

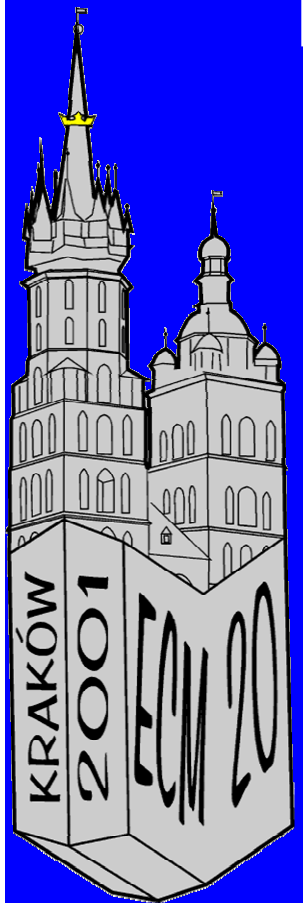
Old-Style Amorphous Structure Modelling. Does it Can Still Bring Something ?

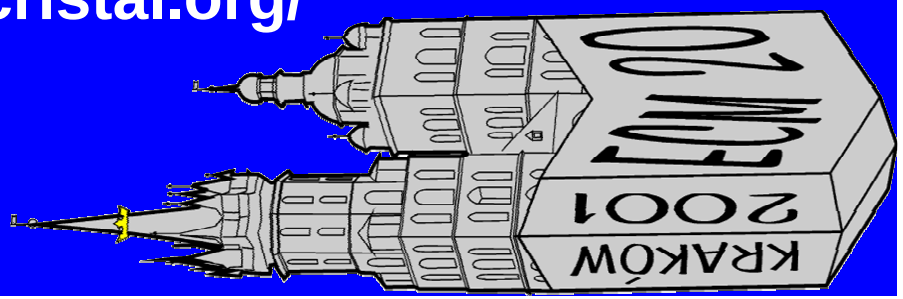
A. Le Bail

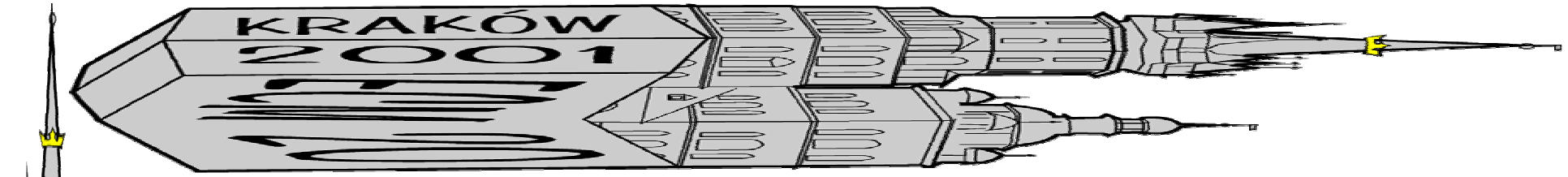
Université du Maine – France

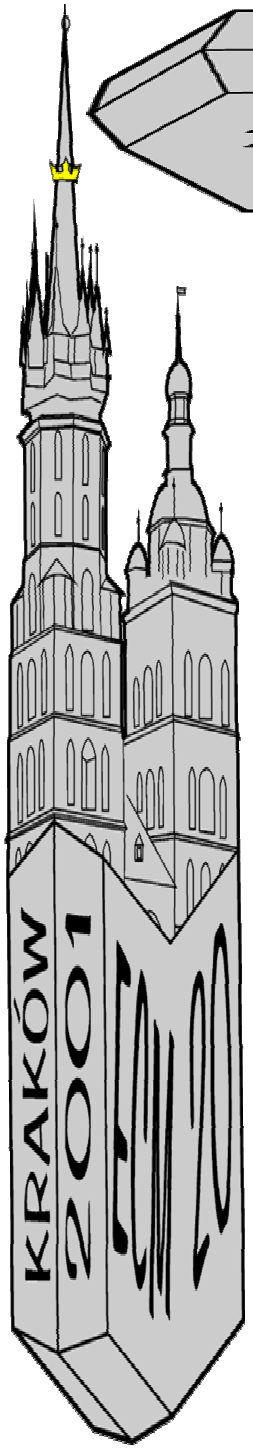
alb@cristal.org

http://www.cristal.org/









Old and new modelling styles

CRN or crystallites (1932-1940)

Paracrystalline models (1950)

Quasi-crystalline models (seventies)

