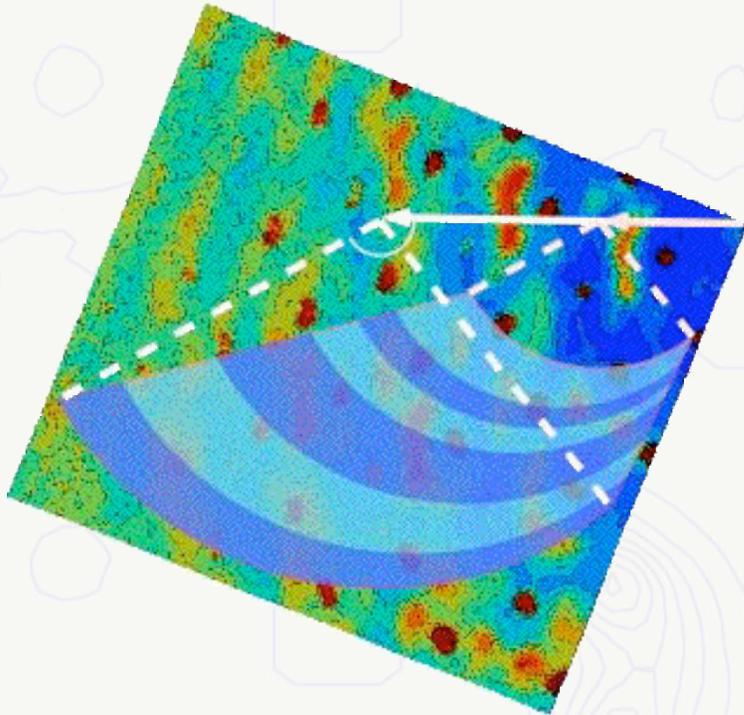


Monte Carlo Based Modeling of Single Crystal Diffuse Scattering



Thomas Proffen

Lujan Neutron Scattering Center
Los Alamos National Laboratory

Richard Welberry

Research School of Chemistry
The Australian National University

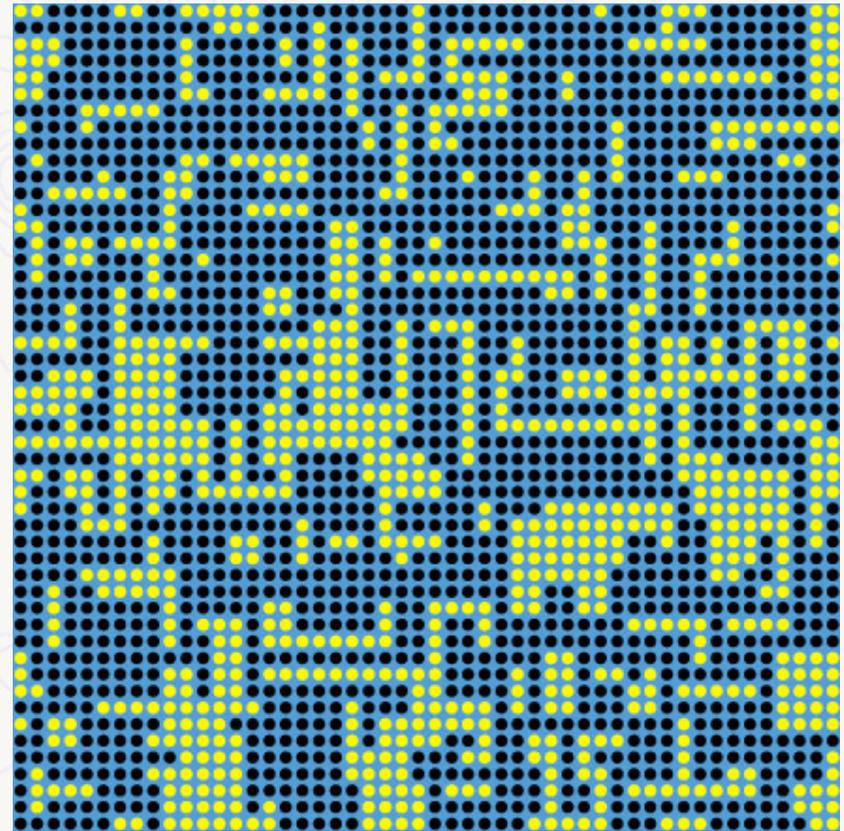
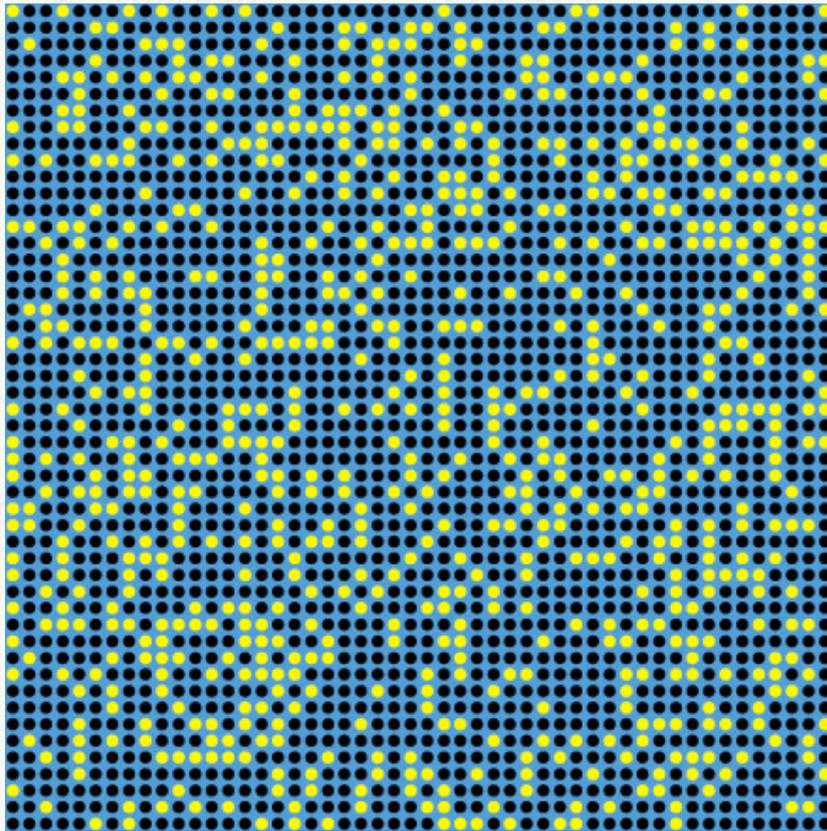


Outline

- **Introduction**
 - Looking between the Bragg peaks
 - Analyzing diffuse scattering
- **The Reverse Monte Carlo (RMC) simulation method**
 - RMC refinements of simulated test structures
 - RMC refinements of cubic stabilized zirconia
- **The Automatic Monte Carlo (AMC) simulation method**
 - AMC refinements of $\text{Fe}_3(\text{CO})_{12}$
- **Summary**



Diffuse scattering ?

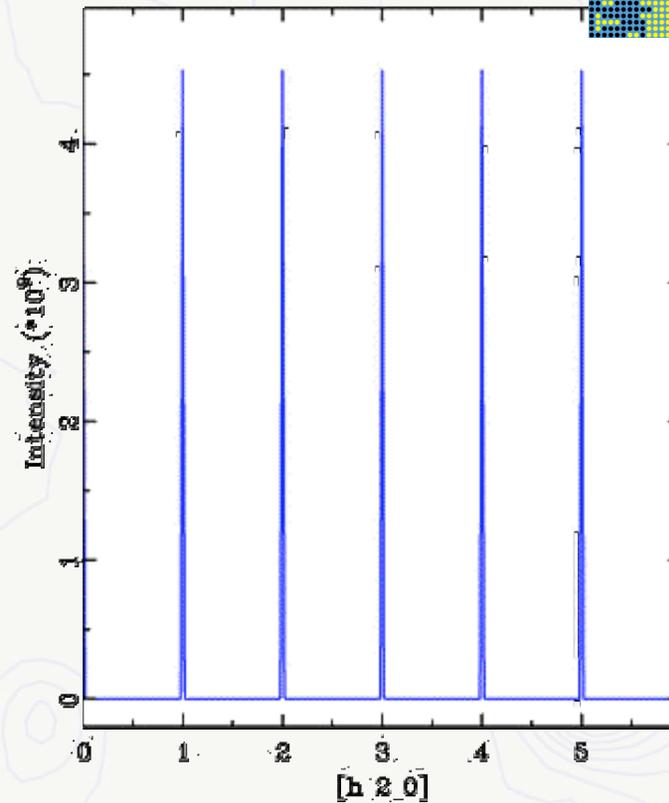
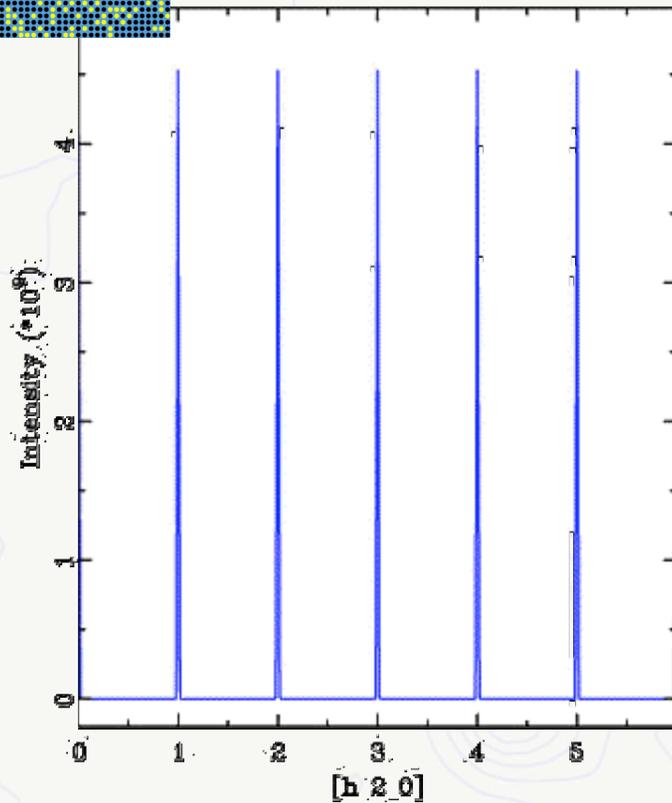
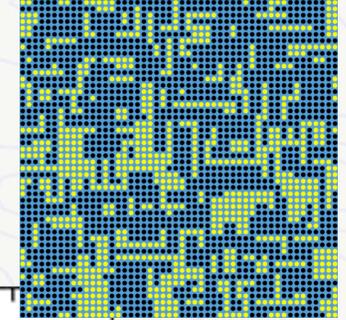
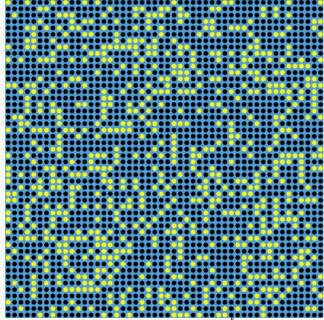


Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !
Properties might depend on vacancy ordering !!



