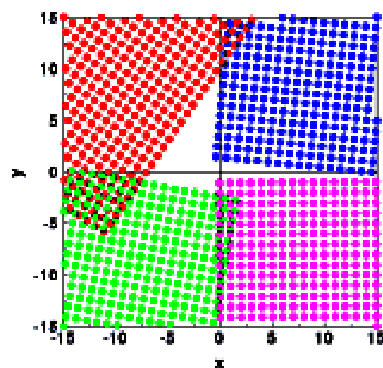
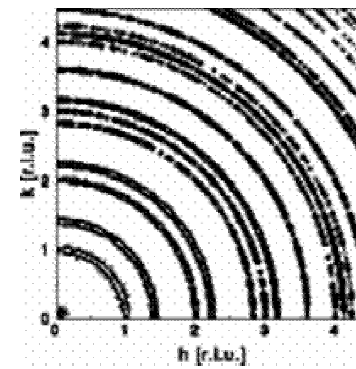
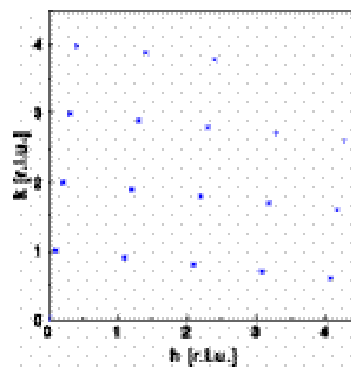
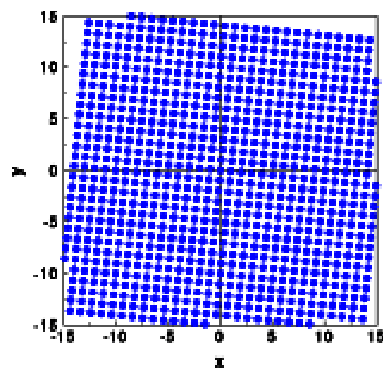


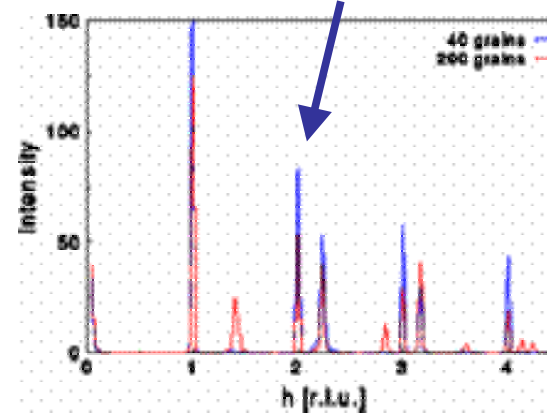


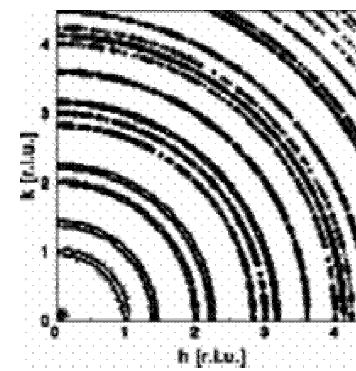
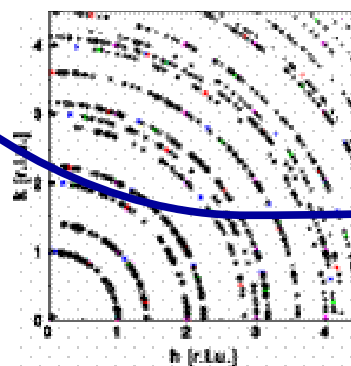
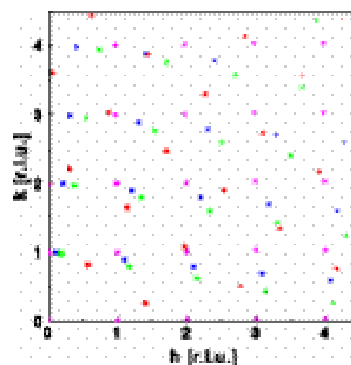
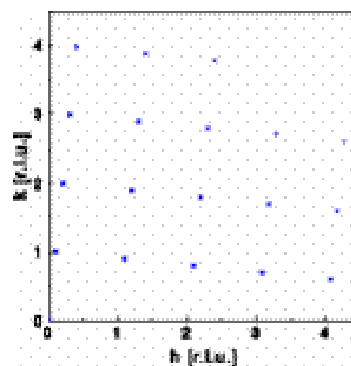
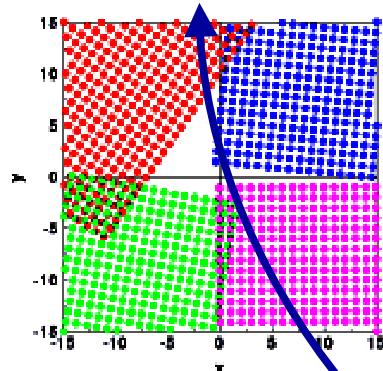
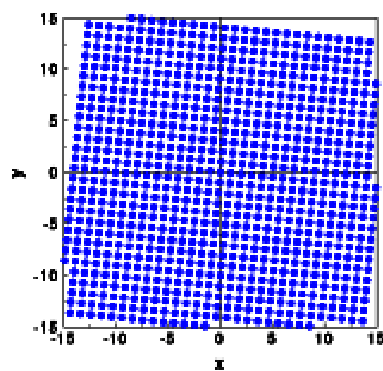


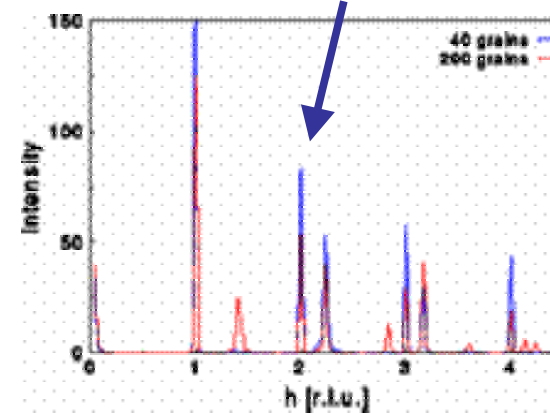




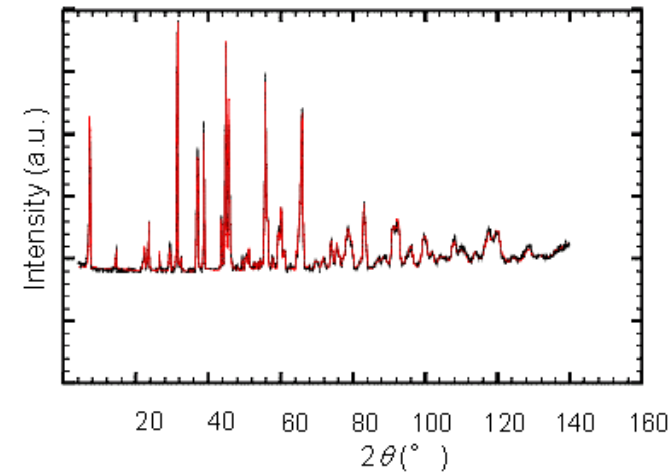


$$I_{hkl}$$




$$I_{hkl}$$


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



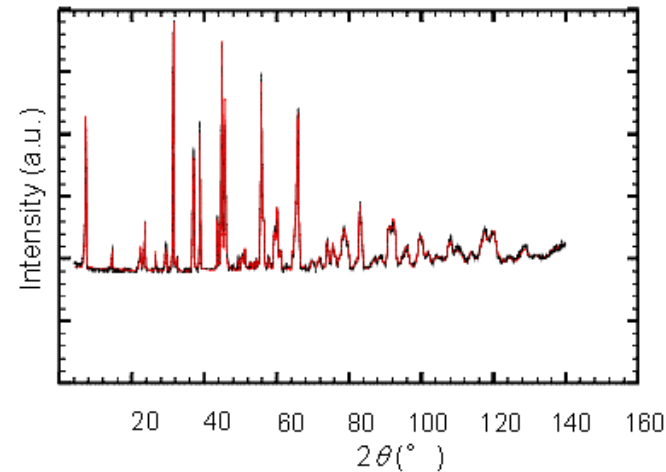
$$F_{hkl} = \sum_{j=1}^{N_j} b_j \exp(2\pi i(hx_j + ky_j + lz_j))$$

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

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

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

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

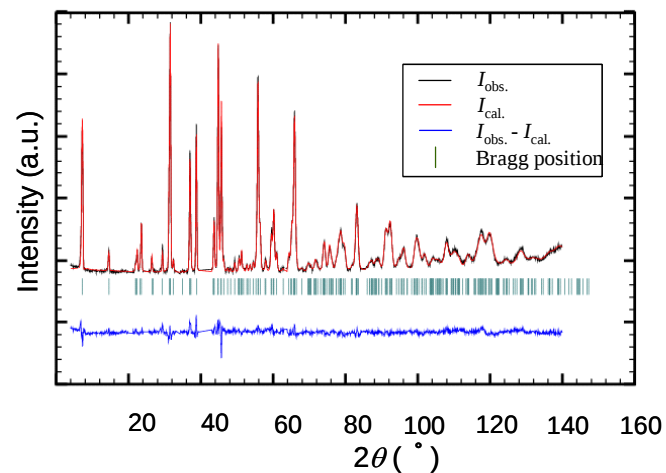
Asymmetry parameters : 0.08420 0.02110

GLOBAL PARAMETERS

Zero-point: -0.0016 0.0028

Background Polynomial Parameters

757.356 -10.6976 0.243093 -0.211296E-02 0.664176E-05



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

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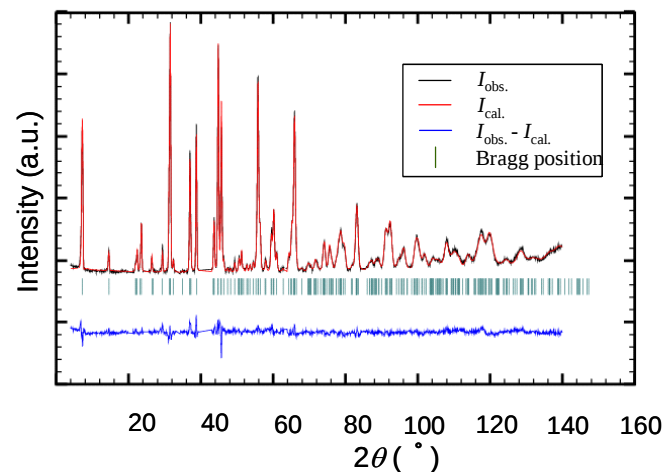
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$$R_p = 4.17, R_{wp} = 5.47, \chi^2 = 3.68$$

Constrained Rietveld refinement

Simulated annealing
(Monte Carlo)

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

Hybrid Monte Carlo
(molecular dynamics)

$$H(t) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2(t) + \chi^2(\mathbf{r}(t))$$
$$\exp(-(E_m - E_0) / T)$$