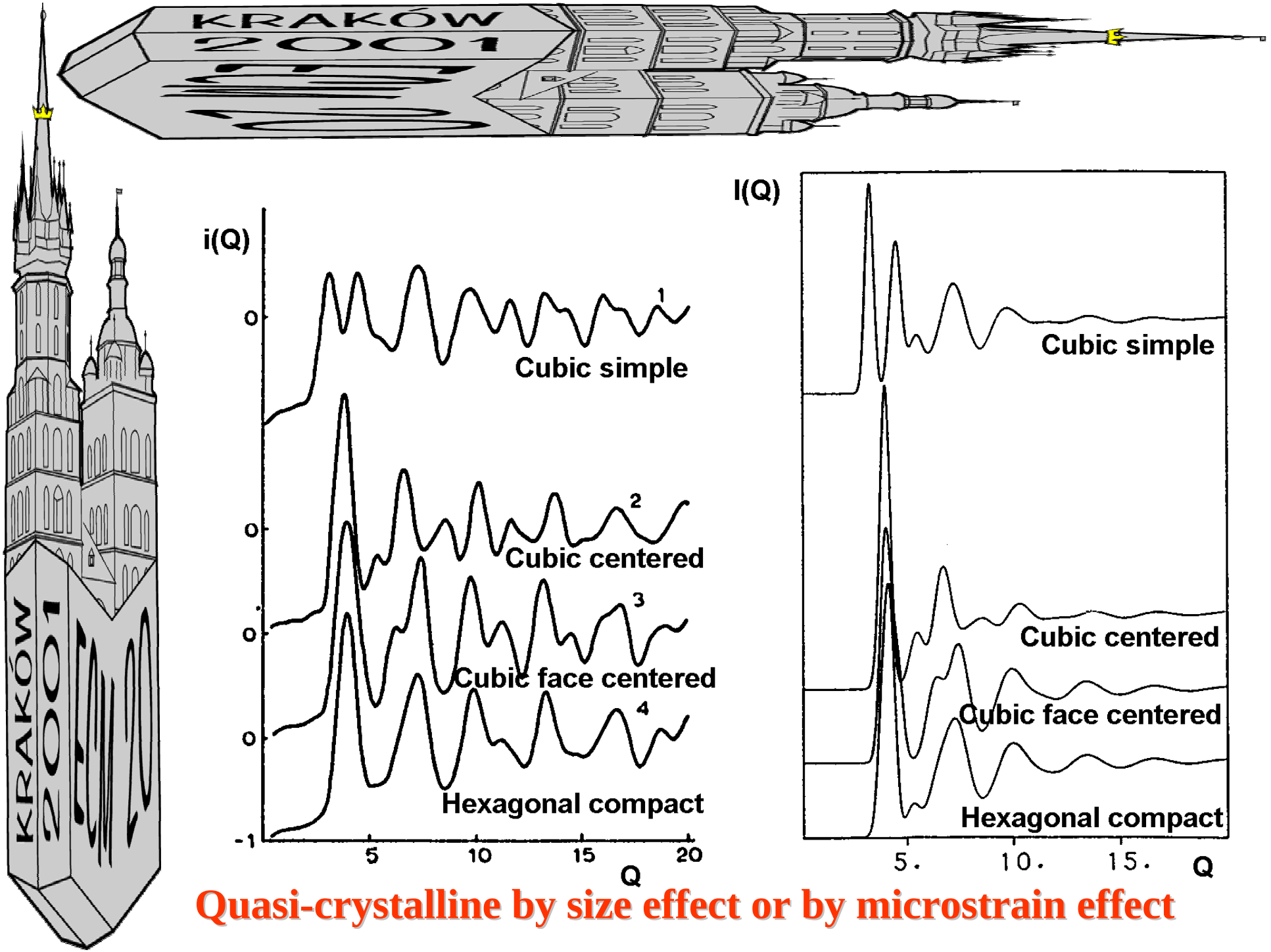
…

Monte Carlo