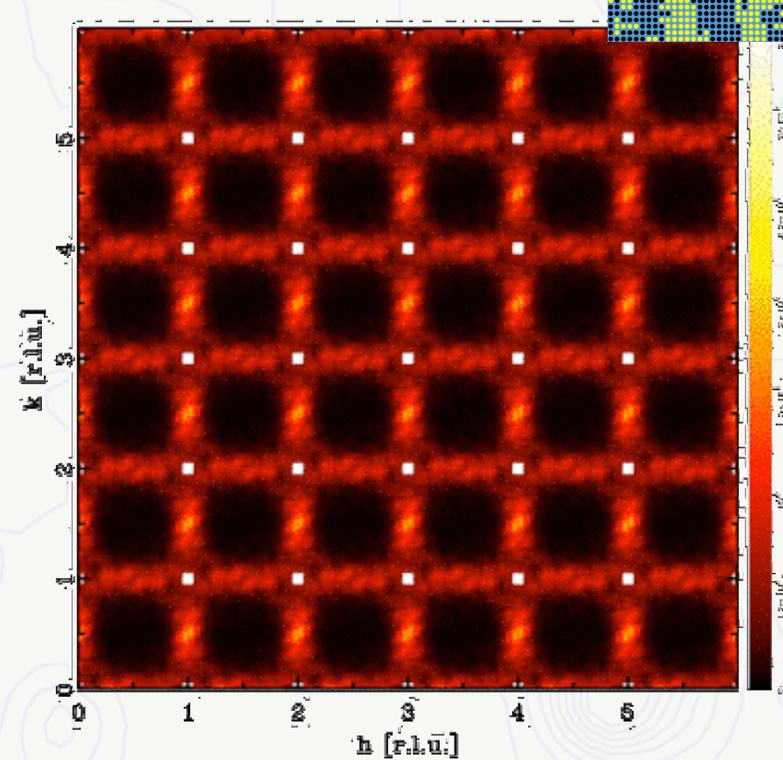
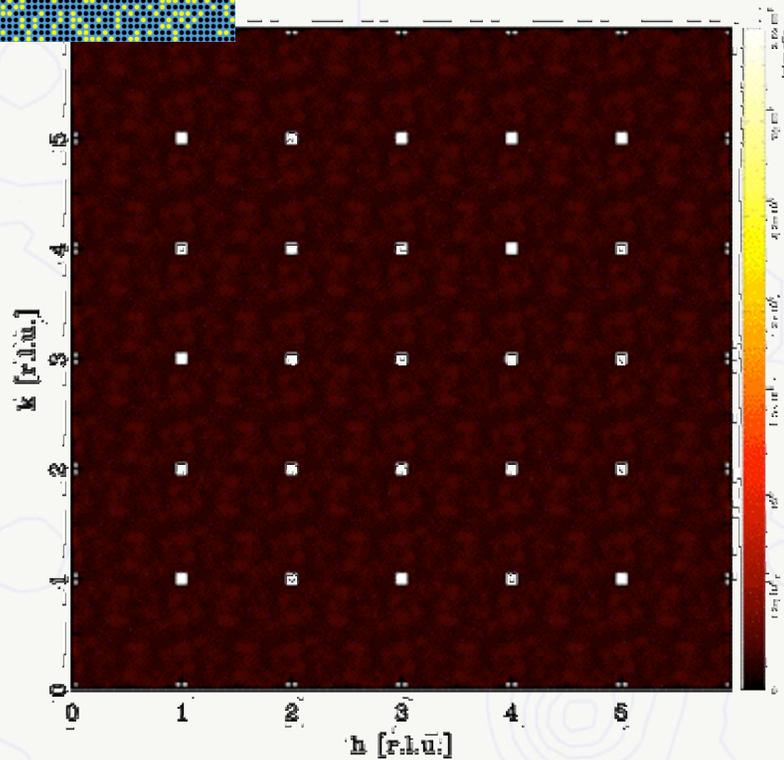
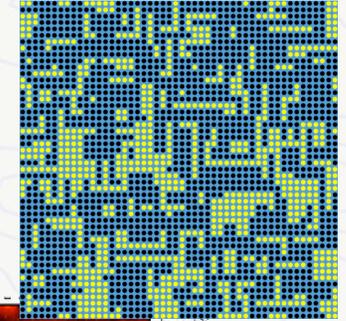
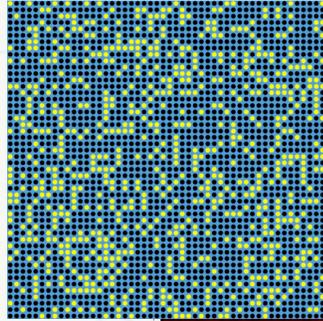
Bragg peaks are blind ..

Bragg scattering: Information about the *average* structure, e.g. average positions, displacement parameters and occupancies.



Diffuse scattering to the rescue ..

Diffuse scattering: Information about *two-body correlations*, i.e. chemical short-range order or local distortions.



See <http://www.totalscattering.org/teaching/>

Short range order simulator - Netscape

Interactive Tutorial about Diffraction Short range order simulator

Disordered structure
MC cycles: 20

x [u.u.]

Scattering: Neutrons
Scale: 1.1 * Average scattering

Intensity

Concentration achieved (%) : 24.040

CORRELATIONS :

a(100):	Target: 0.500	-	Achieved: 0.371
a(010):	Target: -0.200	-	Achieved: -0.108
a(110):	Target: 0.300	-	Achieved: 0.211
a(200):	Target: 0.000	-	Achieved: 0.019
a(020):	Target: 0.000	-	Achieved: 0.027

BRAGG INTENSITIES

(1 0 0) :	1064017.4
(0 1 0) :	1062985.1
(4 0 0) :	1064017.5
(0 4 0) :	1062984.9

Concentration (%) : 25.0
MC cycles: 20

Correlation c₁₀₀: 0.5
c₀₁₀: -0.2
c₁₁₀ = c₁₋₁₀: 0.3
c₂₀₀: 0.0
c₀₂₀: 0.0

Radiation:
X-rays
Neutrons

RUN

[Postscript] [Close window]
Created: 08. Jun 2003 at 05:12 PM

$$I_{\text{sro}} = - \sum_{ij} \sum_{lmn} c_i c_j f_i f_j \alpha_{lmn}^{ij} \cos(2\pi \mathbf{k} \cdot \mathbf{r}_{lmn})$$

Created using the programs [DISCUS](#) and [KUPLOT](#)



Analyzing diffuse scattering

- **Correlation approach:** Expansion of kinematic scattering equation in terms of displacement. Yields set of two-body correlations.
- **Monte Carlo based computer simulations:** Scientist might “win” solution to the problem ..
 - Minimize total energy E : AMC
 - Minimize (observed – calculated)²: RMC
- **More:** “Diffuse Neutron Scattering from Crystalline Materials” by Nield and Keen, Oxford University Press

Table 1. Summary of the properties of the different components of the diffuse intensity.

Term	I_0	I_1	I_2	I_3
Description	Short-range order (SRO) term	Warren Size-effect	Huang Scattering 1st order TDS	3rd order size term
Lattice averages involved	SRO parameters α^{ij}	$\langle X^{ij} \rangle, \langle Y^{ij} \rangle$ etc.	$\langle (X^{ij})^2 \rangle, \langle X^{ij} Y^{ij} \rangle$ etc.	$\langle (X^{ij})^3 \rangle, \langle (X^{ij})^2 Y^{ij} \rangle$ etc.
Type of Summation	cosine	sine	cosine	sine
Symmetry	symmetric	anti-symmetric	symmetric	anti-symmetric
Variation in k -space	nil	linear, <i>i.e.</i> with h_1, h_2 etc.	quadratic, <i>i.e.</i> with $h_1^2, h_1 h_2$ etc.	cubic, <i>i.e.</i> with $h_1^3, h_1^2 h_2$ etc.
Dependence on f_A, f_B for binary	$(f_A - f_B)^2$	$f_A(f_A - f_B), f_B(f_A - f_B)$	$f_A^2, f_A f_B, f_B^2$	$f_A^2, f_A f_B, f_B^2$
Number of components for binary	1	6	18	30



before

now

The Reverse Monte Carlo Method

Input:

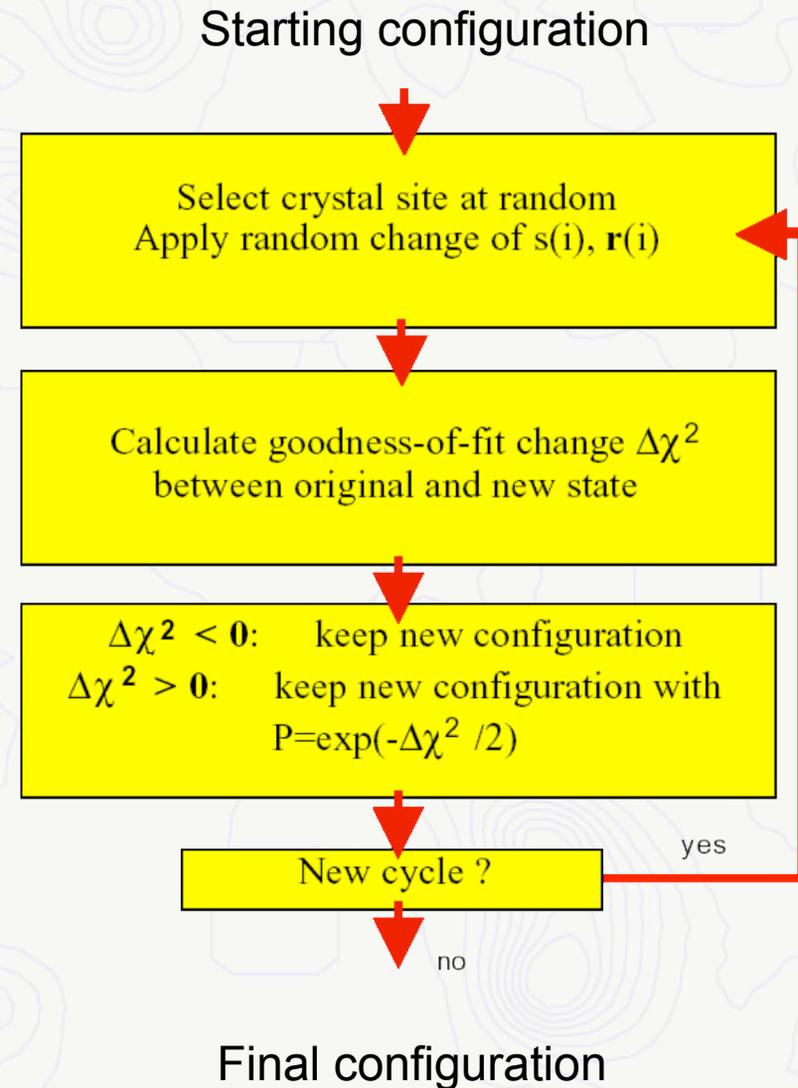
- Observed diffuse scattering
- Starting structure (e.g. average)
- Chemical constraints

Result:

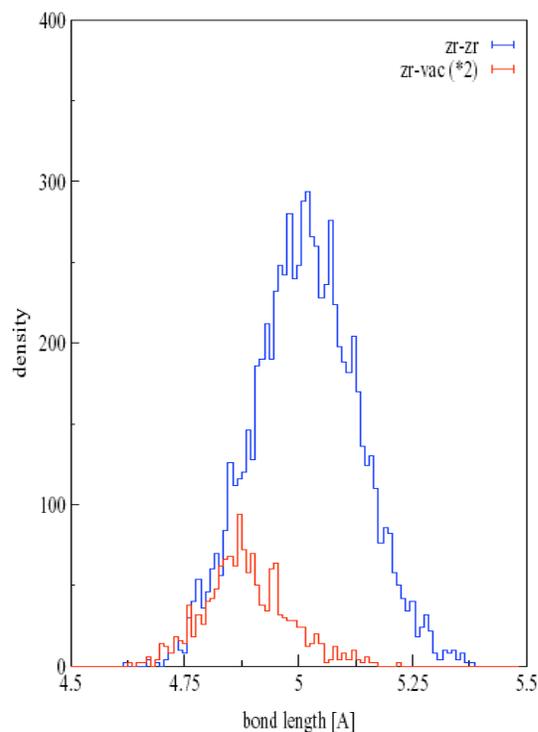
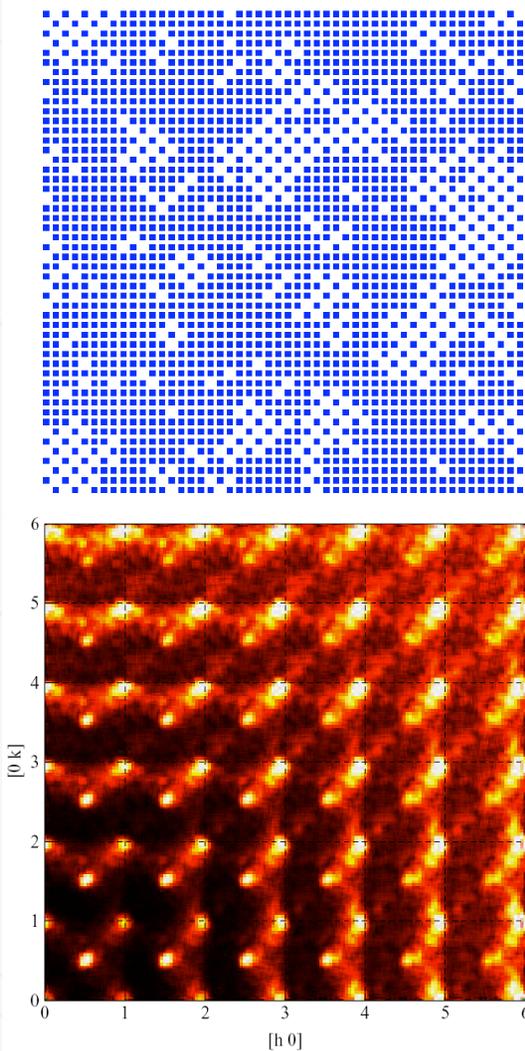
- *One* real space structure consistent with data

Questions:

- Uniqueness / plausibility of result
- Statistical analysis of resulting structure (many atoms)



RMC test simulations



Input data

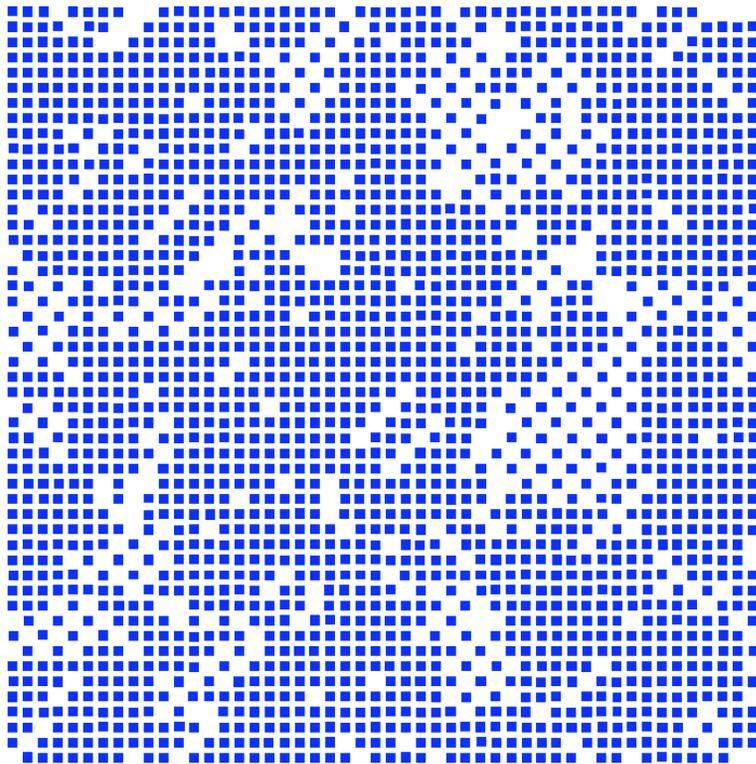
- 50x50 unit cells
- cubic, $a=5\text{\AA}$, Zr on (0,0,0)
- neutron scattering, $\lambda=1\text{\AA}$
- correlations / displacements

$$\Theta = 0.170$$
$$c_{10} = -0.203$$
$$c_{11} = 0.523$$
$$d_{zz} = 5.05 \pm 0.12 \text{\AA}$$
$$d_{zv} = 4.90 \pm 0.12 \text{\AA}$$

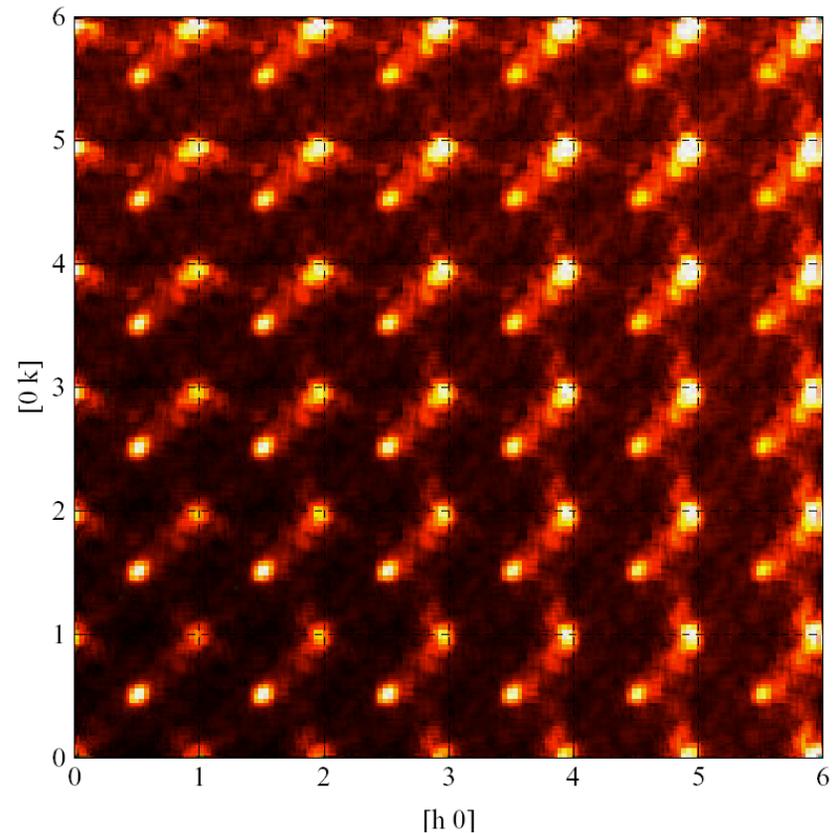
RMC simulations based on simulated scattering data showing occupational **and** displacive disorder.

Proffen and Welberry., *Acta Cryst A* **53**, 202 (1997)

RMC test simulations - results



$$\begin{aligned}\Theta &= 0.170 && (0.170) \\ c_{10} &= -0.076 && (-0.203) \\ c_{11} &= 0.412 && (0.523) \\ d_{zz} &= 5.02 \pm 0.08 \text{ \AA} && (5.05 \pm 0.12 \text{ \AA}) \\ d_{zv} &= 4.97 \pm 0.10 \text{ \AA} && (4.90 \pm 0.12 \text{ \AA})\end{aligned}$$

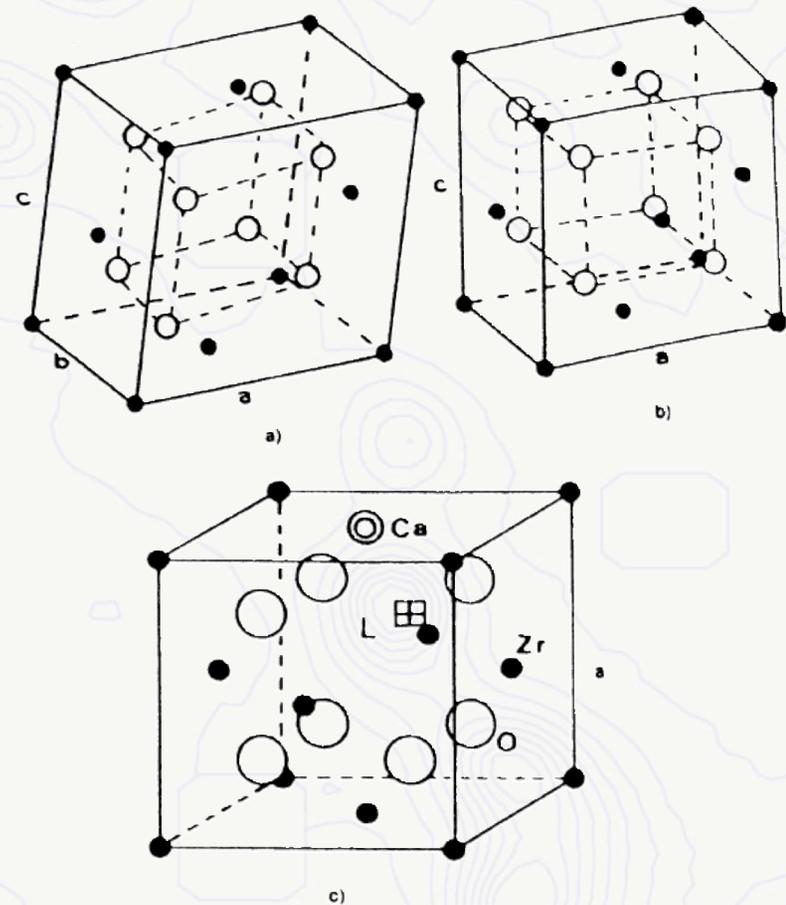


- Mode: swchem-swdisp (10%)
- Start: Random vacancy distr.
- Data: $|\mathbf{Q}| < (4,0,0)$ - all

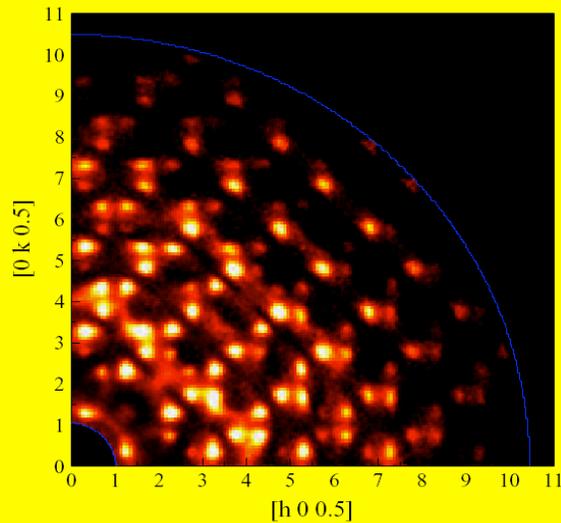


Stabilized Zirconia: Introduction

- **Structures of zirconia**
 - RT: monoclinic ($P2_1/c$)
 - $T > 1410\text{K}$: tetragonal ($P4_2/nmc$)
 - $T > 2525\text{K}$: cubic ($Fm\bar{3}m$)
- Cubic phase can be stabilized at RT by doping with CaO , Y_2O_3 , MgO , ..
- **Disorder:** Oxygen vacancy ordering and relaxation of surrounding metals.