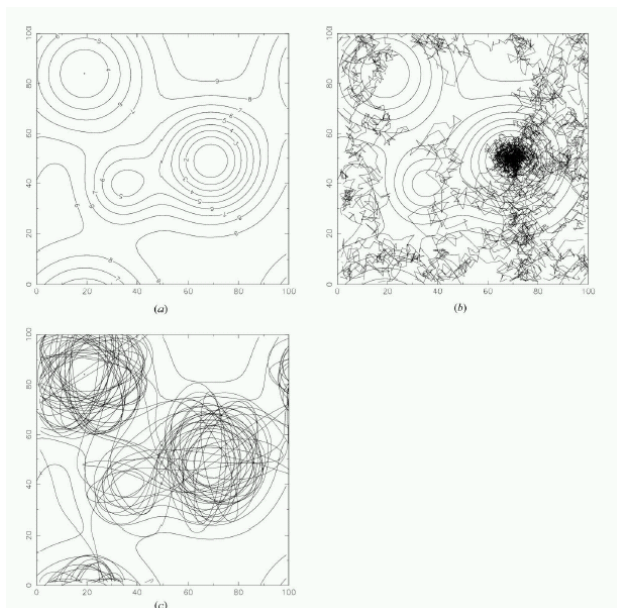
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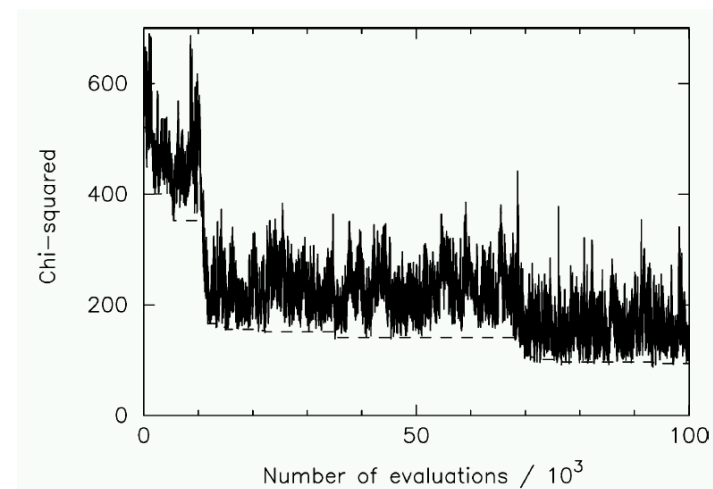
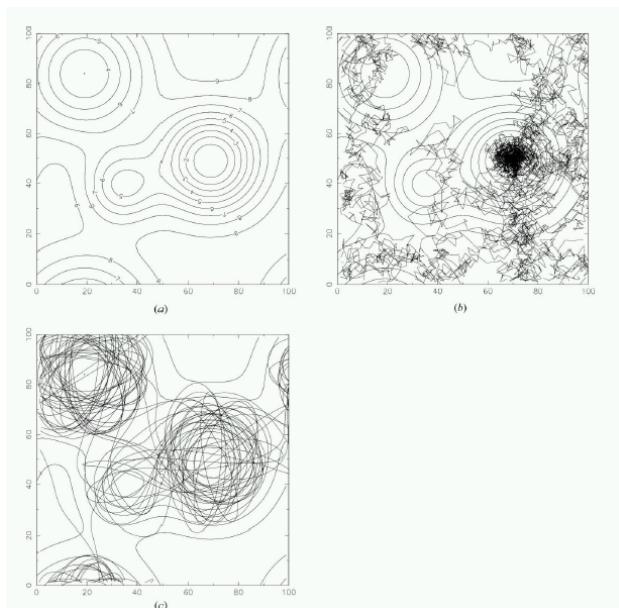
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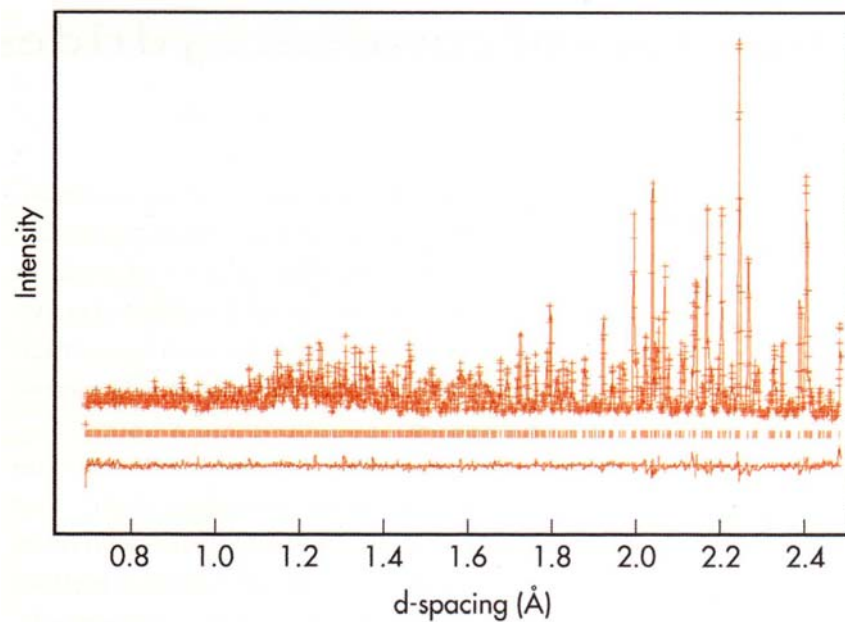
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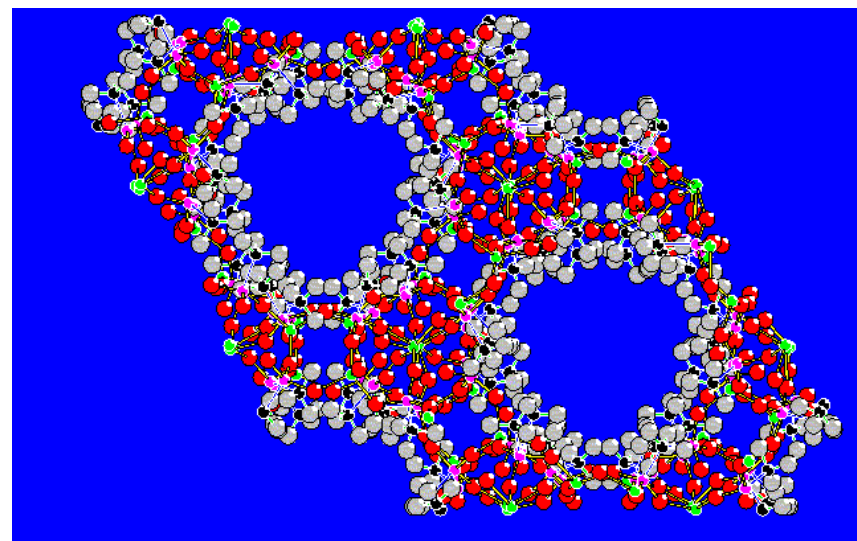
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Johnston, David, Markvardsen, Shankland. Acta Cryst A 58 441 2002



Pushing the 100 atom limit



α -AgI

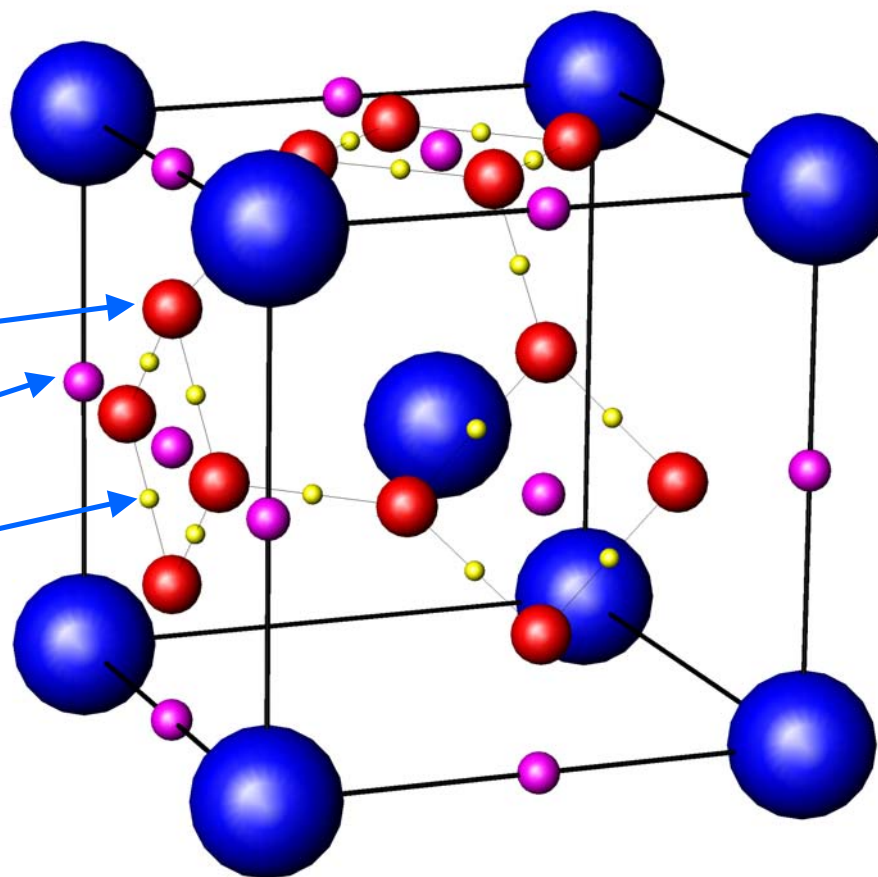
b.c.c. I⁻

Ag⁺ sites.....