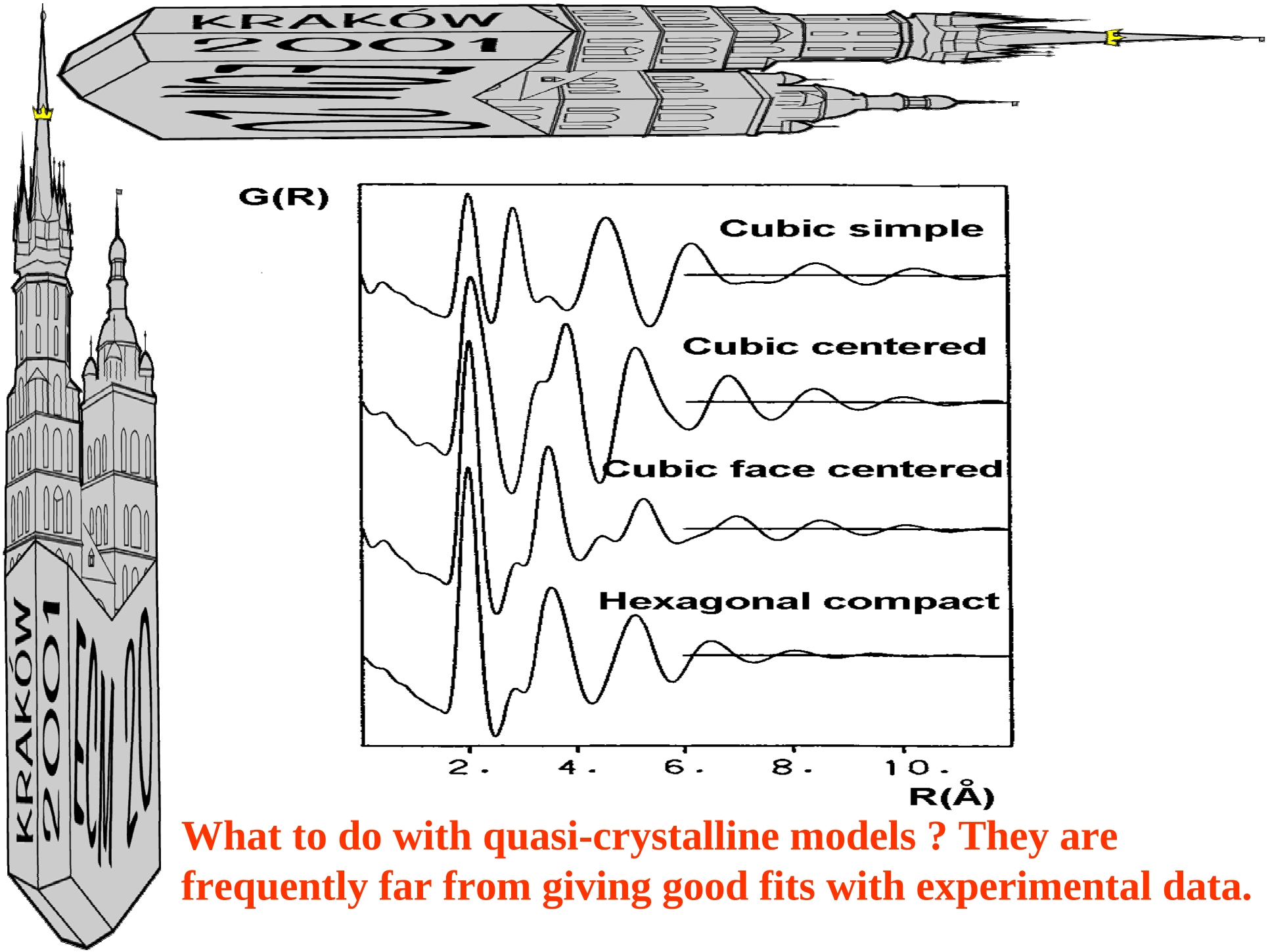
Molecular Dynamics

Reverse Monte Carlo (1988)