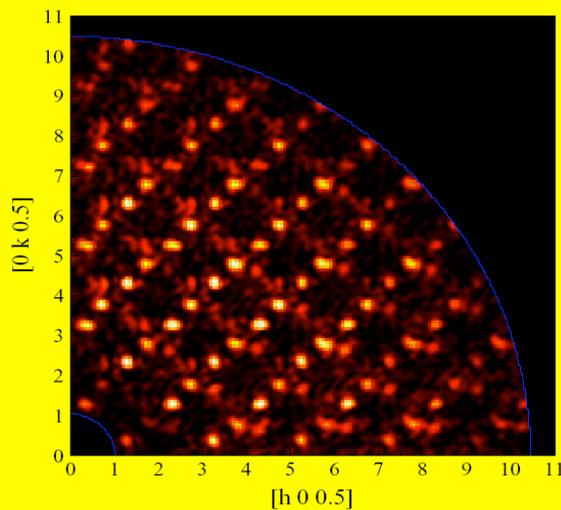
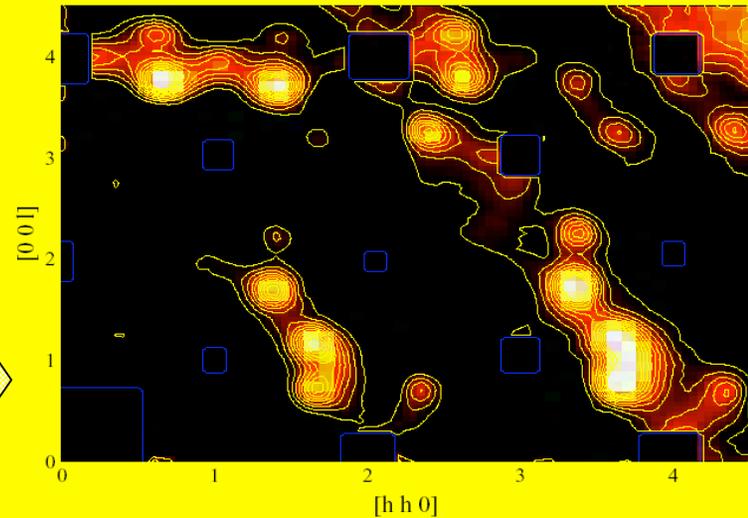
Stabilized Zirconia: RMC simulations



Measured data

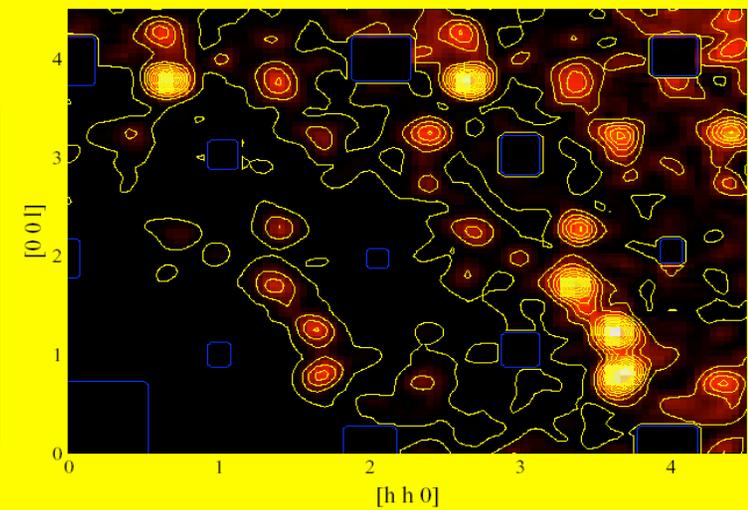
X-ray data
Mo-K α radiation
301x301 points

neutron data
Measured by Neder et. al
FRM I



RMC results

- 5x5x5 unit cells
- Average of 6 runs
- 25 RMC cycles
- R~33%



Stabilized Zirconia: Results

RMC model result

- Preferred vacancy-oxygen pairs along $\frac{1}{2}\langle 111 \rangle$ over “filled” oxygen cubes.
- Avoid Ca-Ca NN and 2NN neighbors
- NN oxygen shift towards vacancy
- Metal NN distance closer if both bridging O sites are occupied, otherwise further apart.

Correlations			
Neighbour	20x20x20 unit cell system	average : 5x5x5 unit cell system	Welberry et al. (1995)
$\square - \square: \frac{1}{2}\langle 100 \rangle$	-0.005	-0.008(11)	-0.044
$\square - \square: \frac{1}{2}\langle 110 \rangle$	-0.014	-0.011(10)	-0.058
$\square - \square: \frac{1}{2}\langle 111 \rangle$	0.006	-0.009(17)	-0.090
$\square - \square: \frac{1}{2}\langle 111 \rangle^*$	0.008	0.015(7)	0.260
Ca - Ca: $\frac{1}{2}\langle 110 \rangle$	-0.037	-0.052(33)	-
Ca - Ca: $\langle 100 \rangle$	-0.009	-0.008(17)	-
Displacements from average position [\AA]			
$\square - \text{O}: \frac{1}{2}\langle 100 \rangle$	-0.011	-0.031(13)	-
$\square - \text{O}: \frac{1}{2}\langle 110 \rangle$	0.003	0.009(5)	-
$\square - \text{O}: \frac{1}{2}\langle 111 \rangle$	0.005	0.014(7)	-
Zr-Zr: $\frac{1}{2}\langle 110 \rangle \square$	0.024	0.064(39)	0.872
Zr-Zr: $\frac{1}{2}\langle 110 \rangle \text{O}$	-0.002	-0.012(6)	-0.218
Zr-Ca: $\frac{1}{2}\langle 110 \rangle \square$	0.020	0.029(35)	-
Zr-Ca: $\frac{1}{2}\langle 110 \rangle \text{O}$	-0.007	-0.019(10)	-

Resulting correlations and displacements.

Proffen and Welberry., *J. Appl. Cryst.* **31**, 318 (1998)

The Automatic Monte Carlo Method

Input:

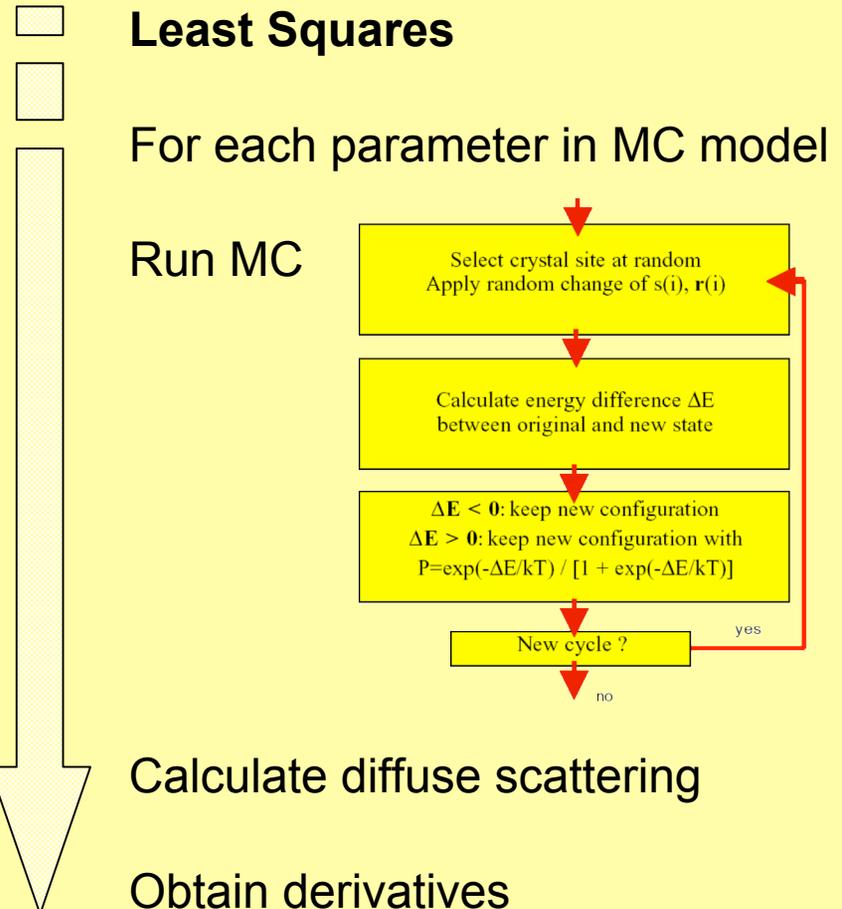
- Observed diffuse scattering
- Starting structure (e.g. average)
- Model for disorder in terms of interaction energies for MC simulation.

Result:

- Set of interaction energies for given model that best match the data.

Questions:

- Finding the right model ..
- It is very slow ..



Some equations ..

- Minimize 'Goodness-of-fit', χ^2

$$\chi^2 = \sum_{h,k,l,m} \omega_{hkml} \{ \Delta I \}^2 \quad \Delta I = I_{obs} - [b_m + f_m I_{calc}]$$

- Least-squares Matrix

$$\mathbf{A}_{ij} = \sum_{hkml} \omega_{hkml} \frac{\partial \Delta I}{\partial p_i} \frac{\partial \Delta I}{\partial p_j} \quad \mathbf{B}_i = - \sum_{hkml} \omega_{hkml} \Delta I_{trial} \frac{\partial \Delta I}{\partial p_i}$$

- Parameter shifts

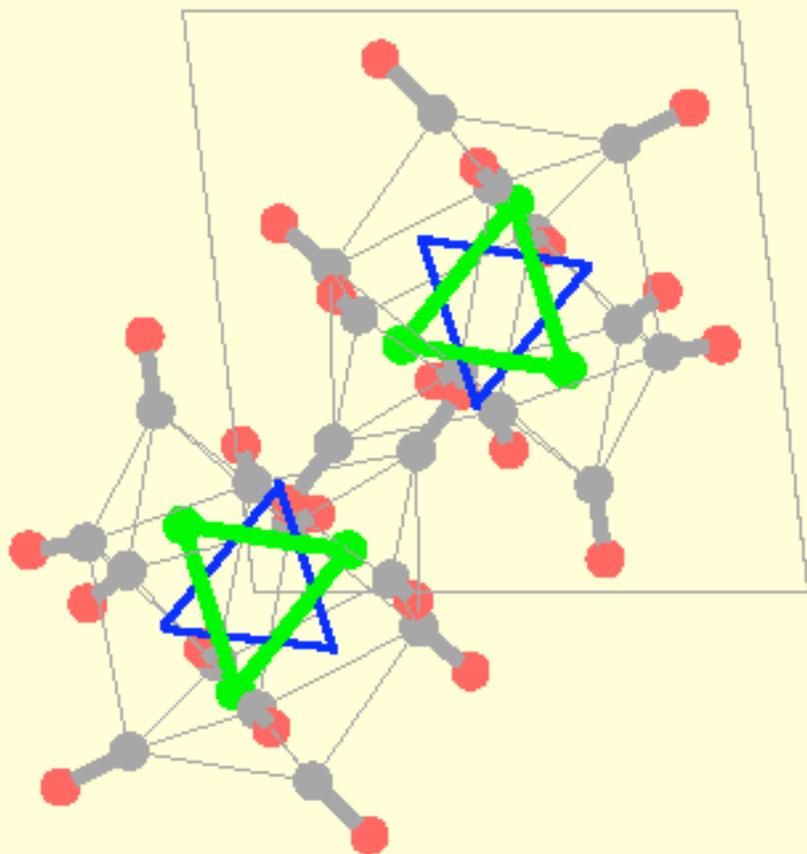
$$\Delta p_i = \sum_{l=1}^{npar} \mathbf{A}_{il}^{-1} \mathbf{B}_l$$