12 $\times$ tetrahedral

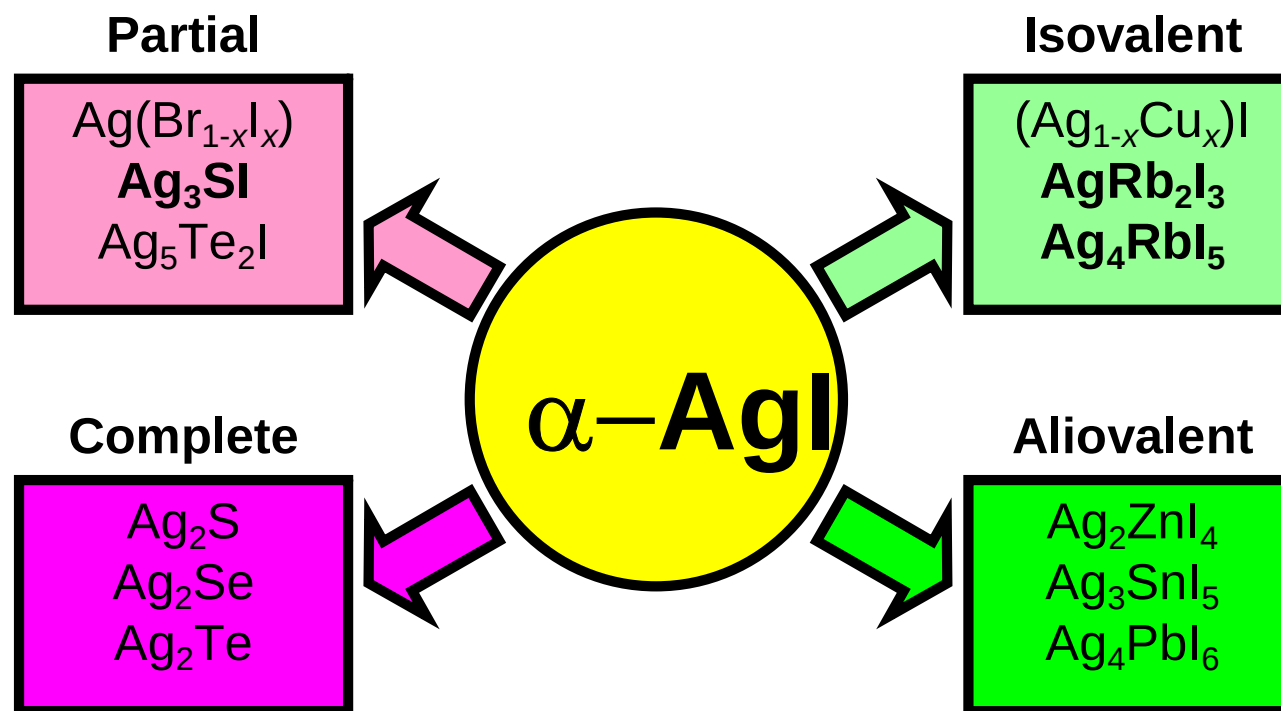
6 $\times$ octahedral

24 $\times$ trigonal



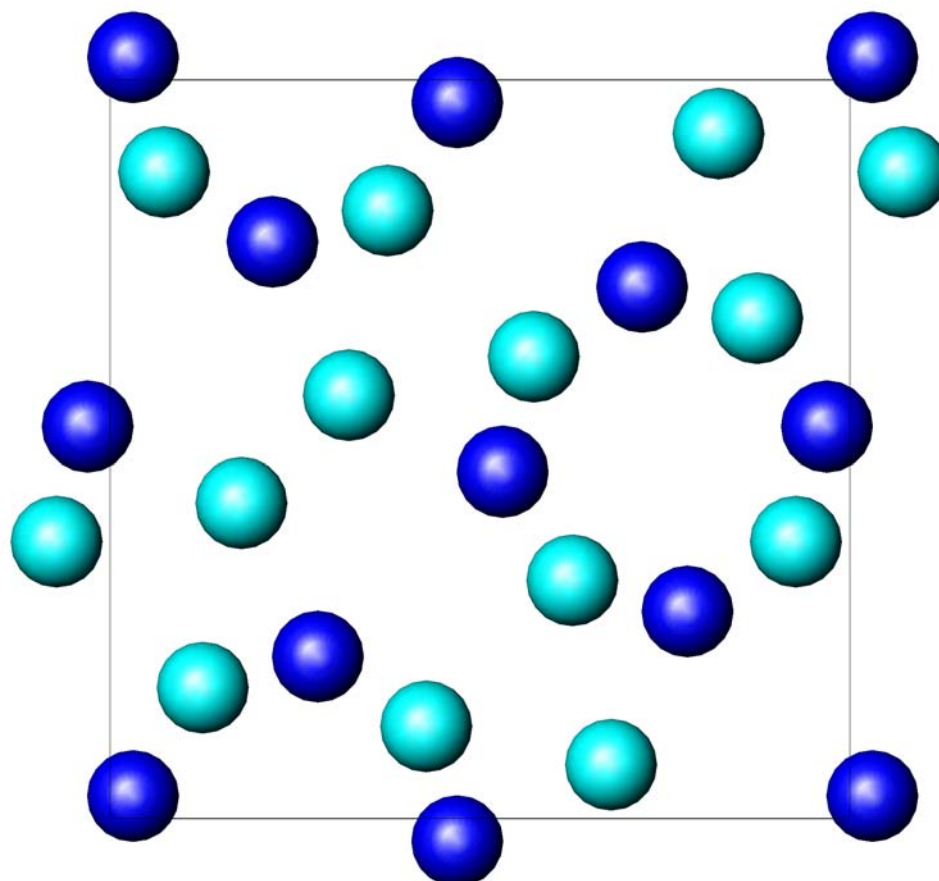
ANION REPLACEMENT

CATION REPLACEMENT



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

Ag_4RbI_5 : IODINE SUBSTRUCTURE



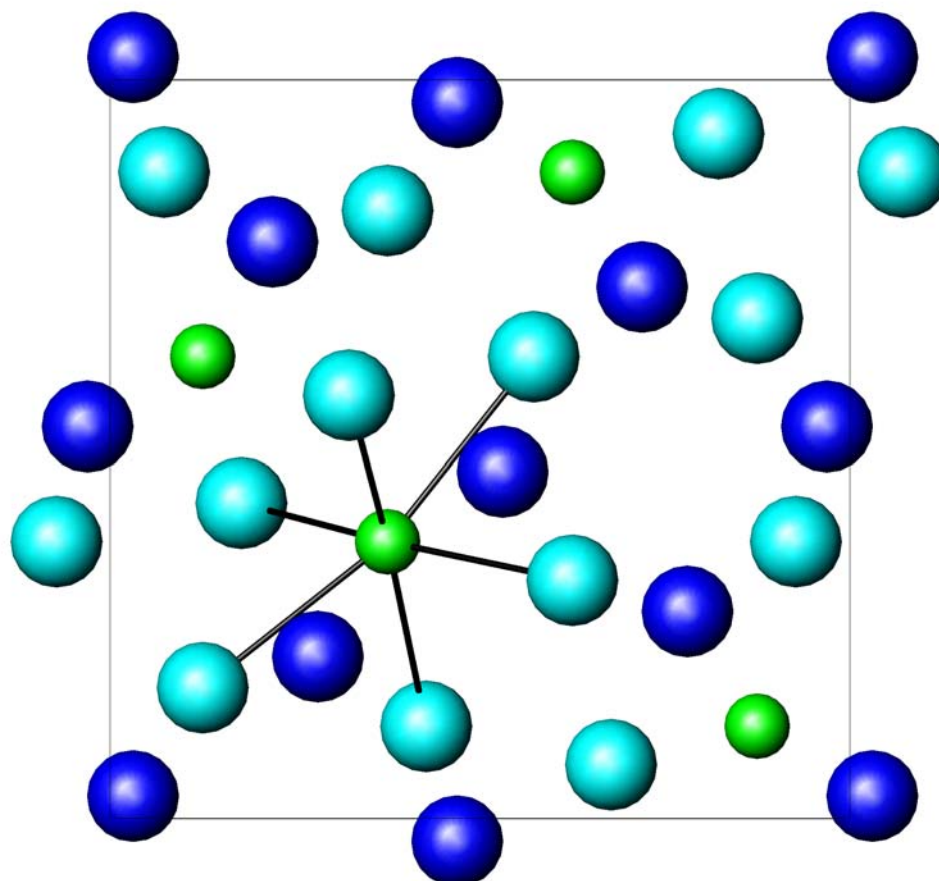
$P 4_132$
 $a \sim 11.24 \text{ \AA}$

I1 in 8(c)
 x, x, x
 $x \sim 0.031$

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

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

Ag_4RbI_5 : Rb POSITIONS

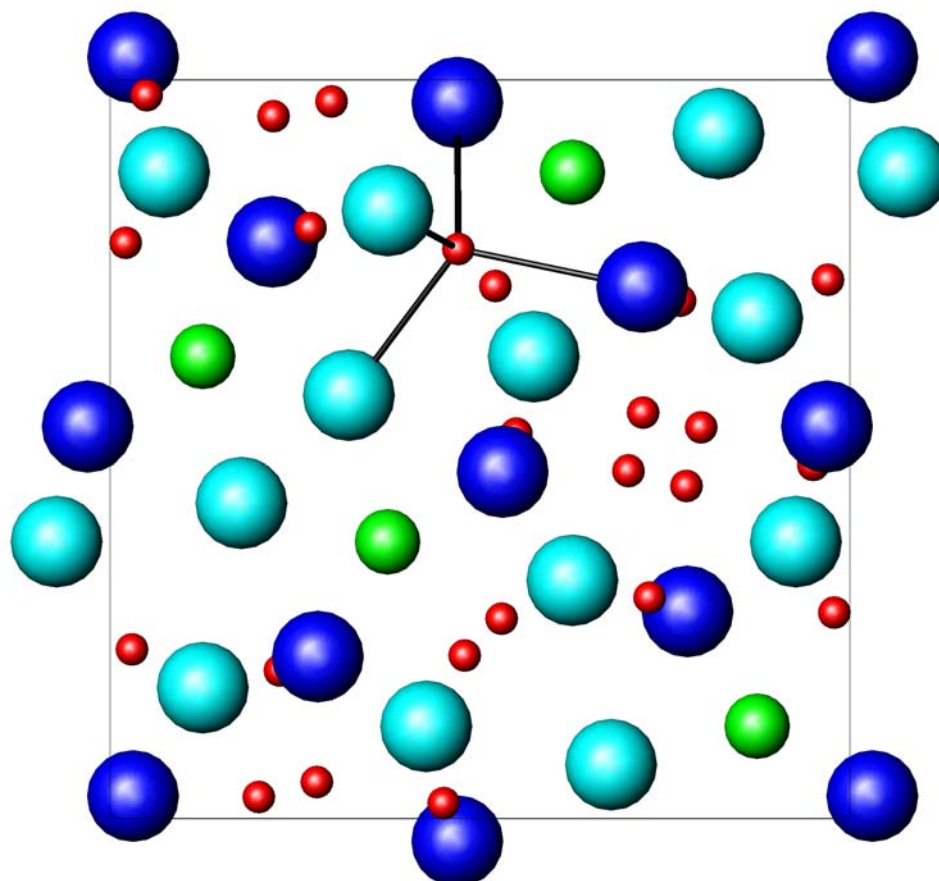


$P 4_132$
 $a \sim 11.24 \text{ \AA}$

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

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

Ag_4RbI_5 : Ag1 SITES

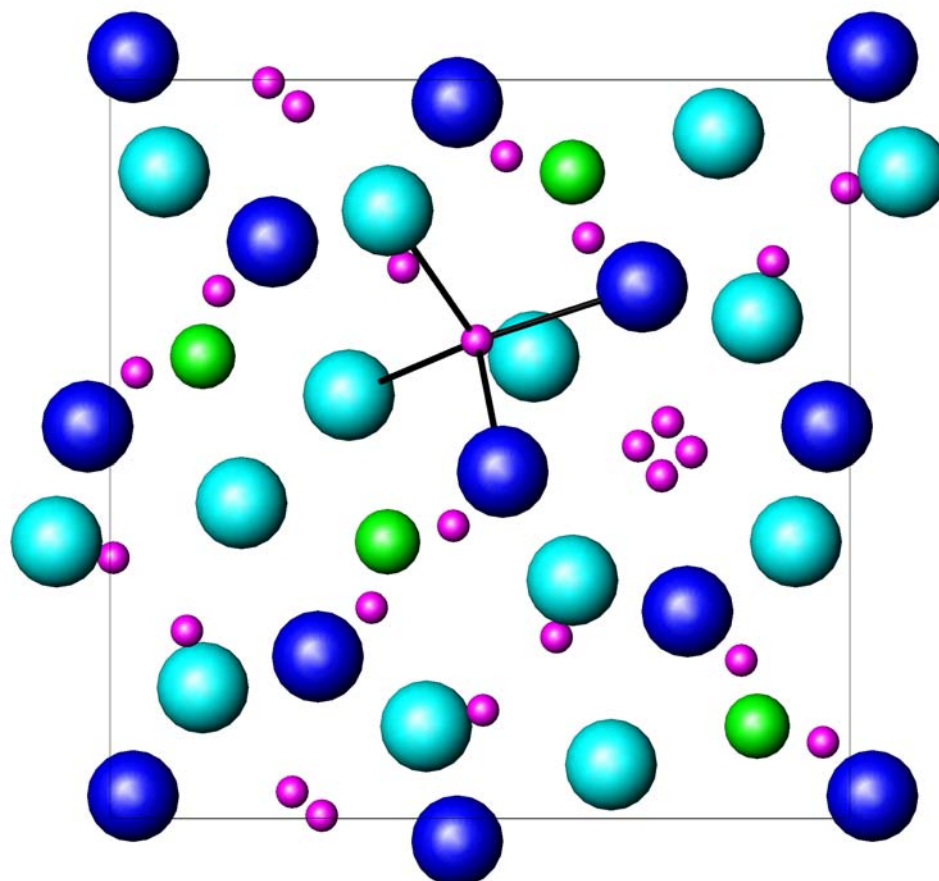


$P 4_132$
 $a \sim 11.24 \text{ \AA}$

Ag1 in 24(e)
 x, y, z
 $x \sim 0.531$
 $y \sim 0.272$
 $z \sim 0.806$

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

Ag_4RbI_5 : Ag2 SITES

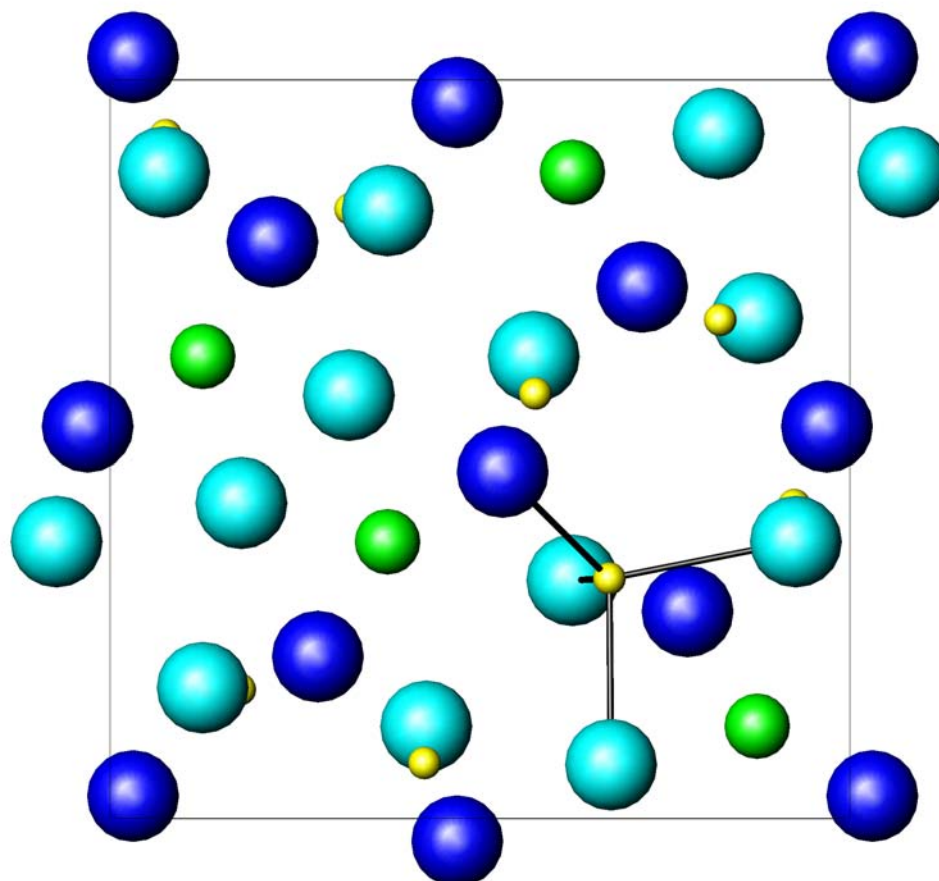


$P 4_132$
 $a \sim 11.24 \text{ \AA}$

Ag2 in 24(e)
 x, y, z
 $x \sim 0.993$
 $y \sim 0.855$
 $z \sim 0.206$