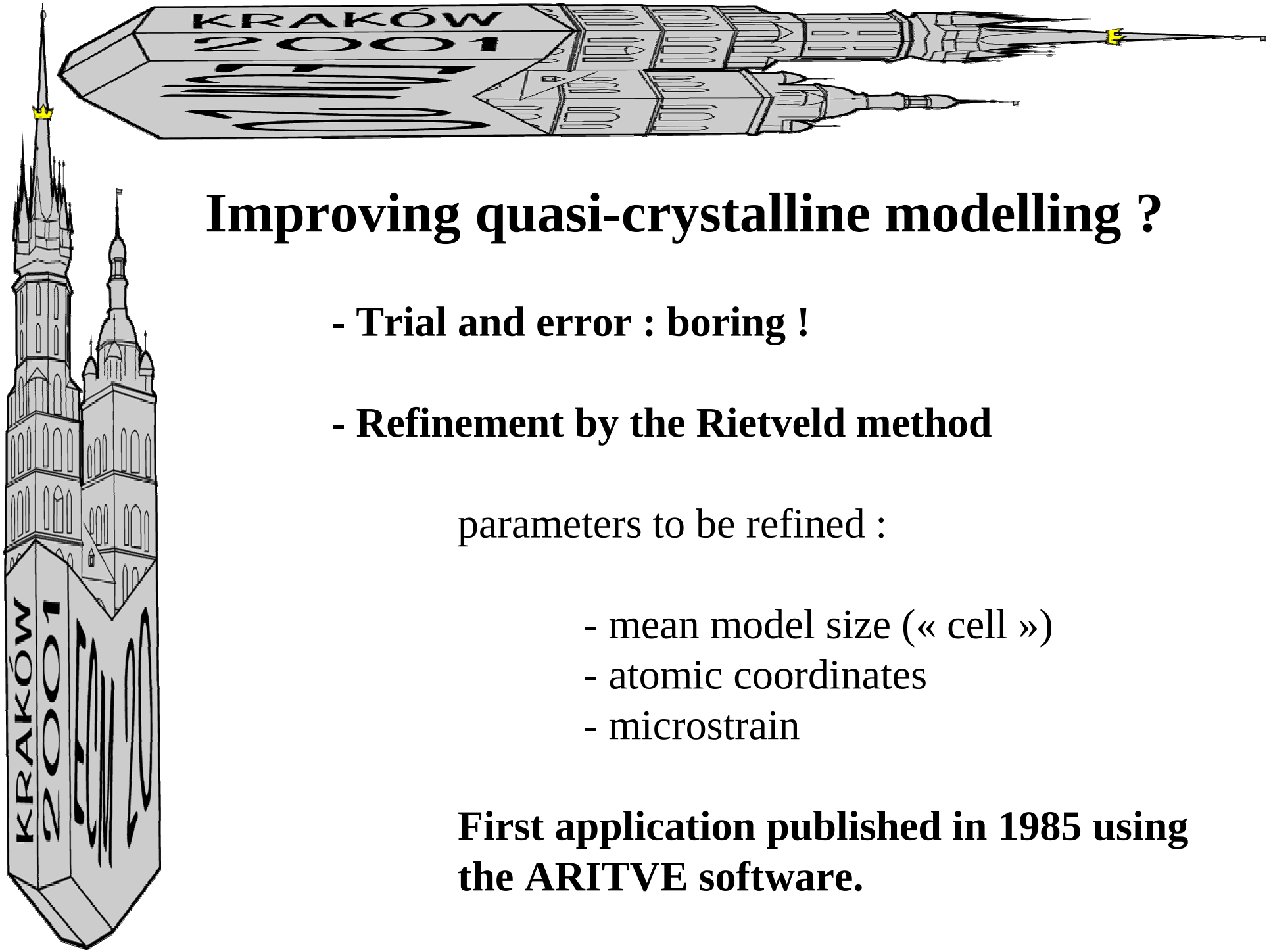
CRN modelling has win, but mostly with periodic boundary conditions ! Models are built in P1 S.G.



Quasi-crystalline by size effect or by microstrain effect



What to do with quasi-crystalline models ? They are frequently far from giving good fits with experimental data.



Improving quasi-crystalline modelling ?

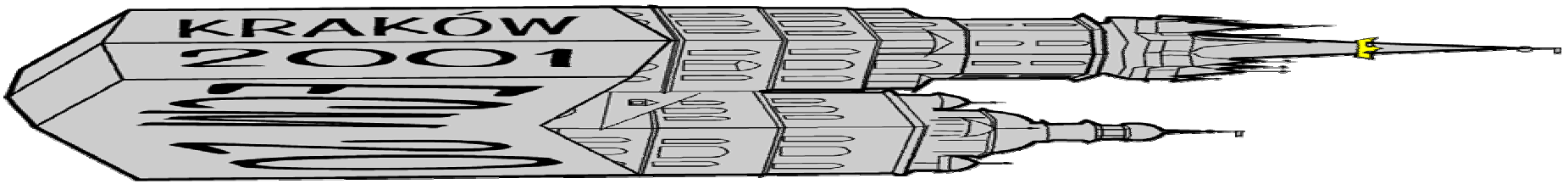
- Trial and error : boring !