- Numerical estimates of Differentials

$$\frac{\partial \Delta I}{\partial p_i} = \sum_{hkml} \frac{(\Delta I_{p+} - \Delta I_{p-})}{2\delta_i}$$



Disorder in $\text{Fe}_3(\text{CO})_{12}$



Basic disorder
is a 180° flip of
 Fe_3 triangle

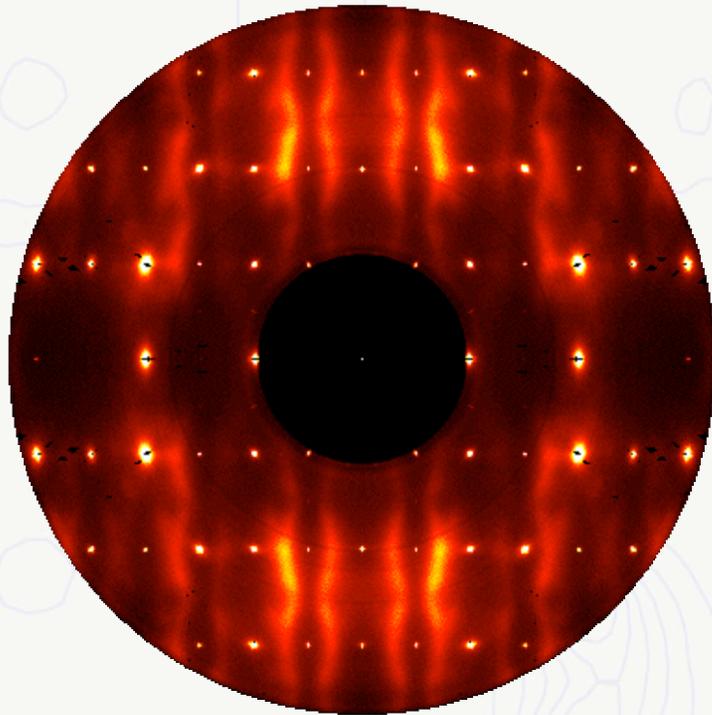
Carbonyls are
disordered too but
main contribution
to the scattering is
from the Fe atoms

Welberry, Proffen and Bown, *Acta Cryst. A* **54**, 661 (1998)

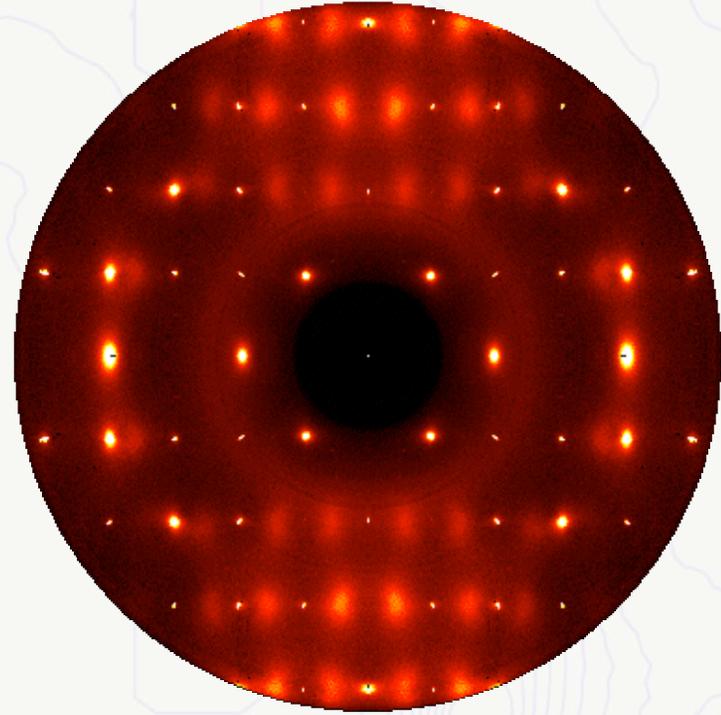
Disorder in $\text{Fe}_3(\text{CO})_{12}$ - Data

X-ray diffraction patterns

$h k -h$

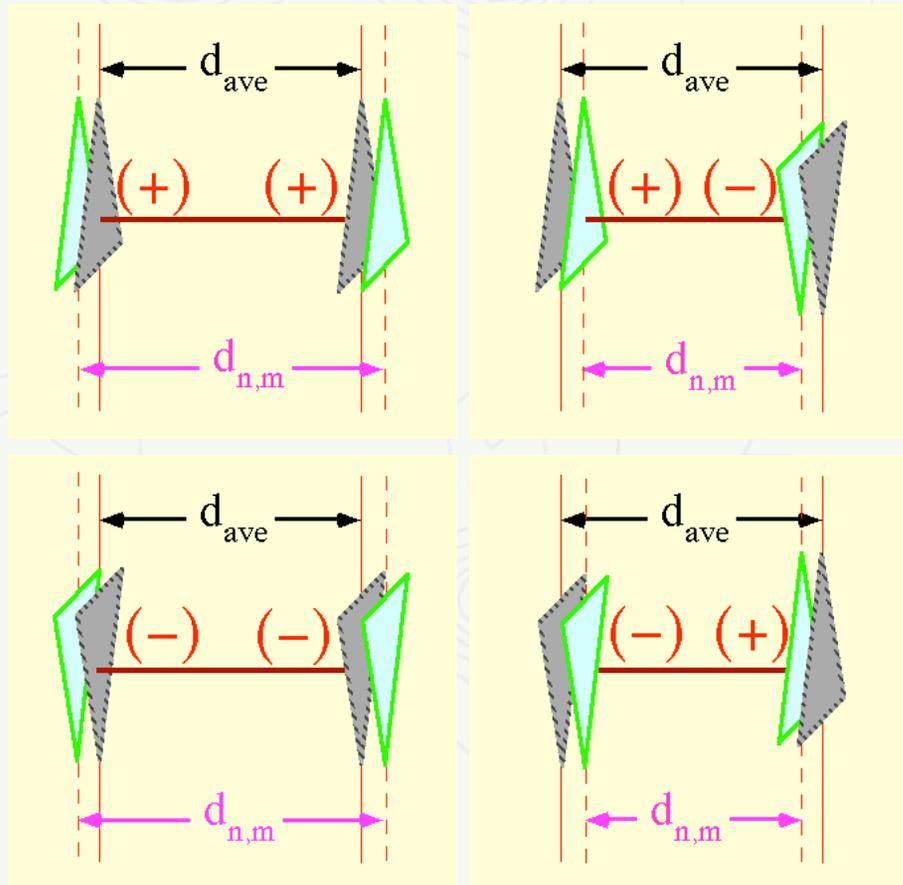


$0 k l$



Disorder in $\text{Fe}_3(\text{CO})_{12}$ – MC model

Center-of-mass relaxation (size-effect)



$$E_2 = \sum_{n,m} \left(d_{n,m} - d_{ave} (1 + \varepsilon_{n,m}) \right)^2$$

$$\varepsilon_{n,m} (++) = g_m + u_m$$

$$\varepsilon_{n,m} (+-) = \varepsilon_{n,m} (-+) = -g_m$$

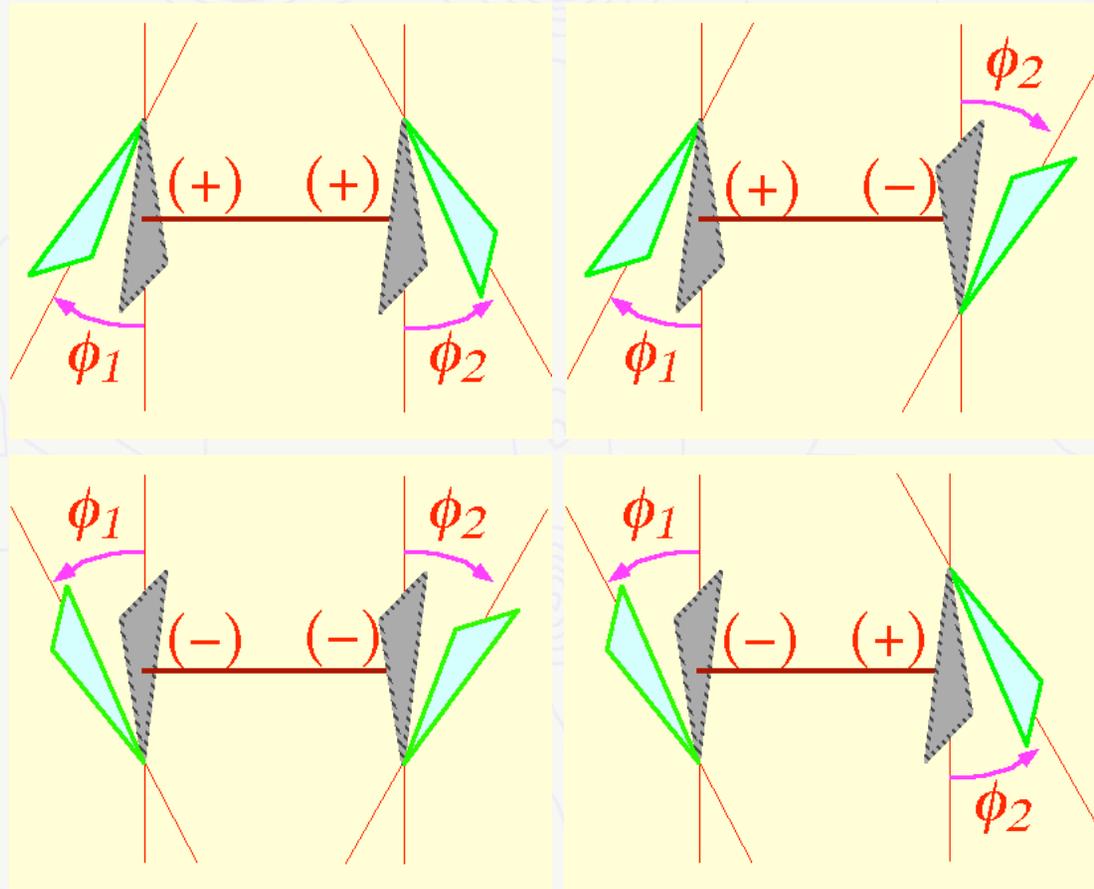
$$\varepsilon_{n,m} (--) = g_m - u_m$$

2 parameters per vector:- symmetric & antisymmetric components



Disorder in $\text{Fe}_3(\text{CO})_{12}$ – MC model

Orientational relaxation (size-effect)



$$E_3 = \sum_{n,m} \left(\Delta\phi_{n,m} - \xi_{n,m} \right)^2$$

$$\xi_{n,m} (++) = \gamma_m + \nu_m$$

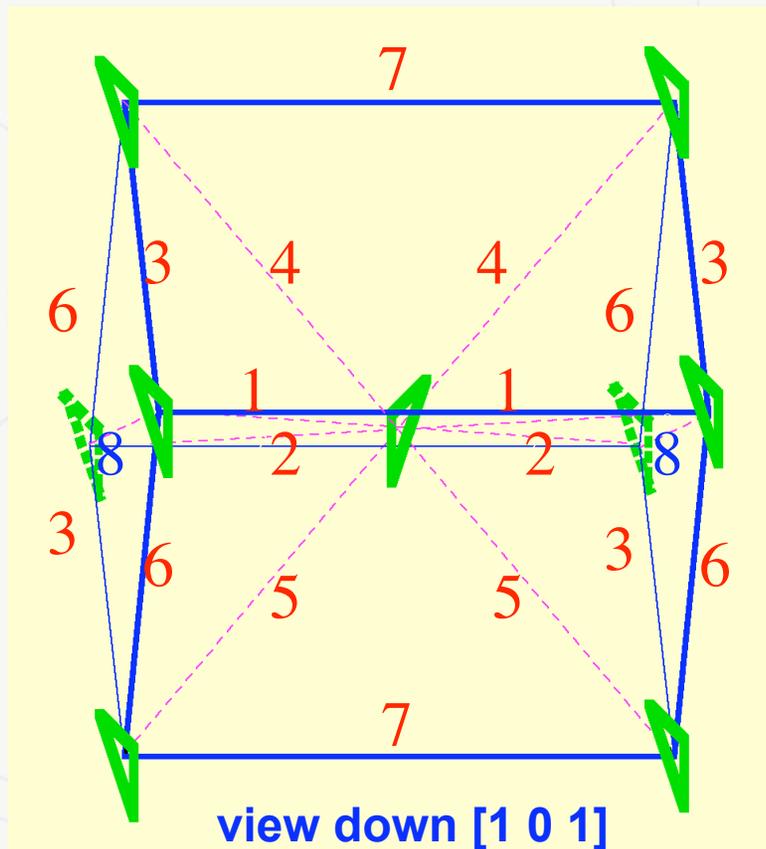
$$\xi_{n,m} (+-) = \xi_{n,m} (-+) = -\gamma_m$$

$$\xi_{n,m} (--) = \gamma_m - \nu_m$$

2 parameters per vector:- symmetric & antisymmetric components

Disorder in $\text{Fe}_3(\text{CO})_{12}$ – MC model

Interactions between central Fe_3 triangle and 8 neighbors.