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

Ag_4RbI_5 : Ag3 SITES

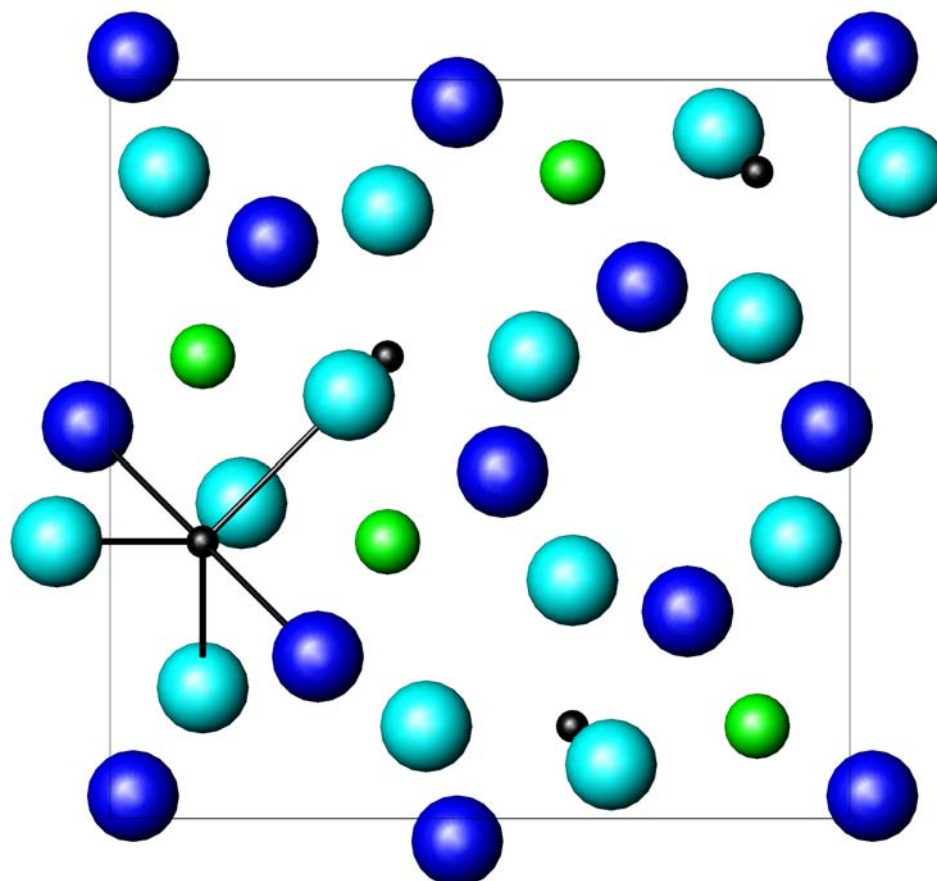


$P 4_132$
 $a \sim 11.24 \text{ \AA}$

Ag3 in 8(c)
 x, x, x
 $x \sim 0.177$

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

Ag_4RbI_5 : Ag4 SITES

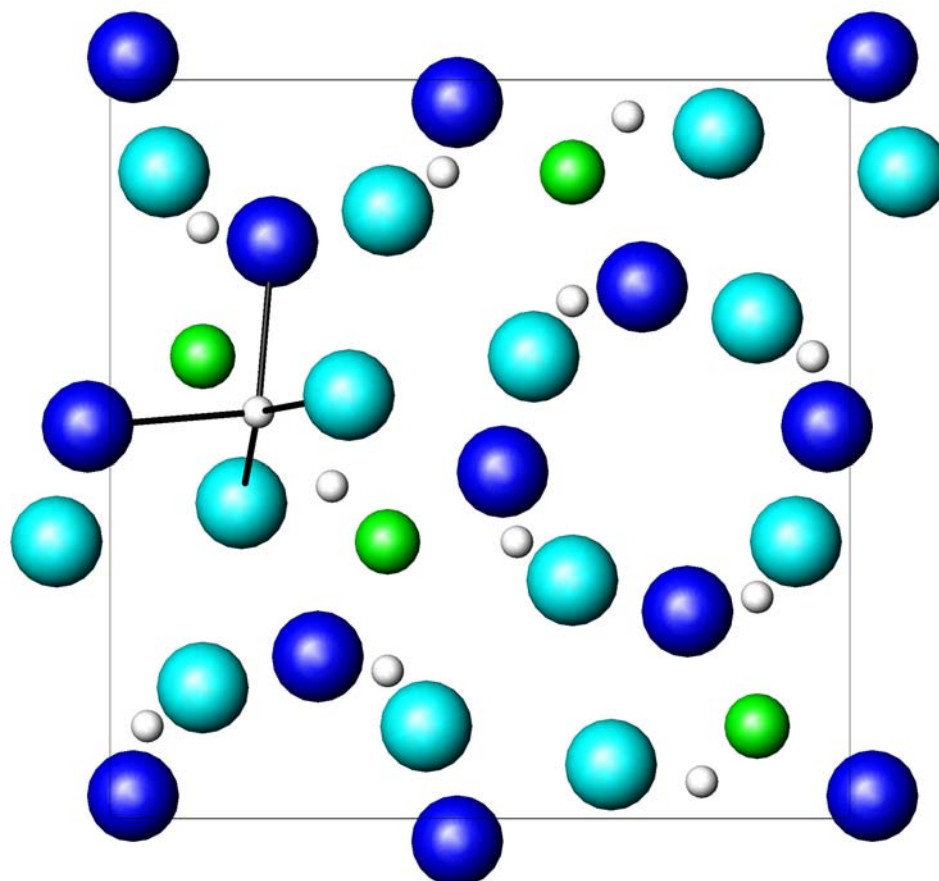


$P 4_132$
a ~11.24Å

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

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

Ag_4RbI_5 : Ag5 SITES

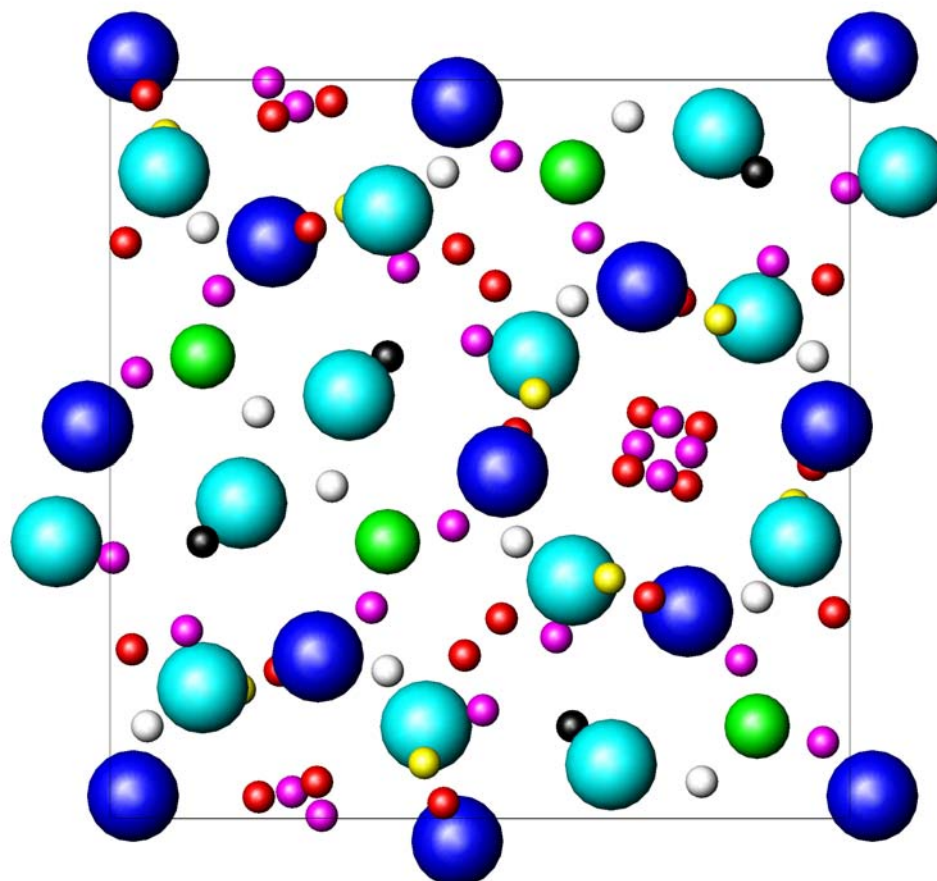


$P 4_132$
 $a \sim 11.24 \text{\AA}$

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

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

Ag_4RbI_5 : Ag SITES



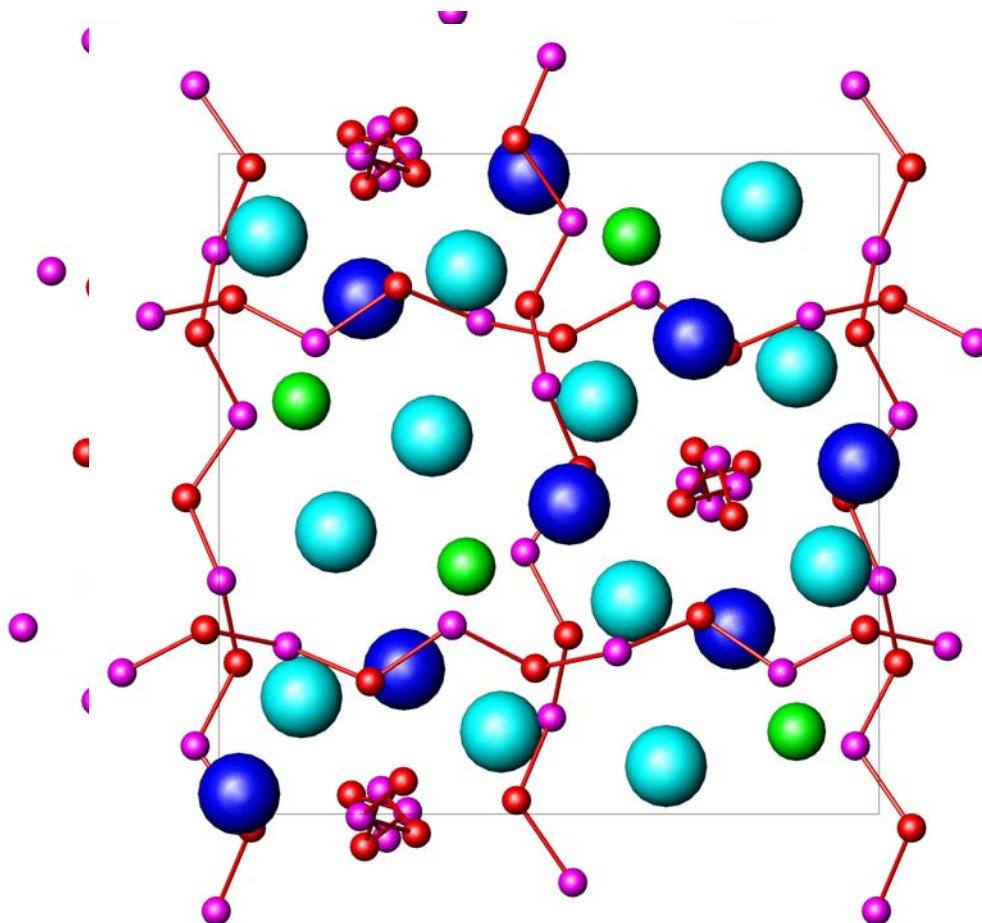
$P 4_132$
a ~11.24Å

$20 \times \text{Ag}^+$
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.

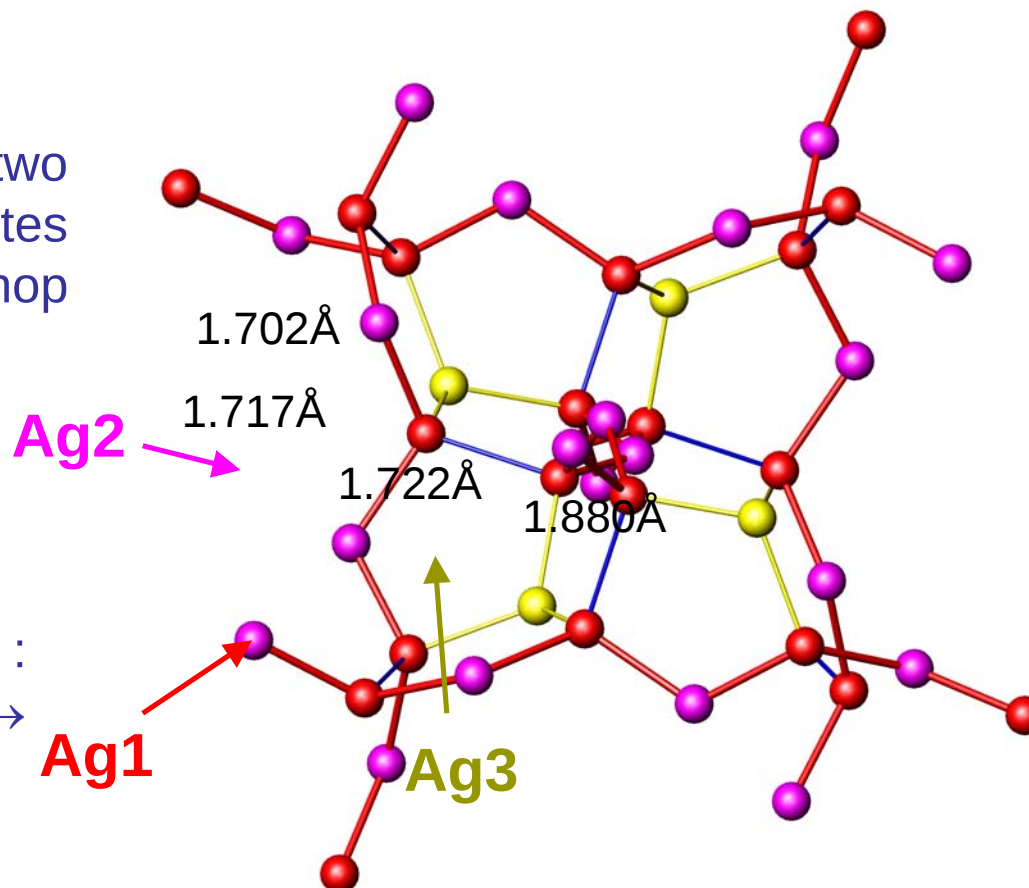
- Ag⁺ hop between pairs of these sites in <001> directions.
- conduction of Ag⁺ occurs along one-dimensional channels.

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

Ag₄RbI₅ : Diffusion between channels

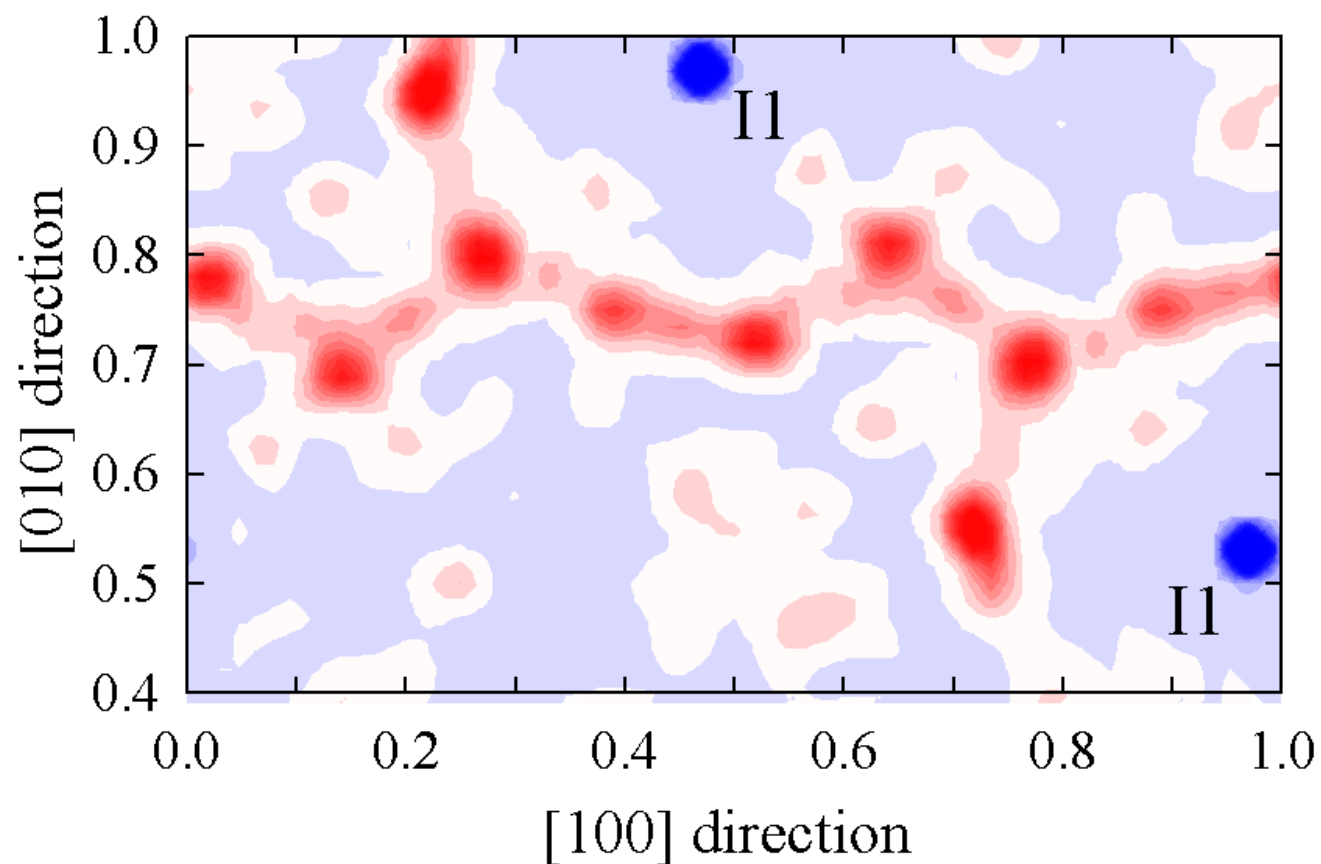
There are two plausible routes for Ag⁺ to hop between channels.