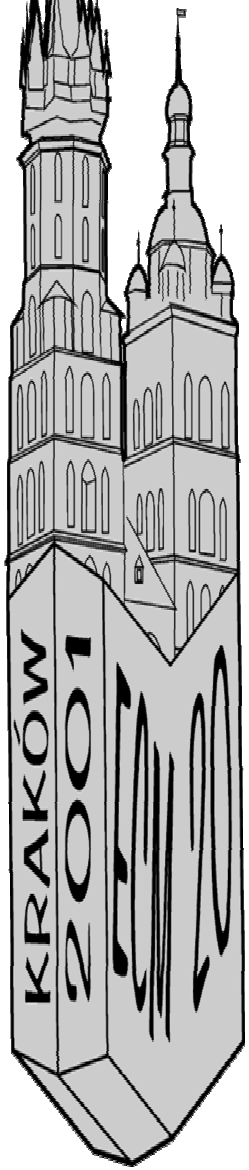
- Refinement by the Rietveld method

parameters to be refined :

- mean model size (« cell »)
- atomic coordinates
- microstrain

First application published in 1985 using the ARITVE software.



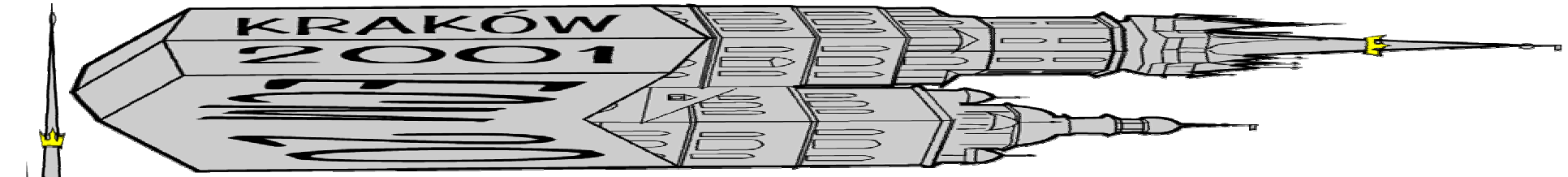


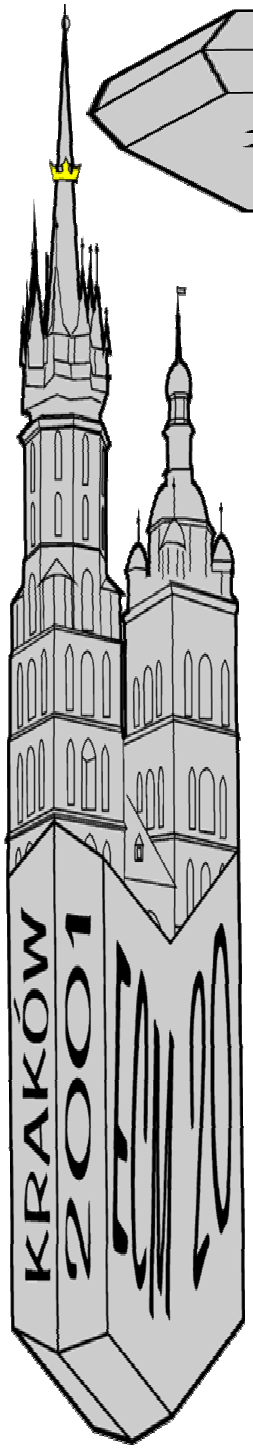
ARITVE

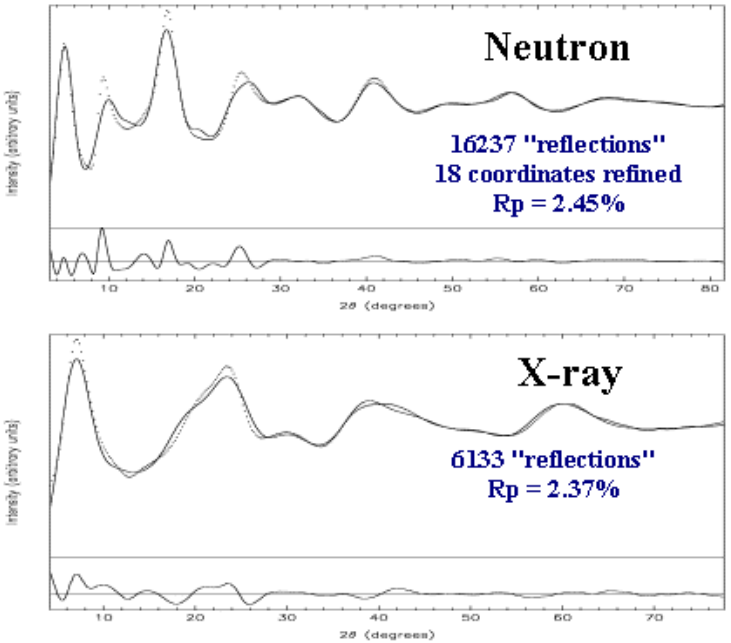
is simply a Rietveld method program allowing :