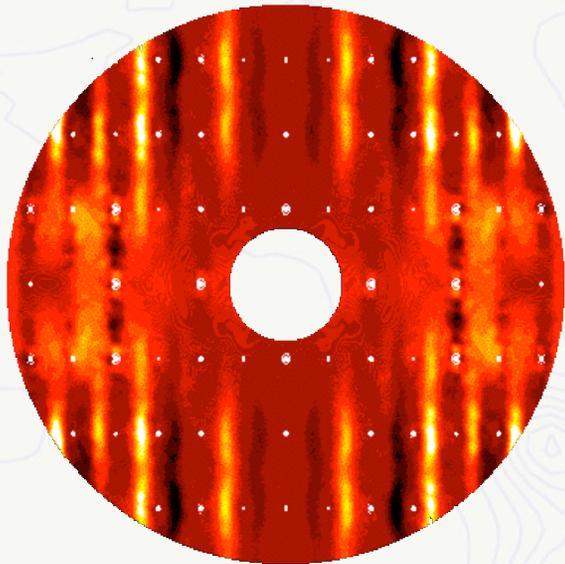
Summary of parameters, p_i , used in the analysis

- 8 occupancy correlations
 - Ising model spin energy
 - along each of 8 vectors (7 vectors initially)
- 4 center-of-mass size-effect
 - 2 each along vectors 1 & 2
- 4 orientational size-effect
 - 2 each along vectors 1 & 2

Disorder in $\text{Fe}_3(\text{CO})_{12}$ – AMC refinement

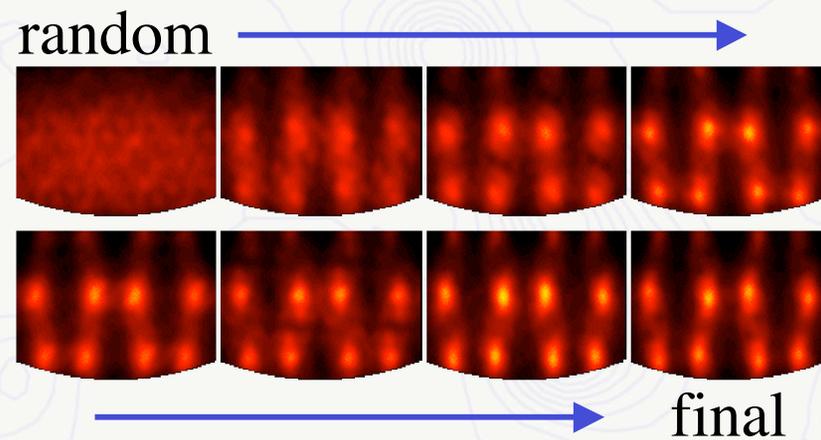
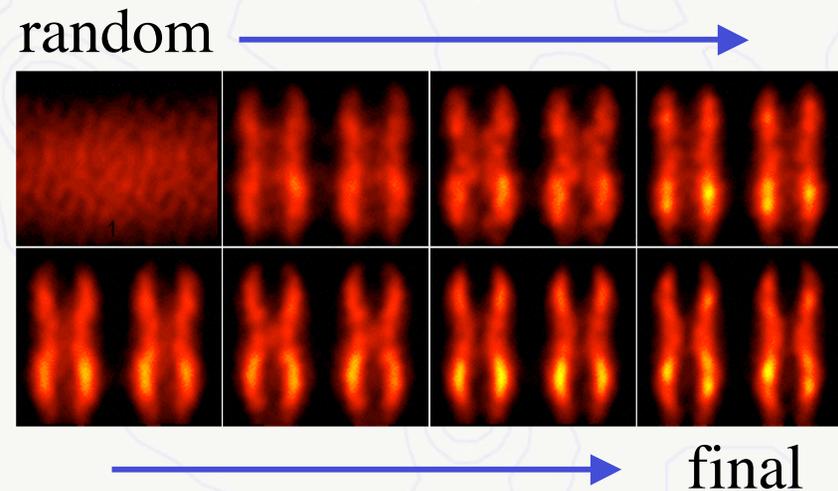
Numerical estimates
of Differentials

$$\frac{\partial \Delta I}{\partial p_i} = \sum_{hklm} \frac{(\Delta I_{p+} - \Delta I_{p-})}{2\delta_i}$$



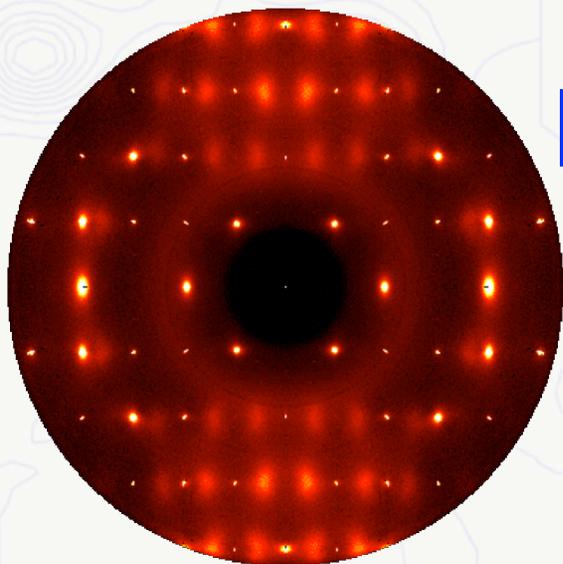
Difference between two calculated
diffraction patterns

Progress of refinement



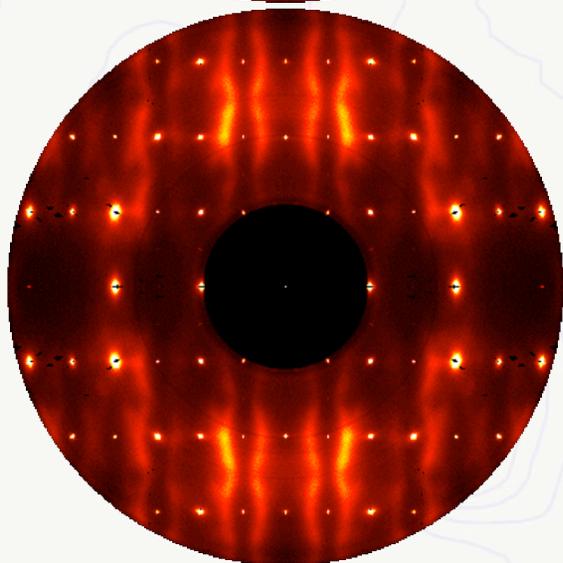
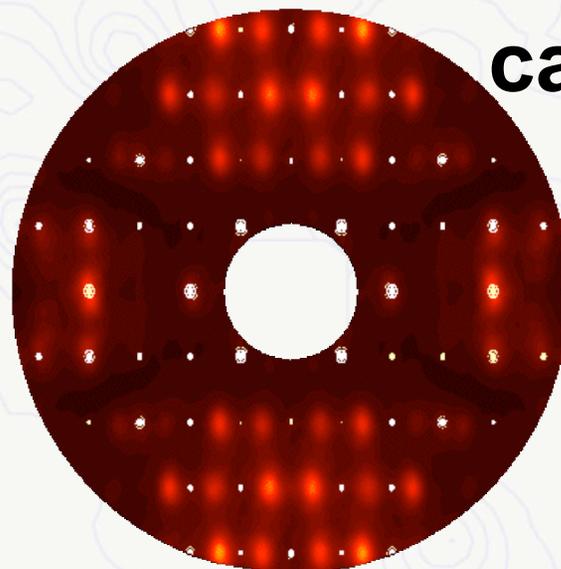
Disorder in $\text{Fe}_3(\text{CO})_{12}$ – AMC refinement

Data

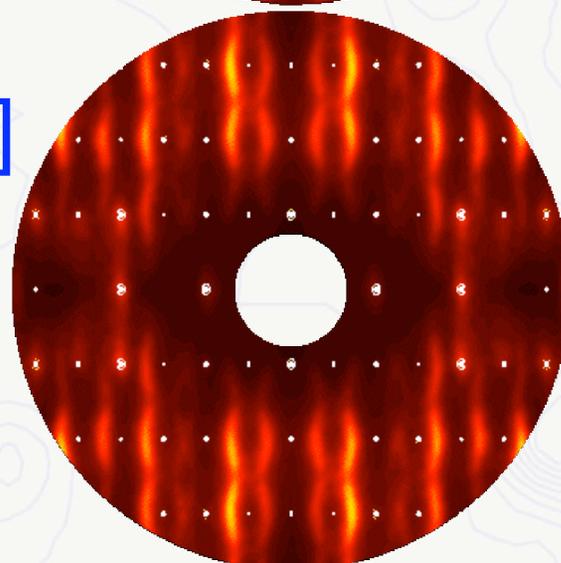


[100]

calculated

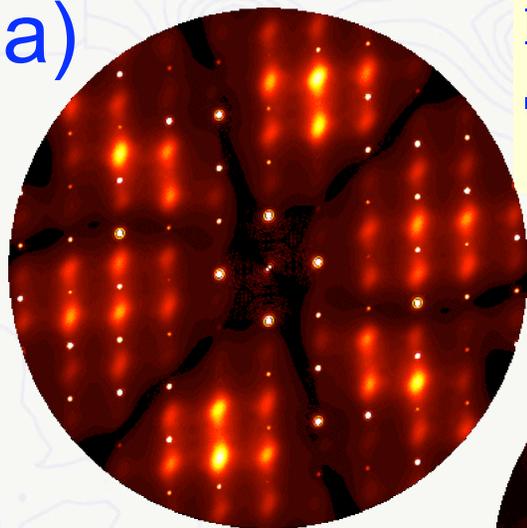


[101]

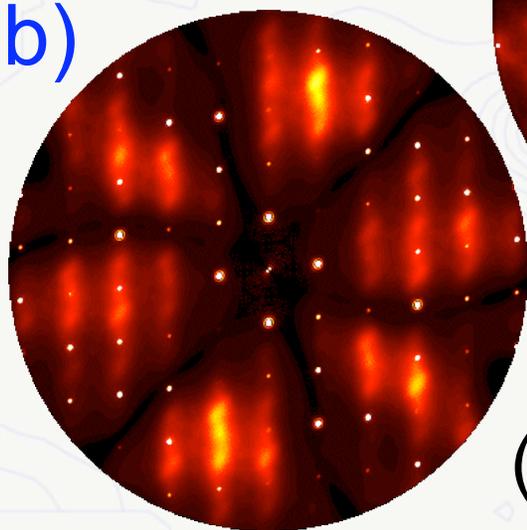


Disorder in $\text{Fe}_3(\text{CO})_{12}$ – Unique solution ?