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



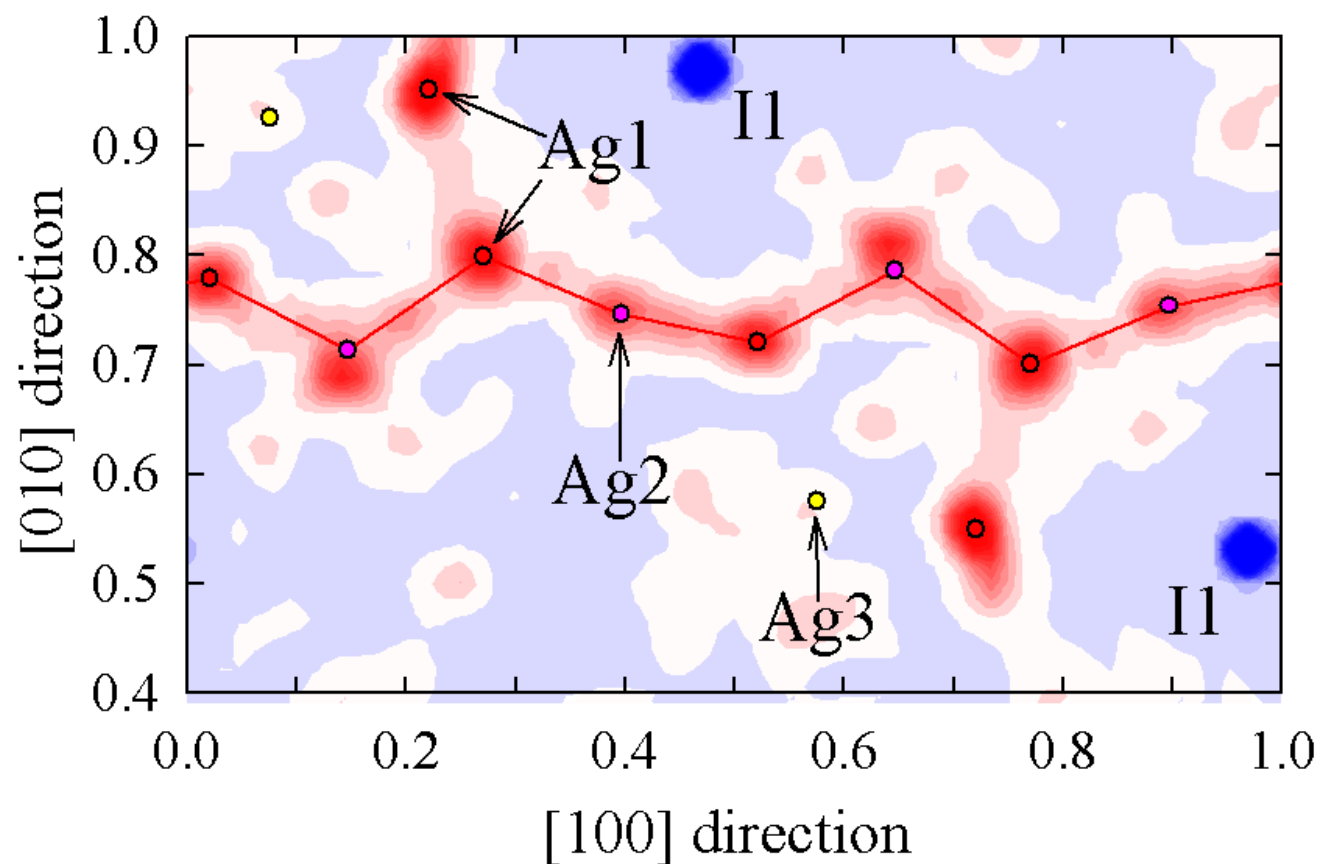
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag_4RbI_5 : Maximum entropy Fourier map



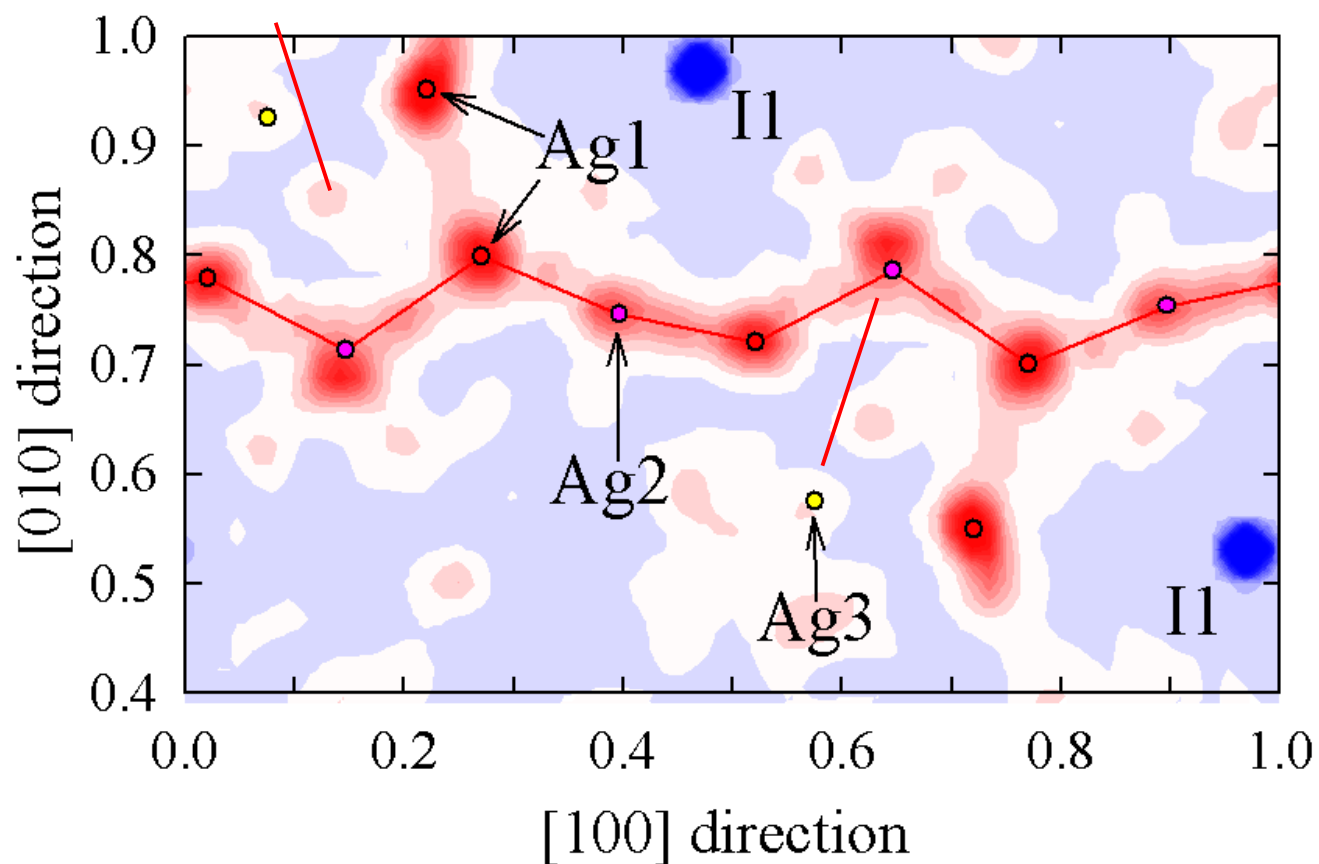
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

Ag_4RbI_5 : Maximum entropy Fourier map

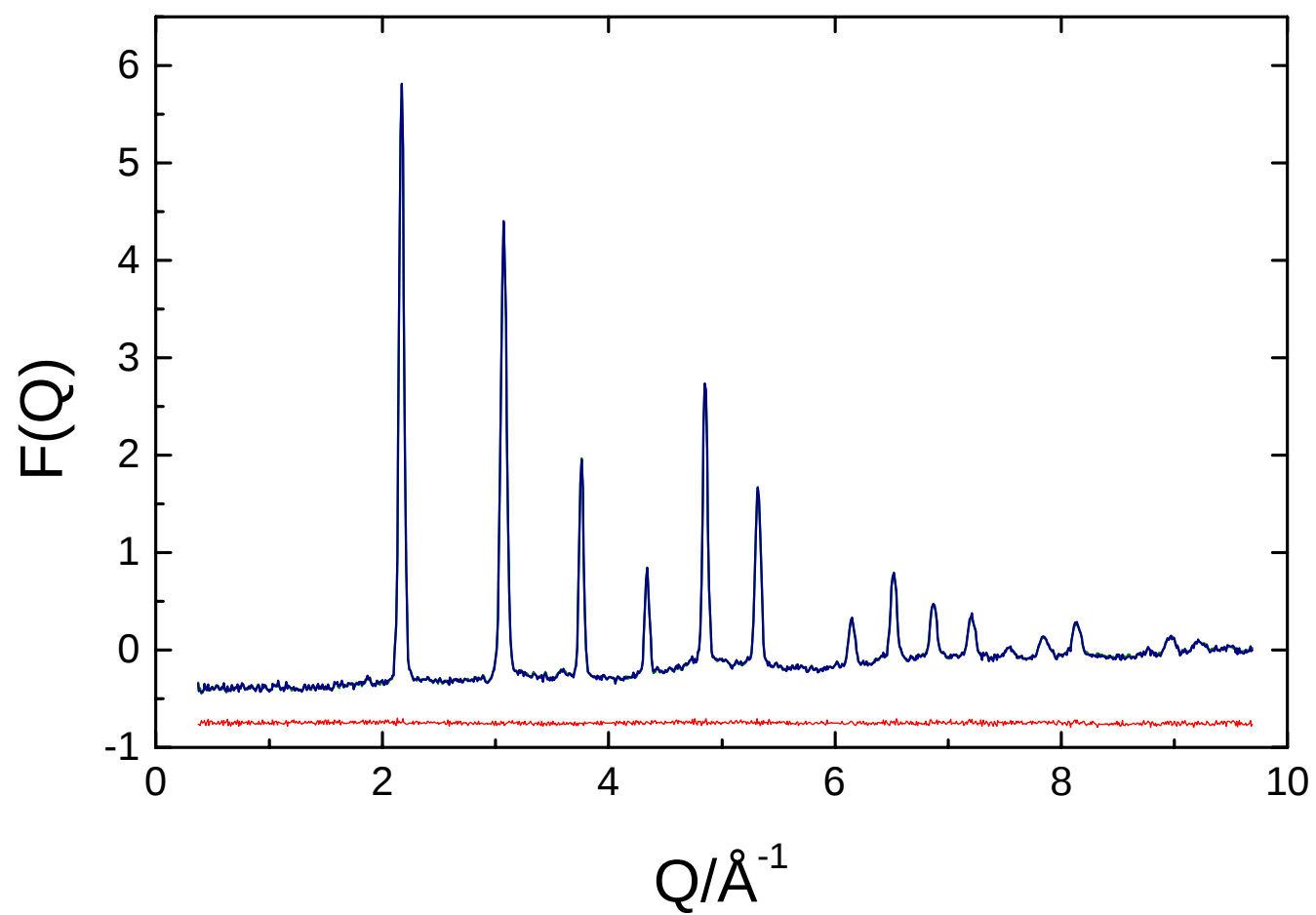


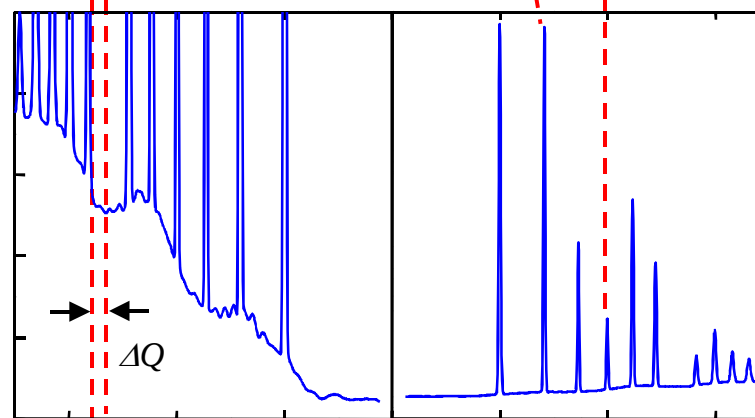
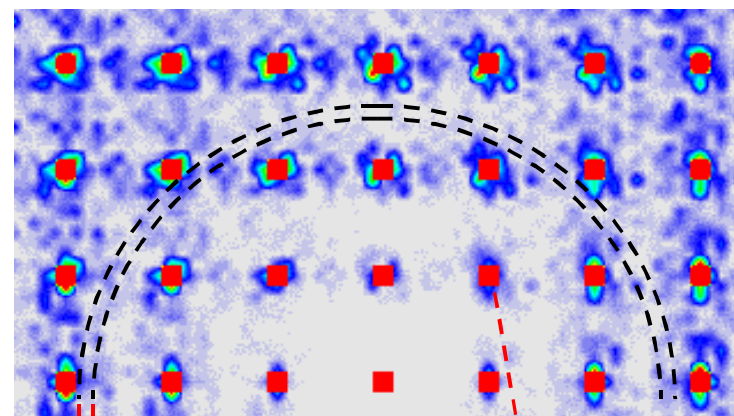
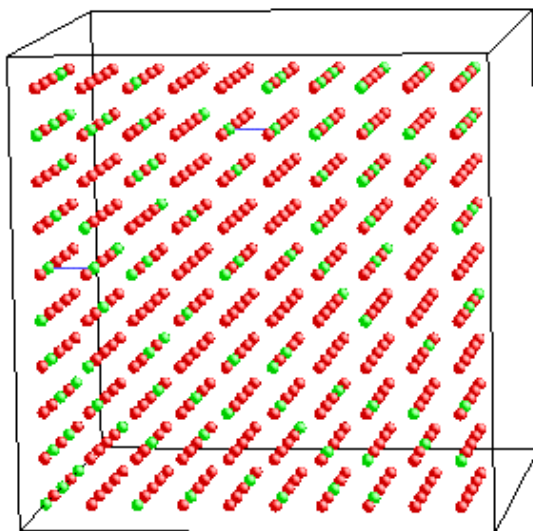
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