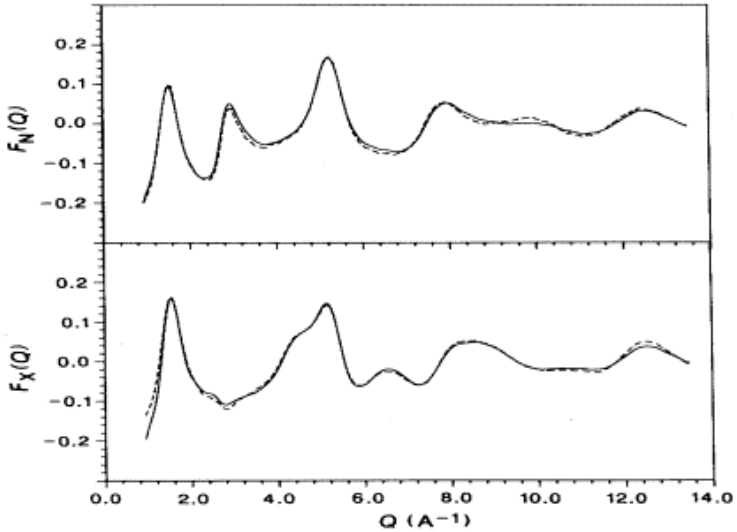
- **a huge limit of reflection number (60000 on each pattern)**
- **3 interference functions maximum fitted simultaneously**
- **a huge limit of reflections overlapping at the same angle (20000)**
- **a small number of parameters to be refined (max = 75)**
- **only Gaussian peak shape**
- **line broadening following the Caglioti law**

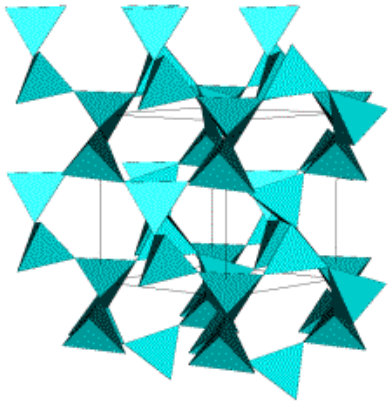
= RDM : Rietveld for Disordered Materials