(a)



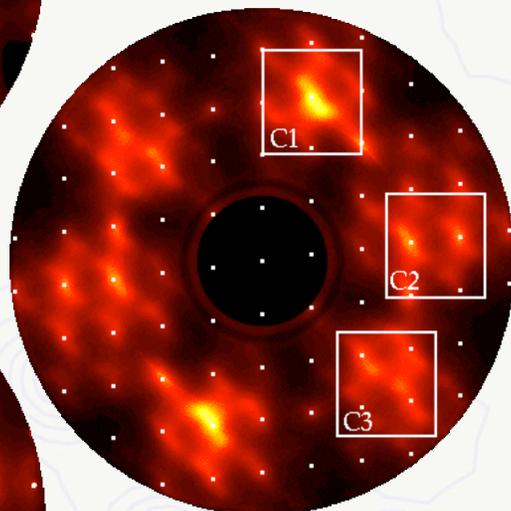
(b)



Parameter

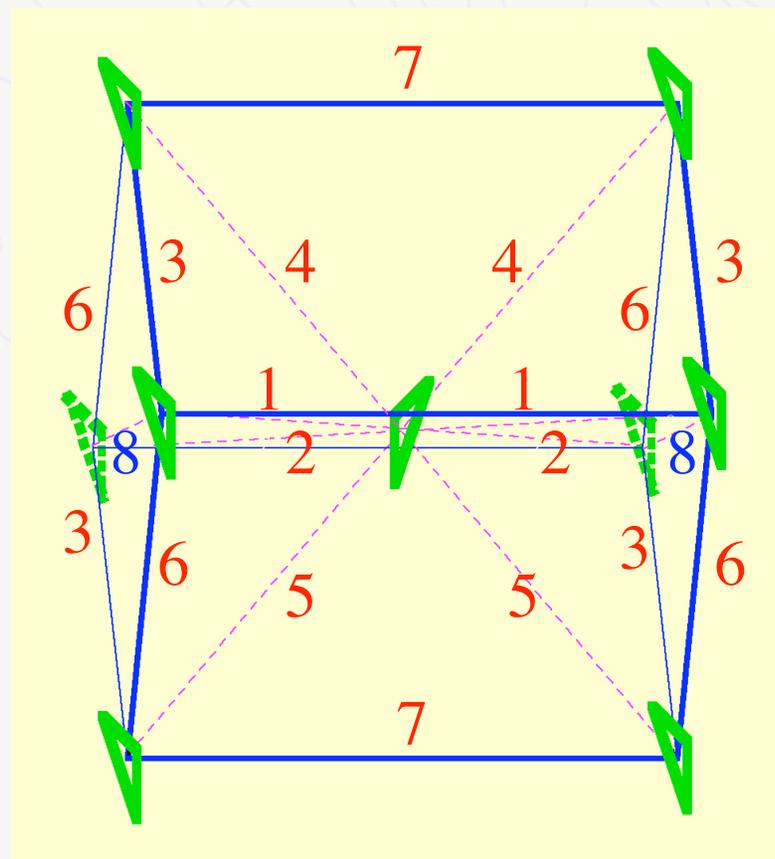
Correlation

	1	2	3	4	5	6	7
(a)	0.23	0.14	-0.21	-0.04	-0.02	0.30	-0.40
(b)	0.48	0.01	-0.17	-0.17	0.09	0.25	-0.40



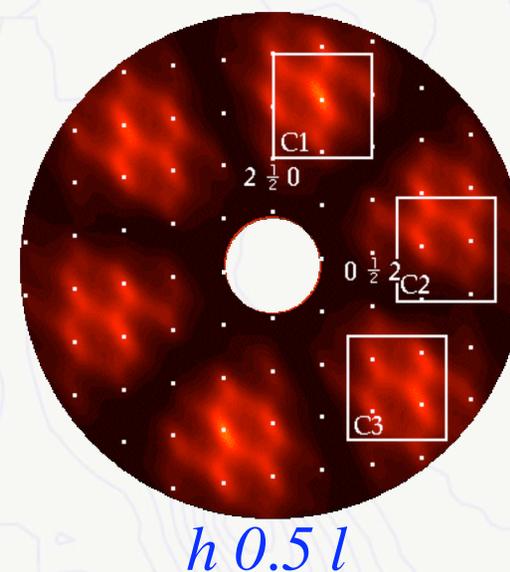
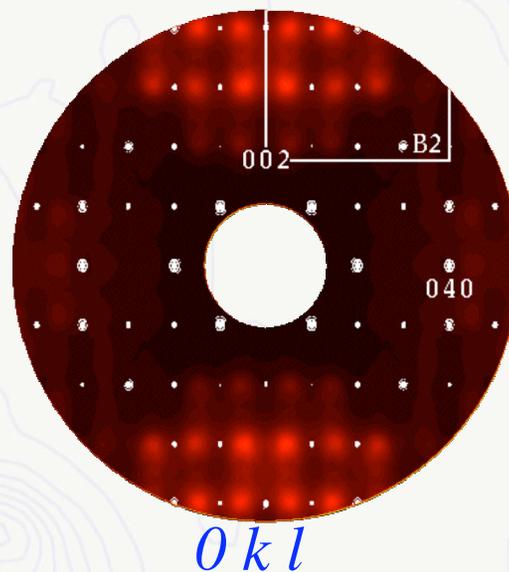
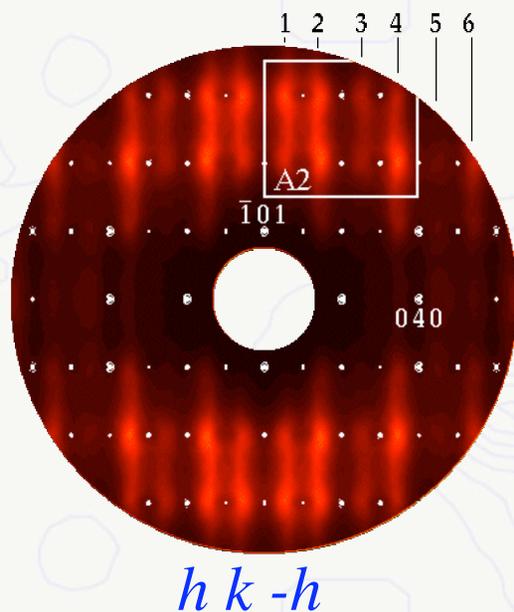
Data

($h\ 0.5\ l$) section



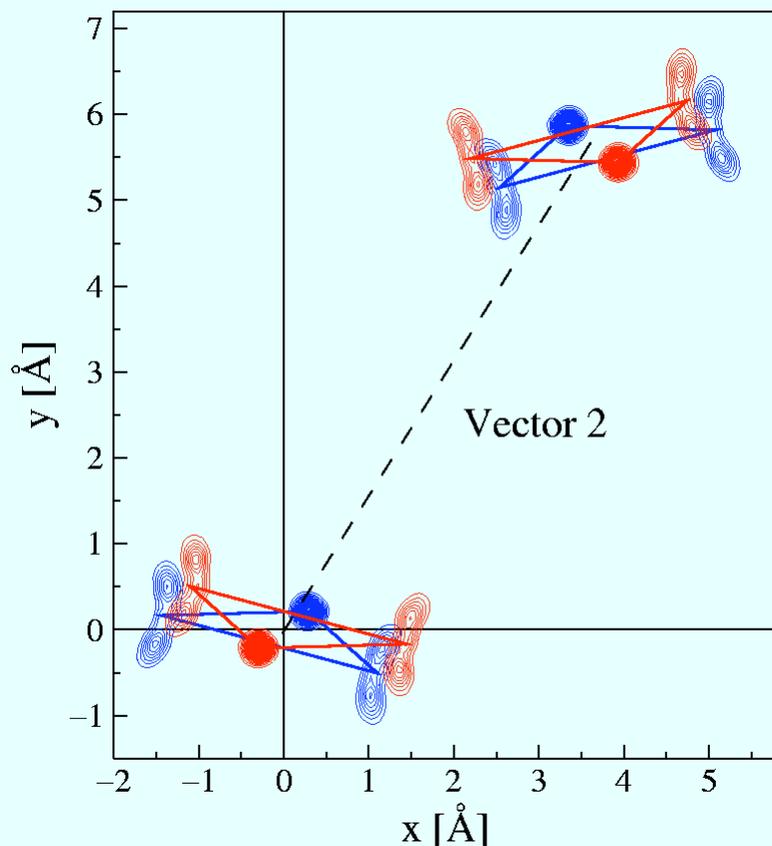
Disorder in $\text{Fe}_3(\text{CO})_{12}$ – AMC again

Calculated intensities after new AMC refinement including vector 8 ..



Disorder in $\text{Fe}_3(\text{CO})_{12}$ – resulting structure

Averaged Fe positions from MC model.



Results from Bragg scattering

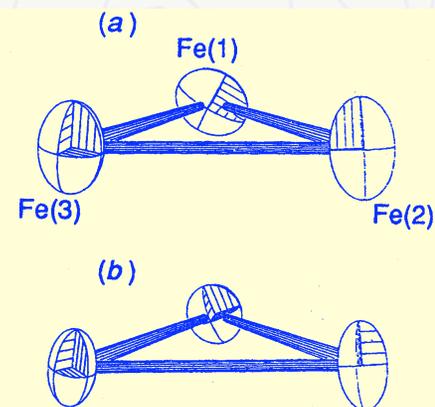
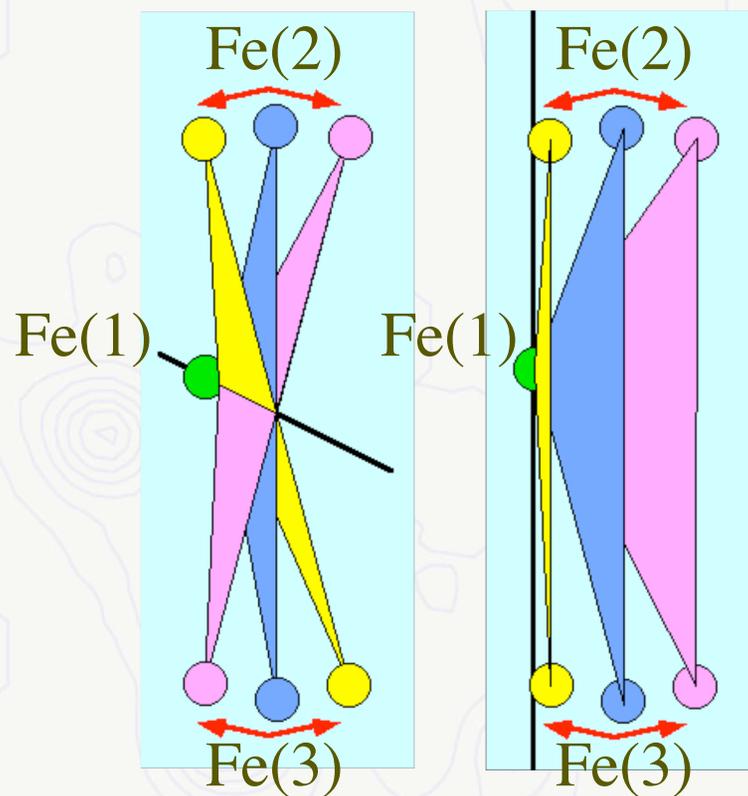