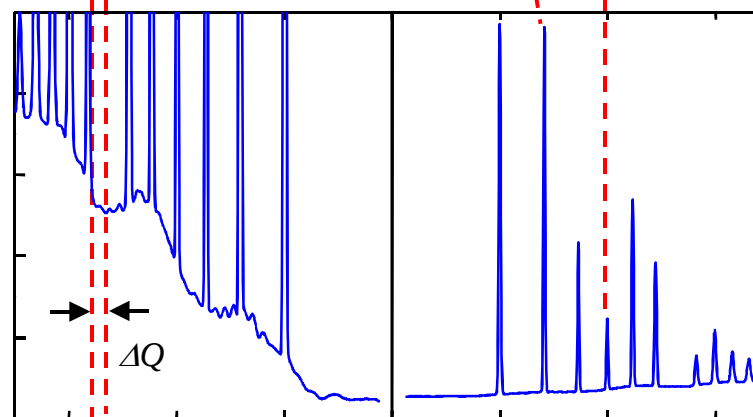
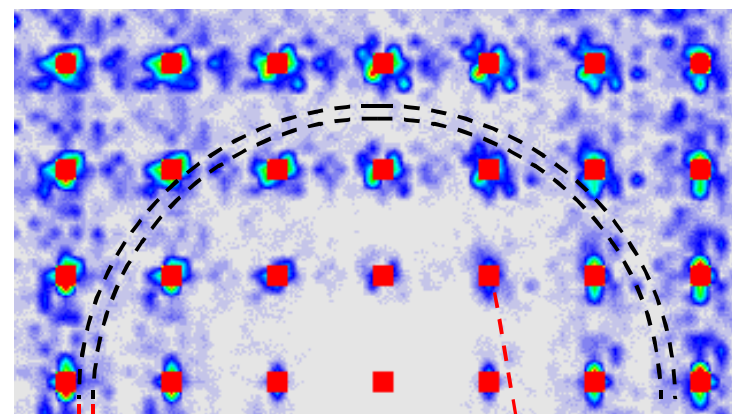
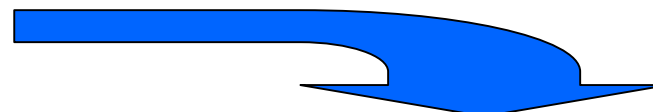
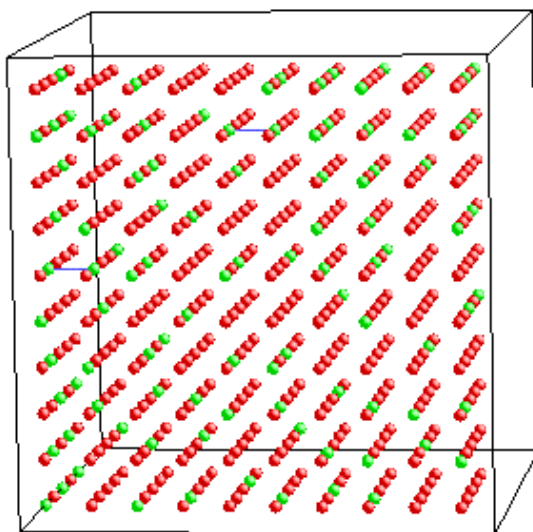
Ag_4RbI_5 : Maximum entropy Fourier map

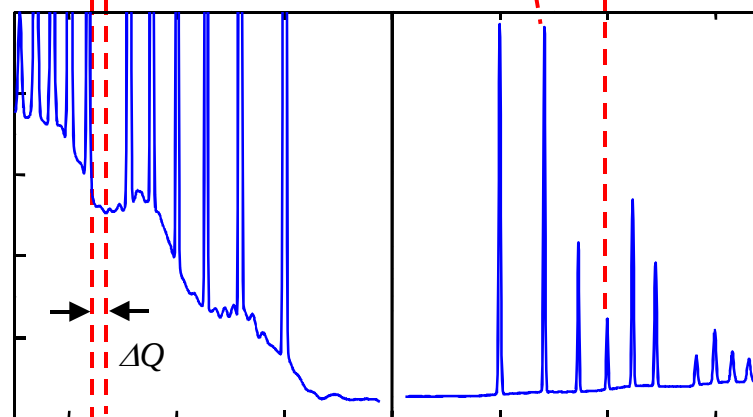
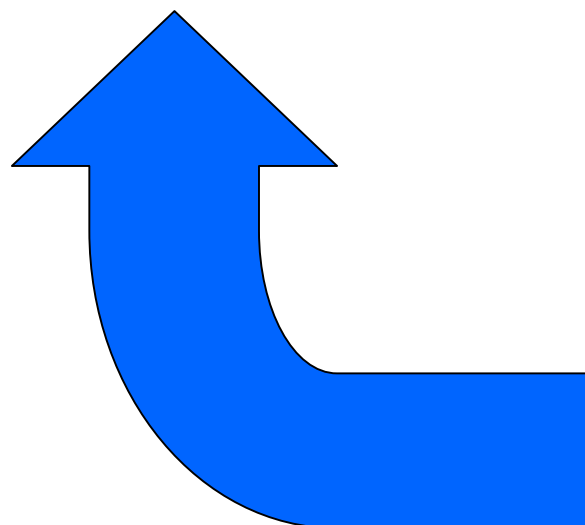
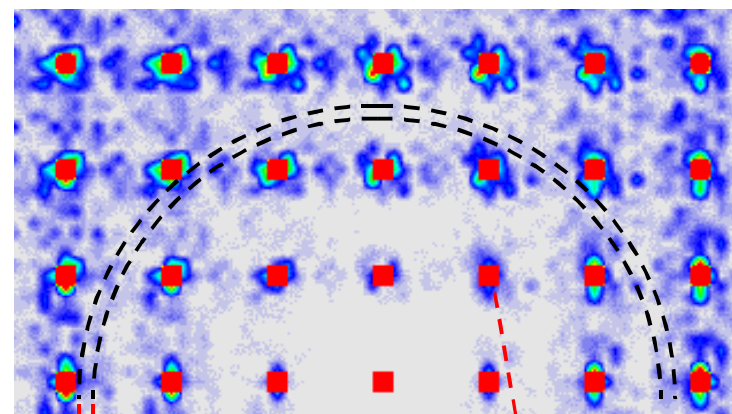
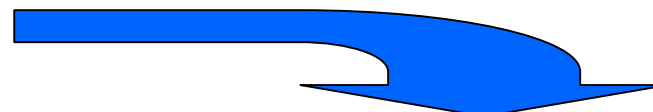
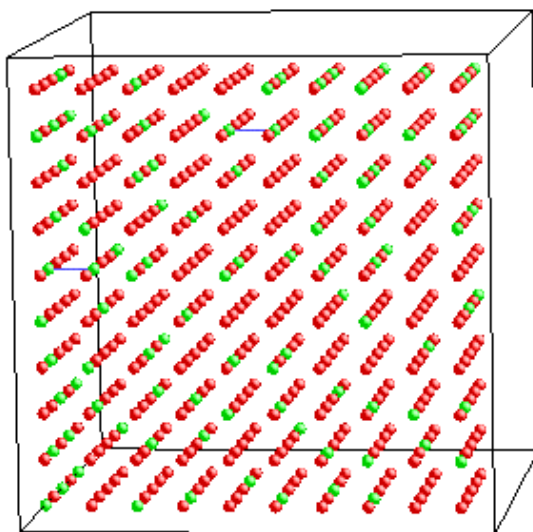


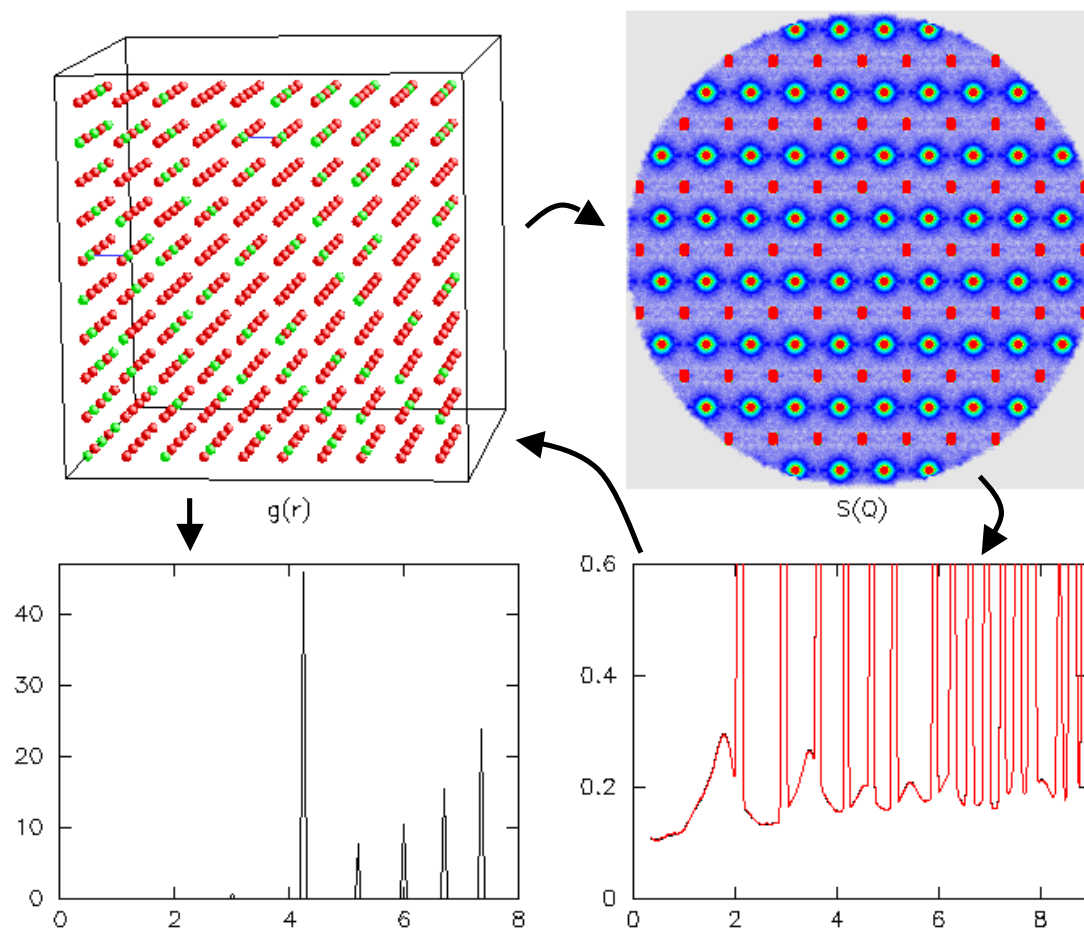
AgI : CHEMICAL DOPING (Hull et al. 2002, ISIS)