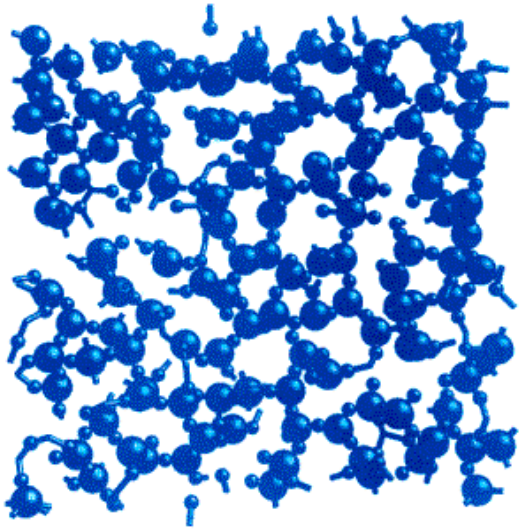




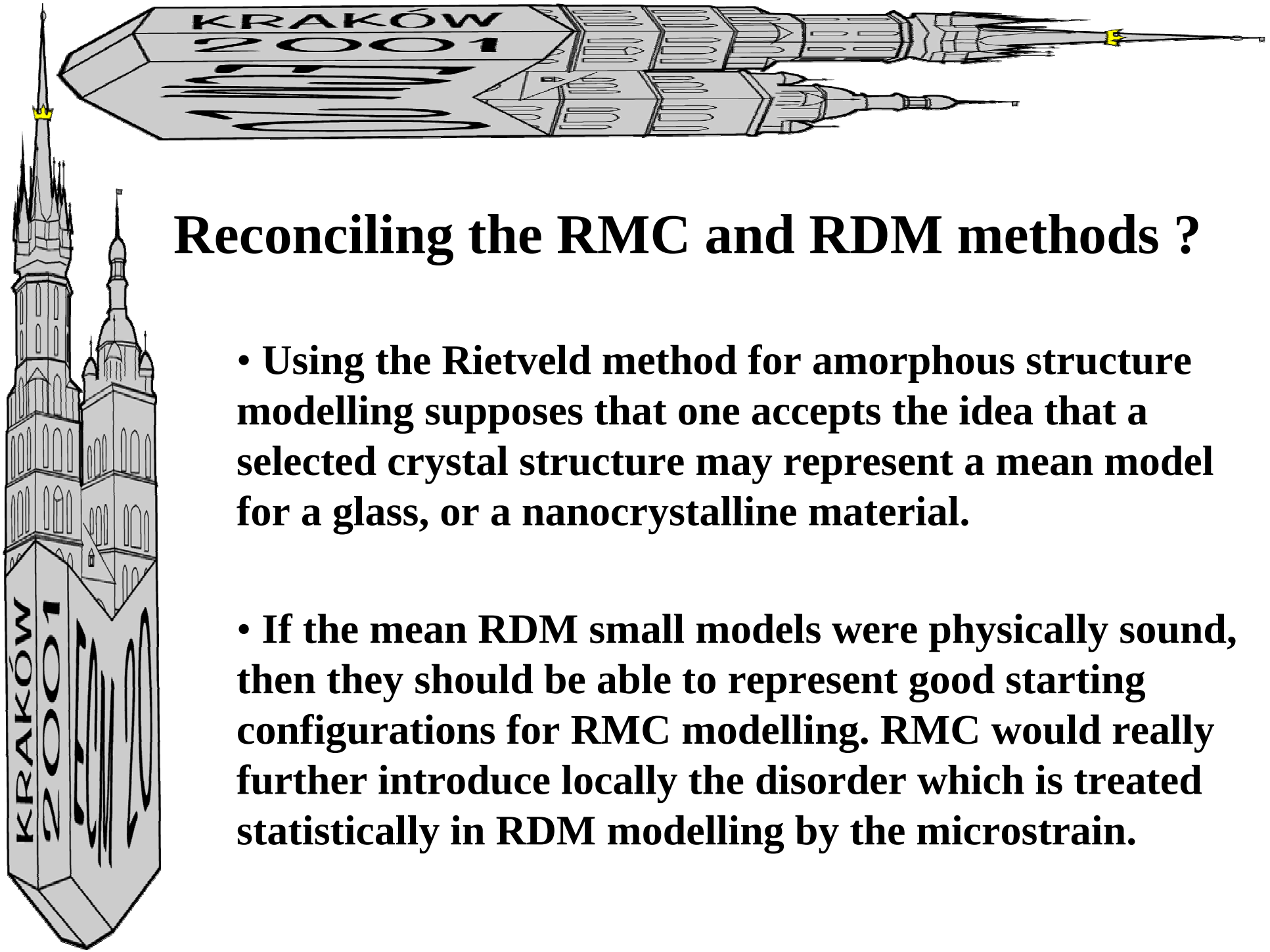




α-carnegieite



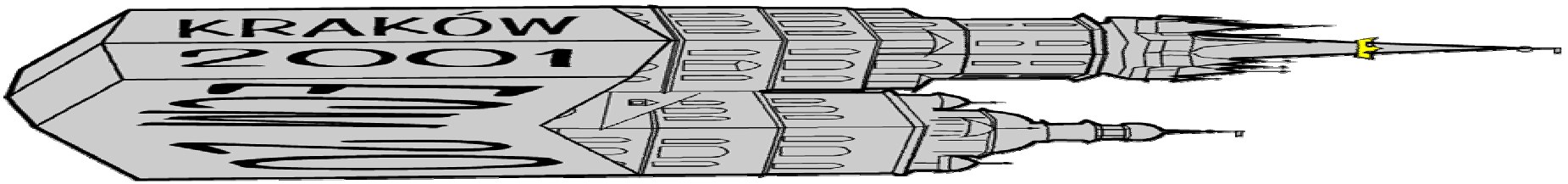
From :
D.A. Keen & R.L. McGreevy, *Nature* 344 (1990) 423-425