Table 5 Libration of the iron triangle around either a three- or two-fold axis

T/K	Rigid-body libration tensor/(degree) ²		IMG additional motion tensor/(degree) ²	
	Two-fold axis	Three-fold axis	Two-fold axis	Three-fold axis
320	12.2(4.0)	12.2(4.0)	130(11)	0.9(2)
295 ^{7b}	13.9(4.0)	13.1(4.0)	109(8.5)	-1(6)
250	12.2(4.0)	9.5(3.0)	80.2(9.1)	1(2)
160	8.8(3.0)	6.3(3.0)	38.9(6.2)	1(2)
100	6.7(3.0)	5.4(2.0)	25.0(4.0)	-1(1)

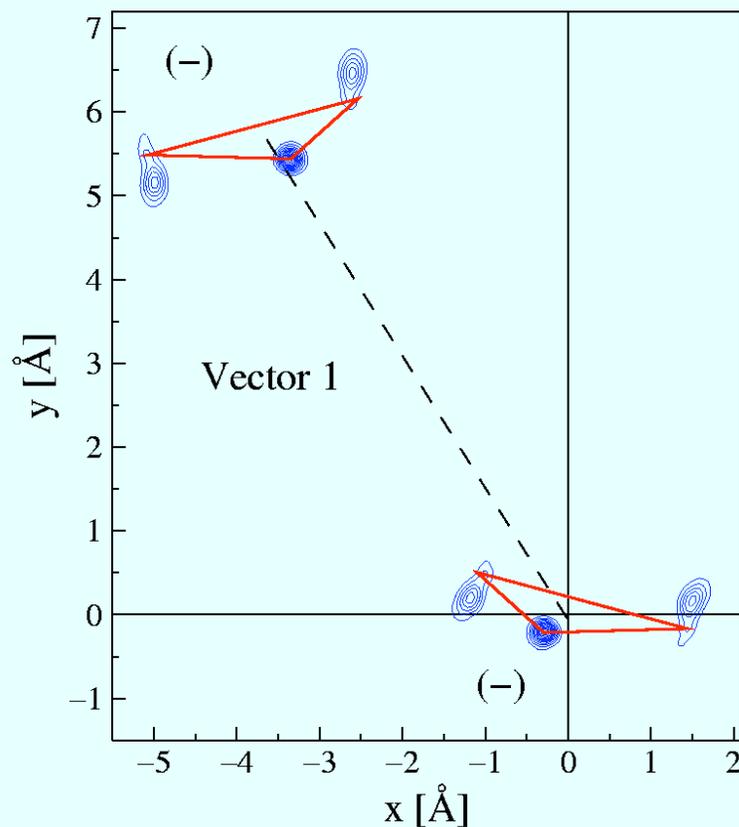
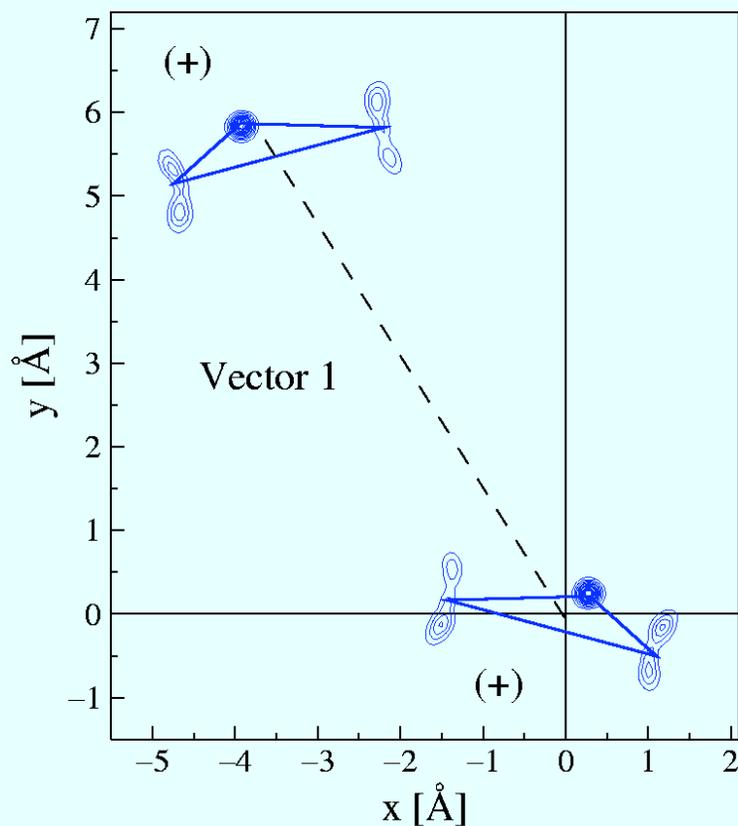
Disorder in $\text{Fe}_3(\text{CO})_{12}$ – resulting structure

Two modes of libration not distinguished by Bragg scattering



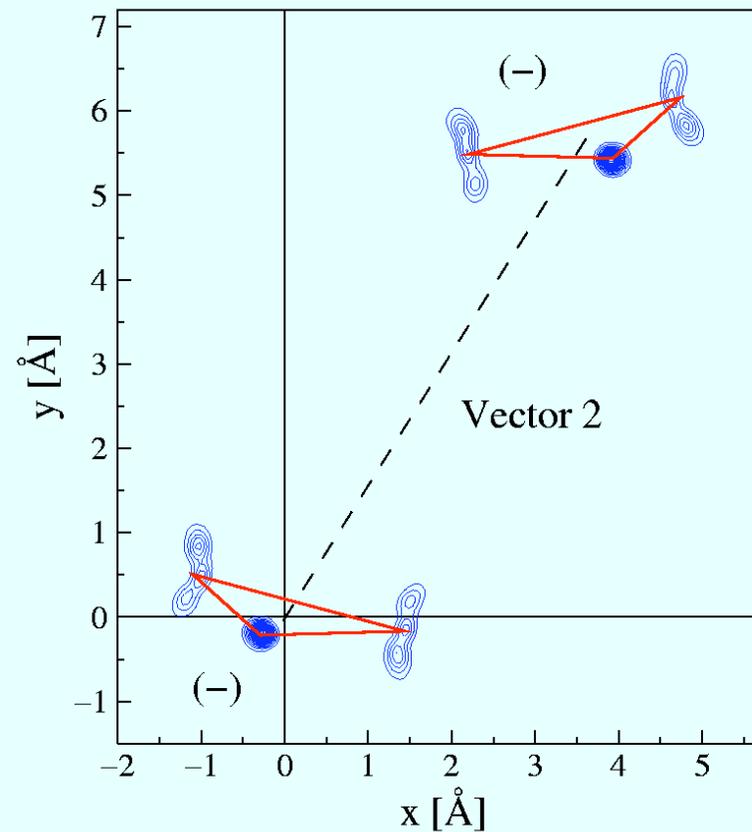
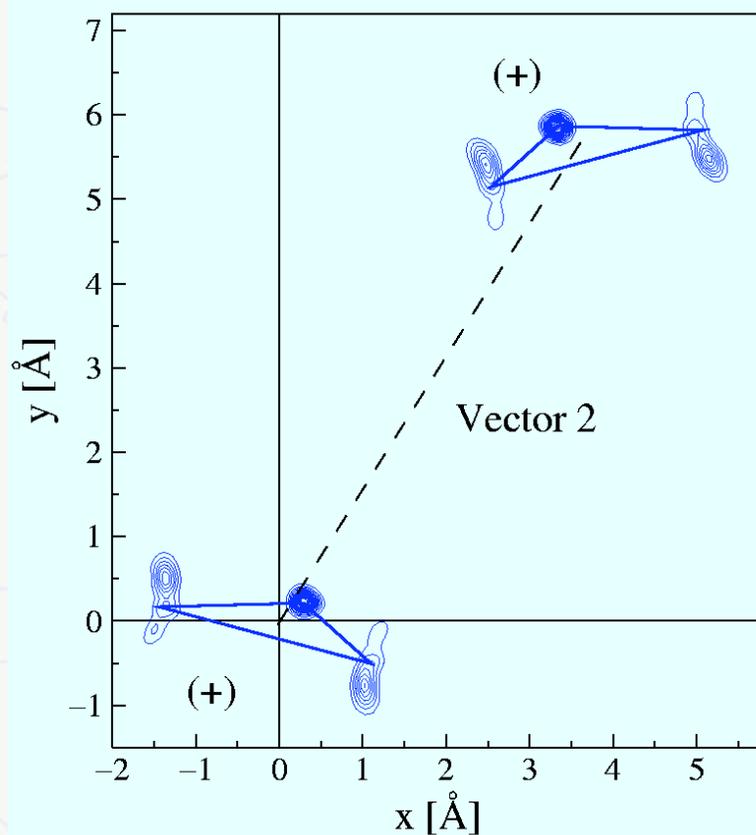
Disorder in $\text{Fe}_3(\text{CO})_{12}$ – resulting structure

Positions of Fe averaged over unit cells containing either (+ +) or (- -) combinations on nearest-neighbor vector 1.



Disorder in $\text{Fe}_3(\text{CO})_{12}$ – resulting structure

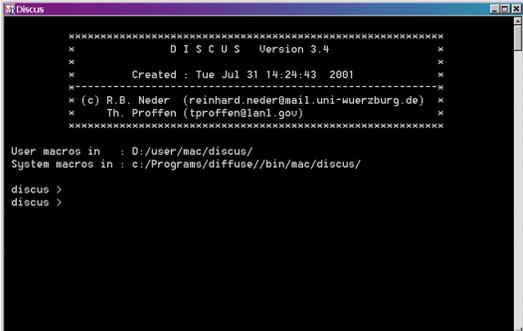
Positions of Fe over unit cells containing either (+ +) or (- -) combinations on nearest-neighbor vector 2.



DISCUS – defect structure simulation

Program features

- Controlled by FORTRAN style command language including loops and IF statements.
- Calculation of Fourier transform, inverse and difference Fourier.
- Expand structure from asymmetric unit and space group symbol.
- Structure “statistics”: correlations, real space lots, ...
- PDF calculations.
- Monte Carlo simulations.
- Reverse Monte Carlo simulations – diffuse scattering & PDF.
- Symmetry & unit cell transformations.
- Interfaces with PDFFIT, KUPLOT and ATOMS.
- Online help function.



```
DISCUS
*****
D I S C U S   Version 3.4
*
*   Created : Tue Jul 31 14:24:43 2001
*-----*
* (c) R.B. Neder (reinhard.neder@mail.uni-wuerzburg.de) *
*   Th. Proffen (tproffen@lanl.gov)
*****
User macros in : D:/user/mac/discus/
System macros in : c:/Programs/diffuse/bin/mac/discus/
discus >
discus >
```

<http://www.totalscattering.org/programs/discus/>

Proffen et al., *J. Appl. Cryst.* **30**, 171 (1997)

Conclusions

- **Diffuse scattering analysis gives local structure of materials, holding key to their properties.**
- **Monte Carlo based modeling**
 - RMC: Constraints important !
 - AMC: Initial MC model required !
 - Obtain complete 3D data sets ..
 - Combine with other data ..
 - More computing power ..
- <http://www.totalscattering.org>