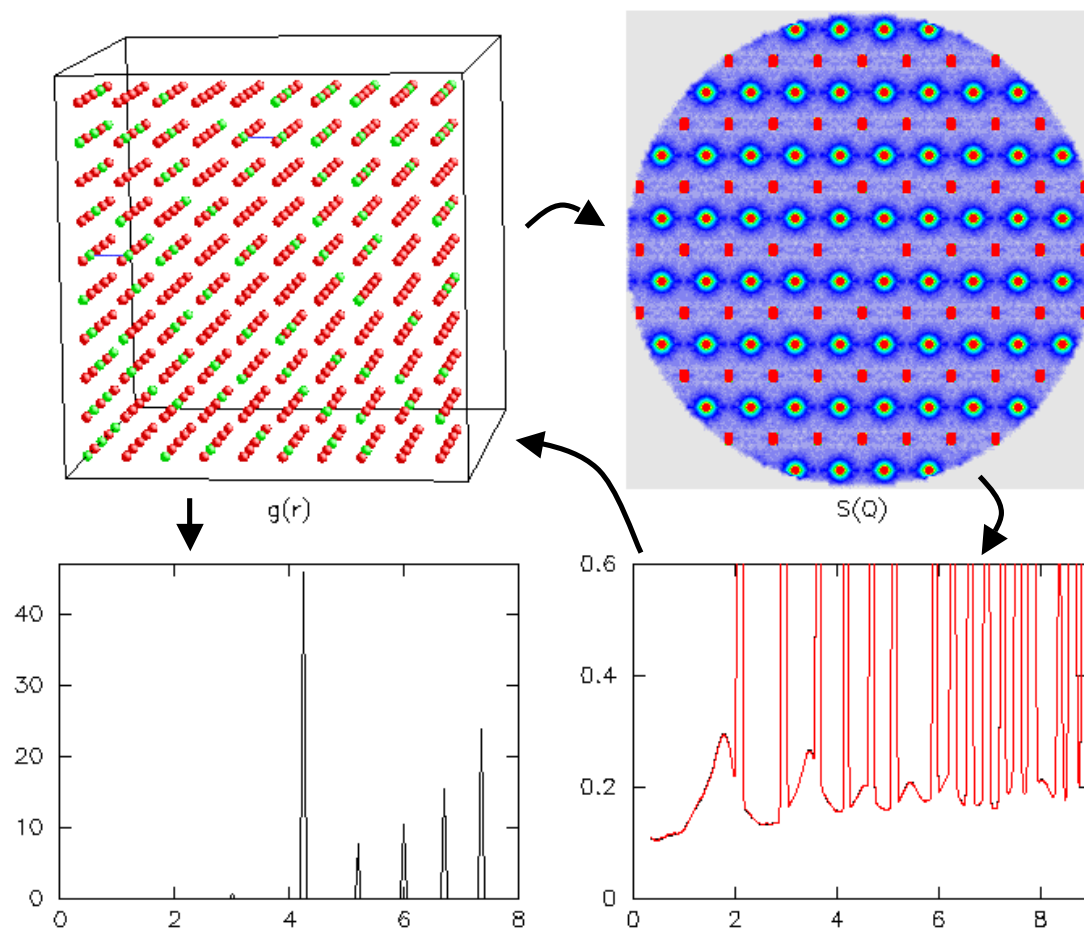


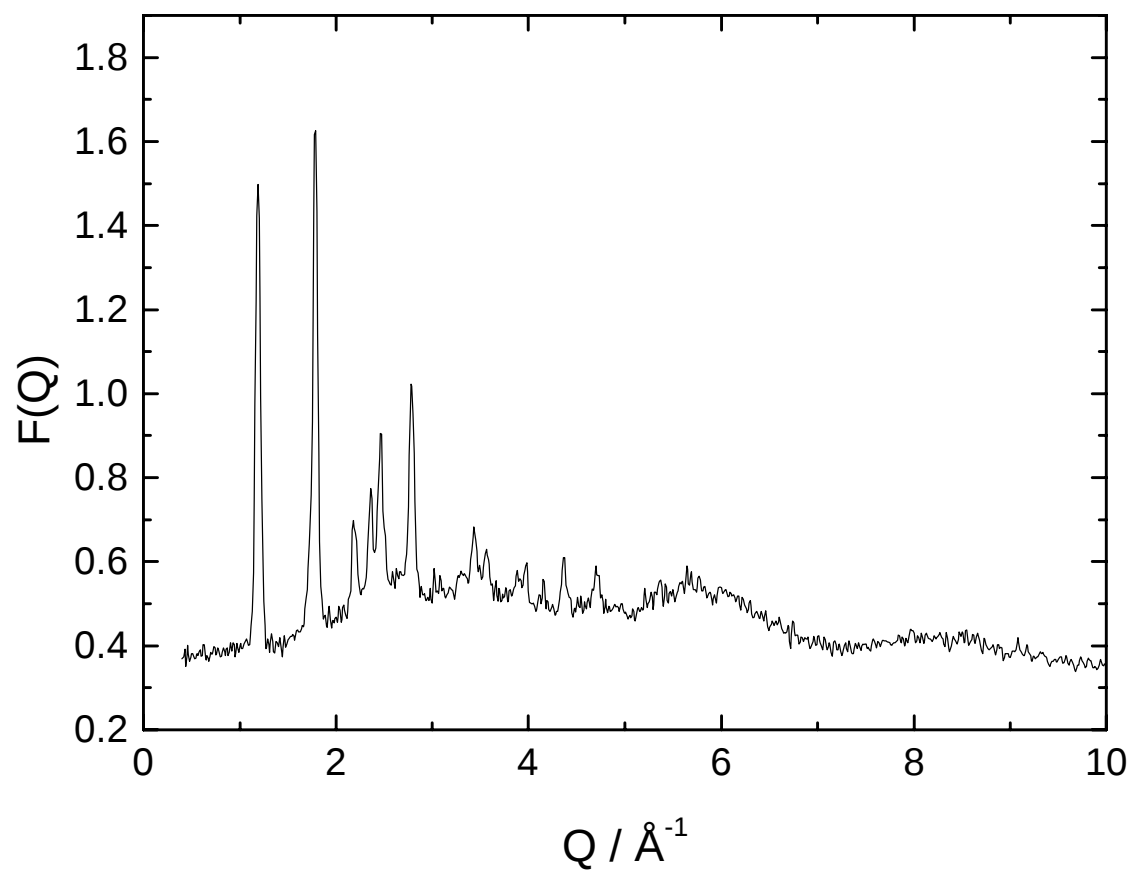




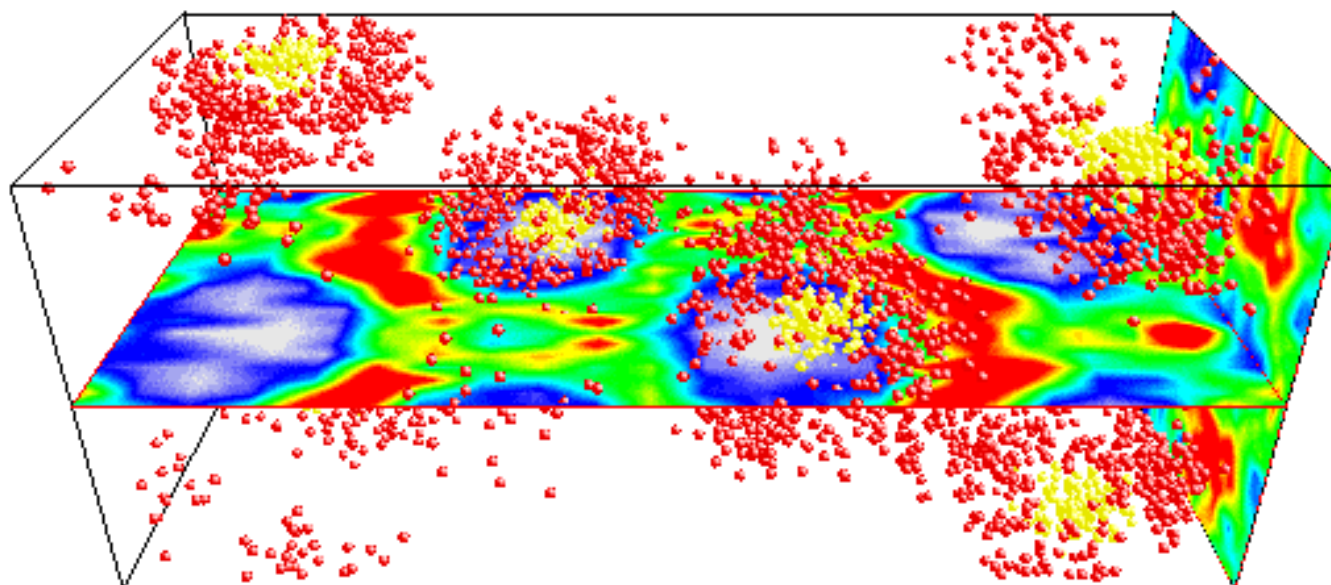




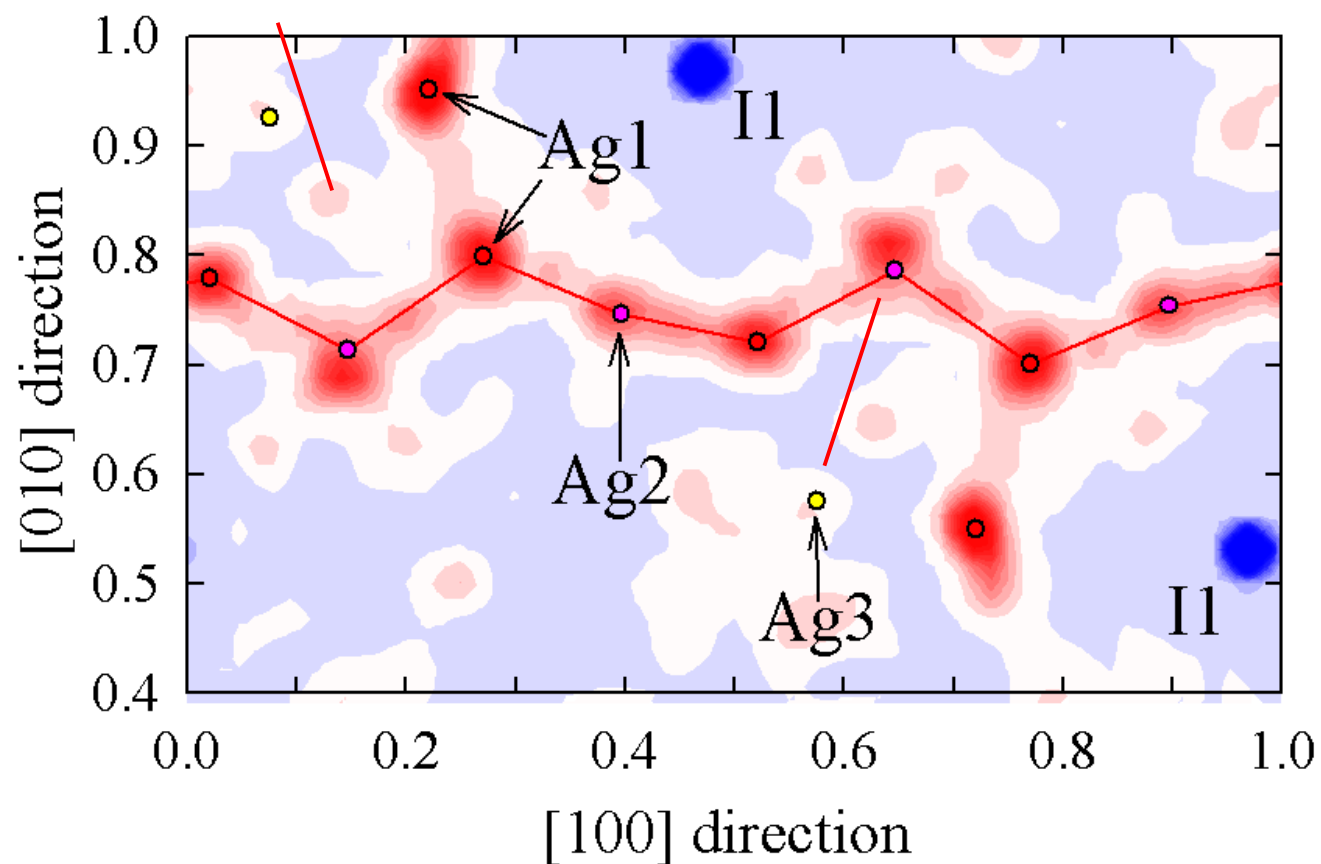




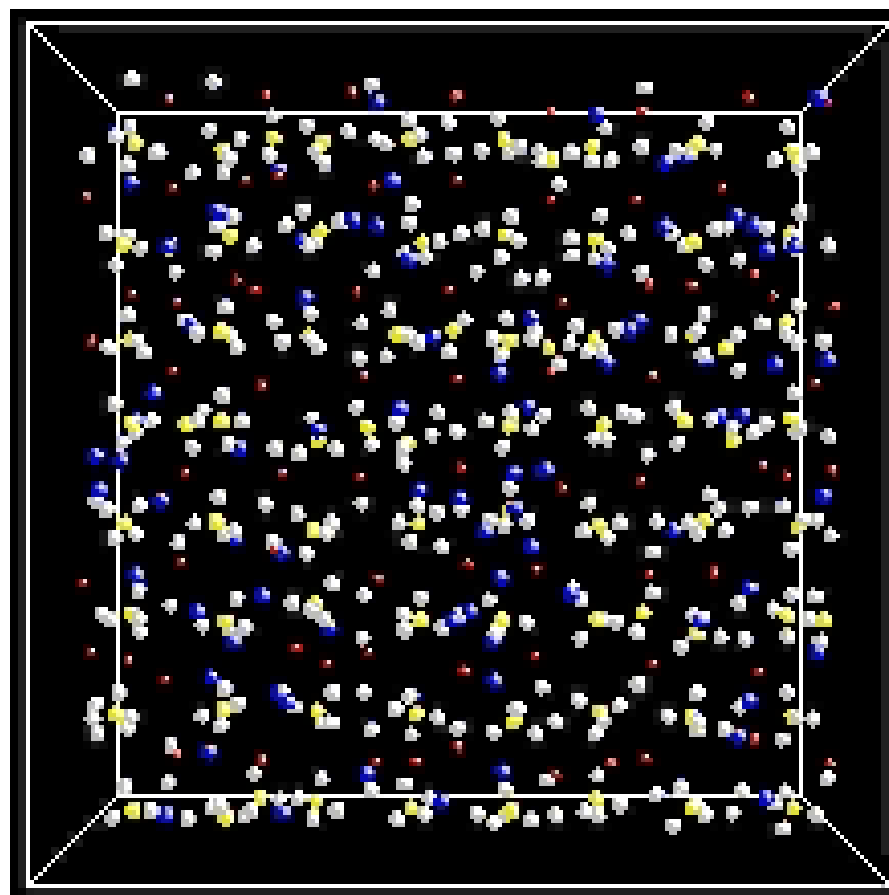
CsDSO_4

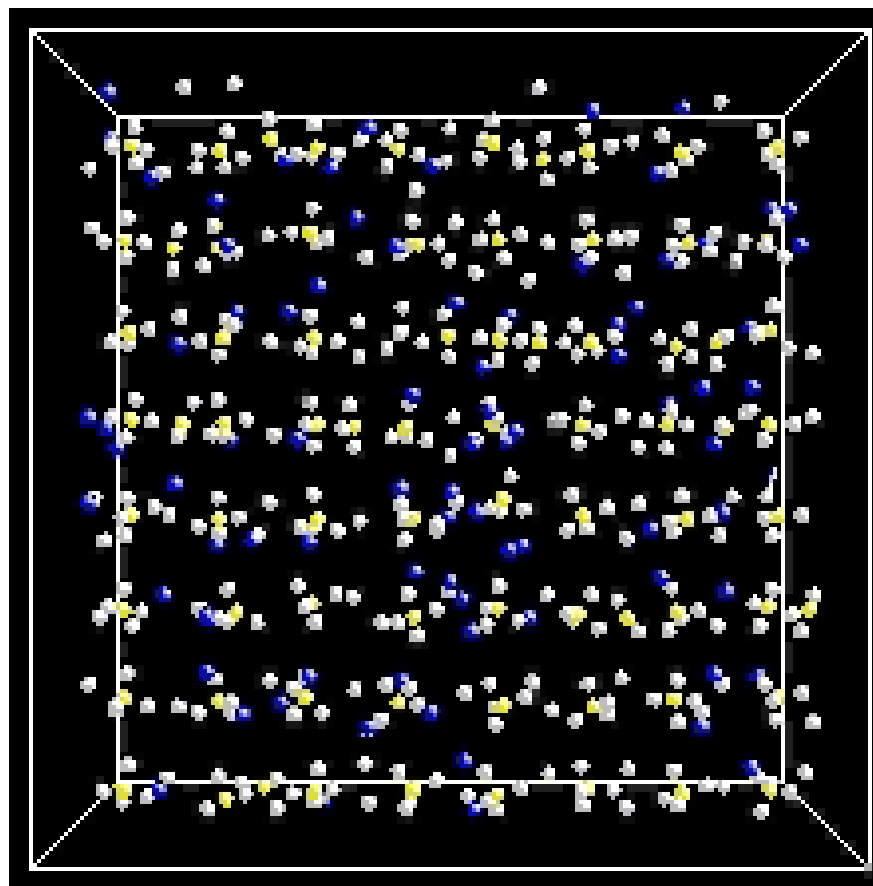


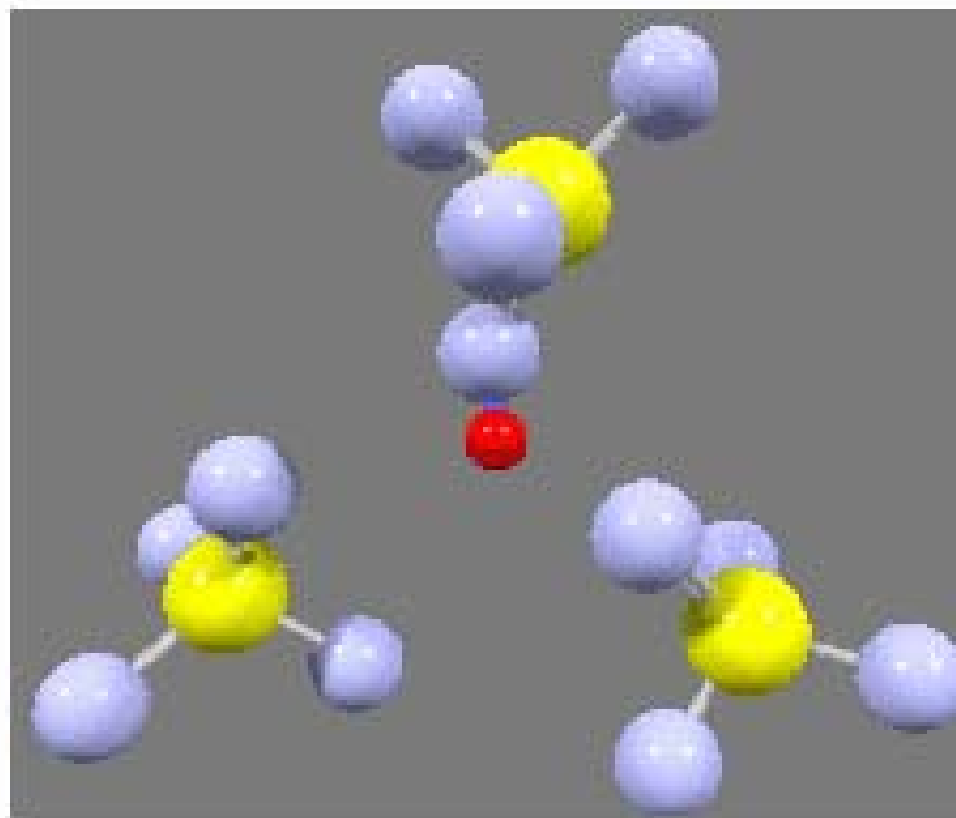
Ag_4RbI_5 : Maximum entropy Fourier map



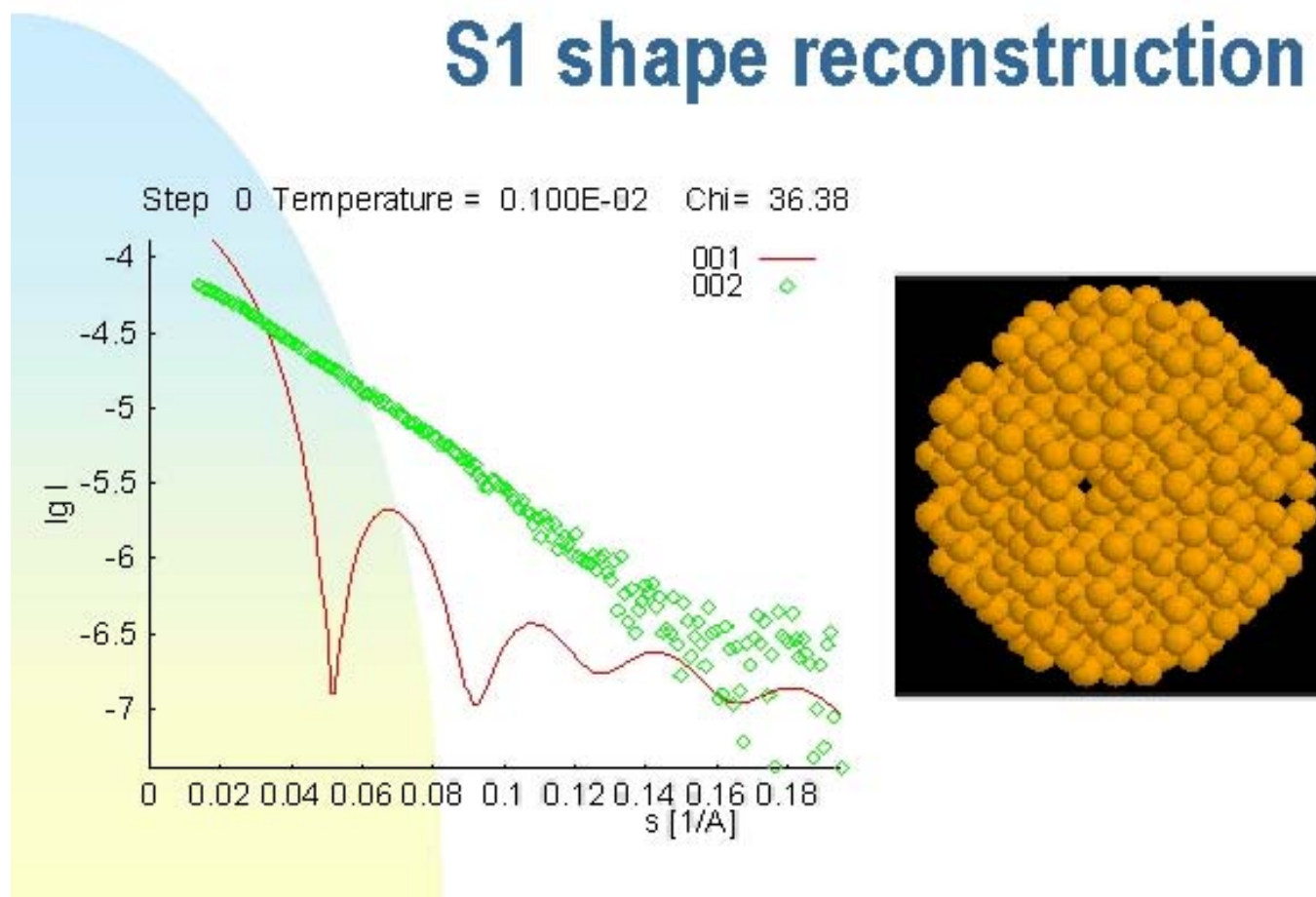
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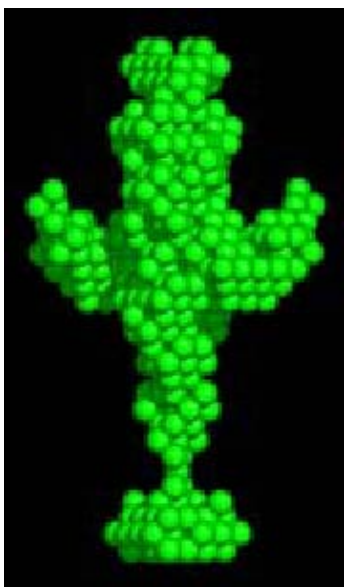


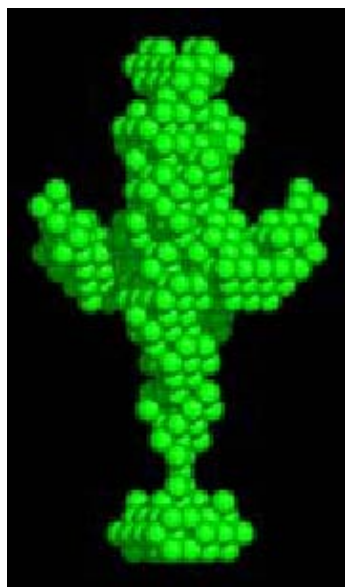


S1 shape reconstruction

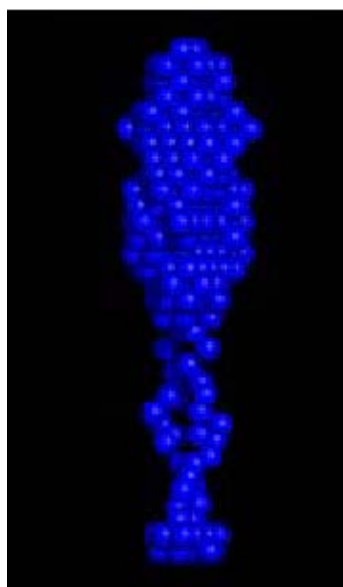


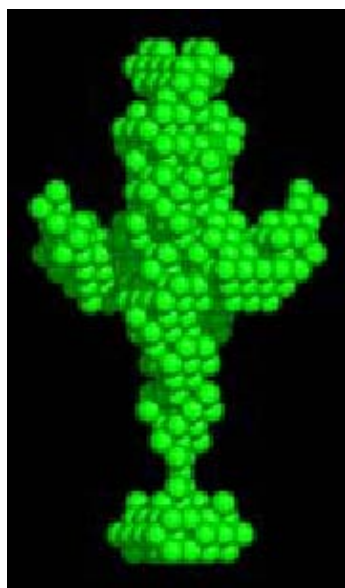




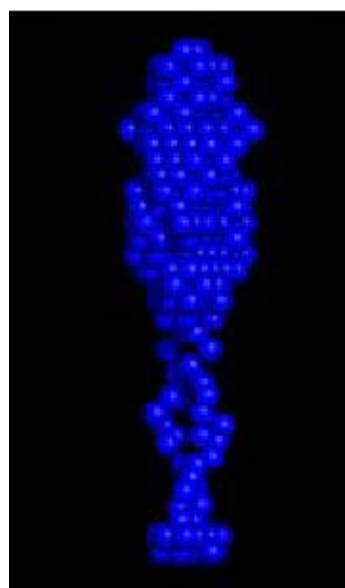


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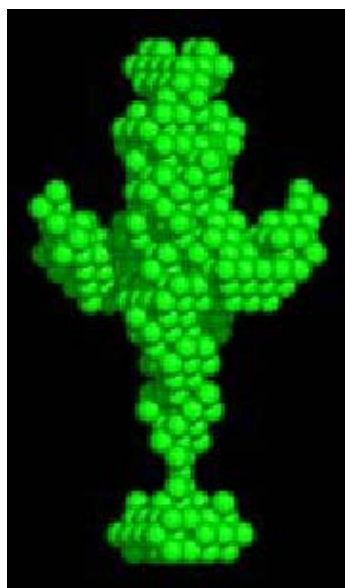


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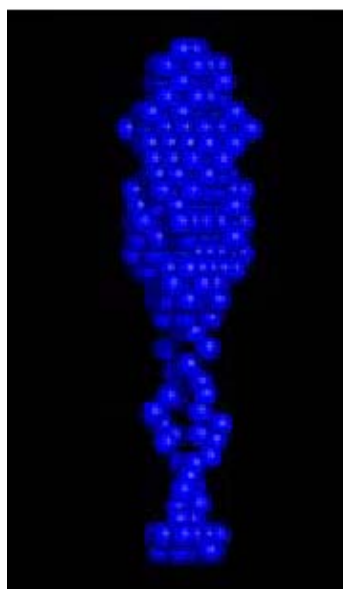


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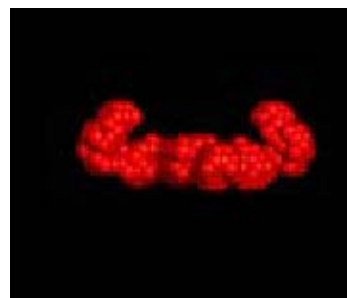




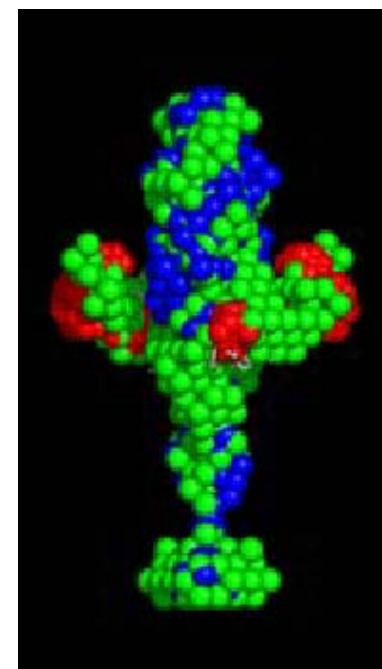
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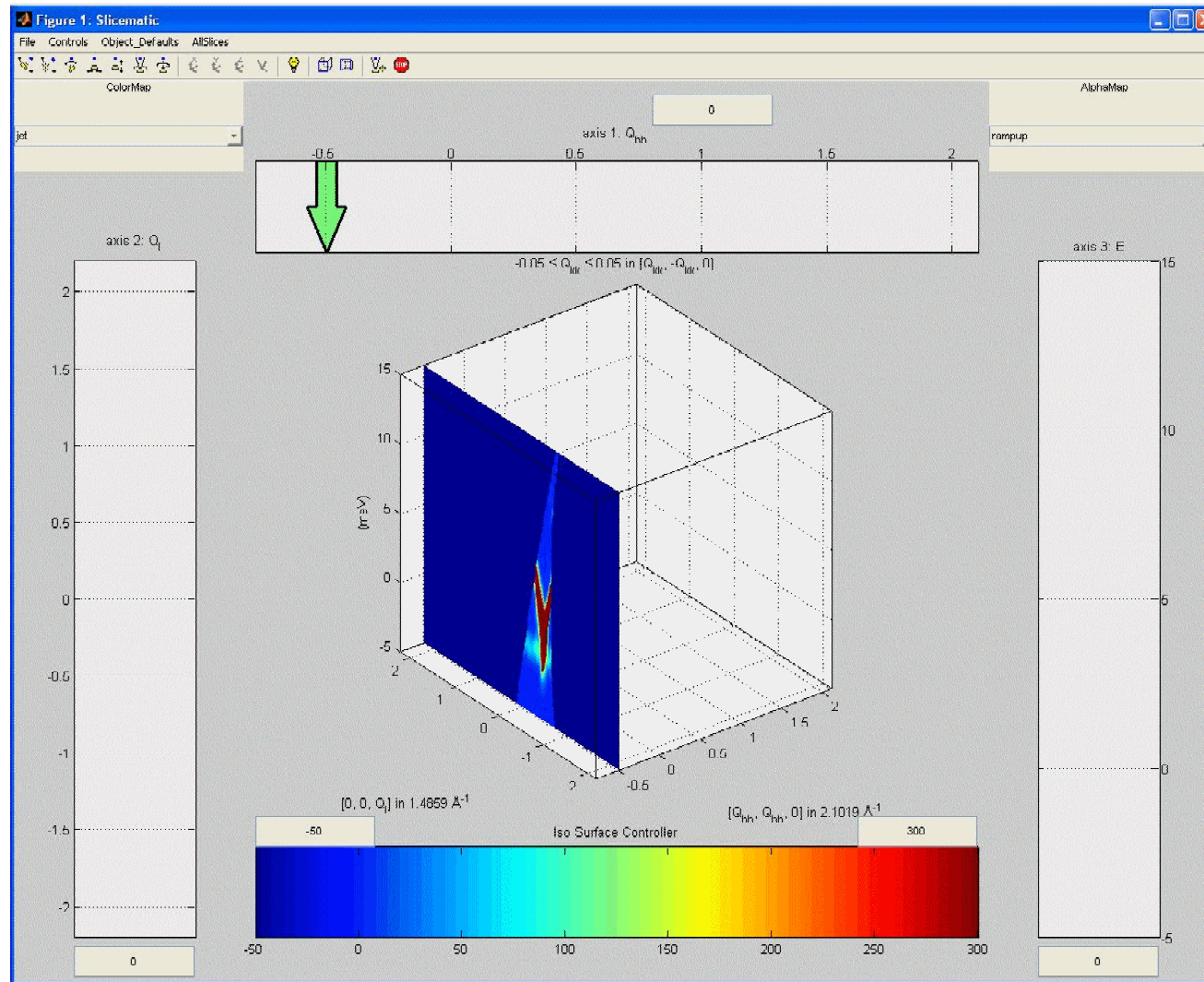


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Neutron Scattering Data Analysis

Robert McGreevy

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Chilton, Didcot, OX11 0QX, UK.*

From here to there