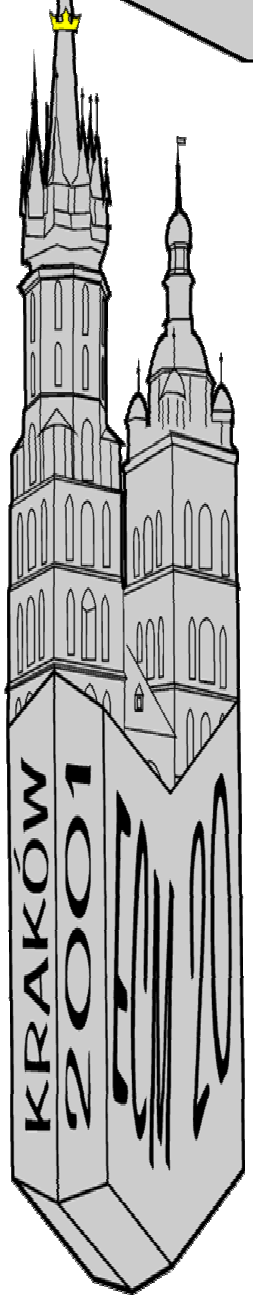


Reconciling the RMC and RDM methods ?

• **Using the Rietveld method for amorphous structure modelling supposes that one accepts the idea that a selected crystal structure may represent a mean model for a glass, or a nanocrystalline material.**

• **If the mean RDM small models were physically sound, then they should be able to represent good starting configurations for RMC modelling. RMC would really further introduce locally the disorder which is treated statistically in RDM modelling by the microstrain.**

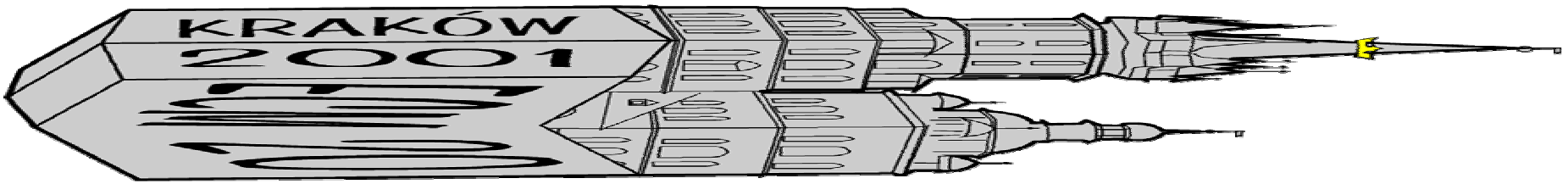


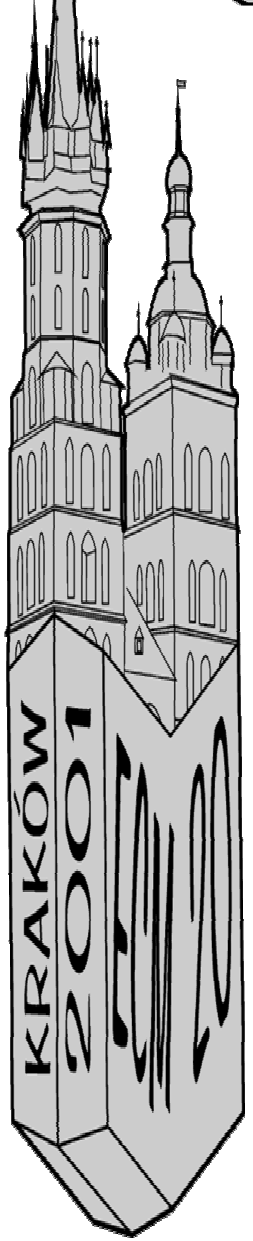


How was it proceeded ?

• It was decided to enlarge some previously established RDM models, so as to build starting RMC configurations to be tested.

• In all cases presented hereafter, some initial coordinations were constrained during the Monte Carlo process, so that the final RMC models were obtained from small random atom moves, keeping essentially the crystal structure features of the RDM starting models.

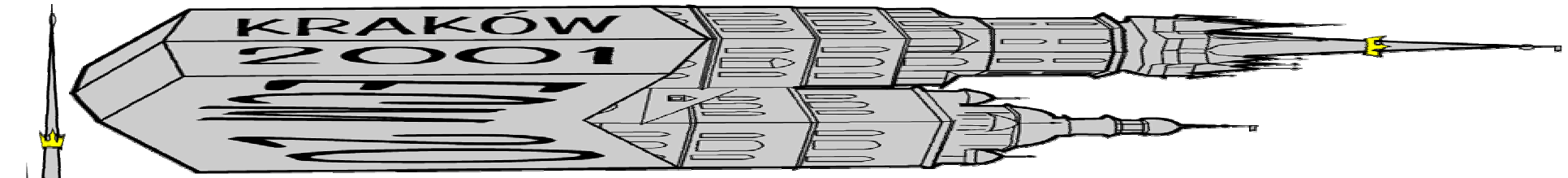


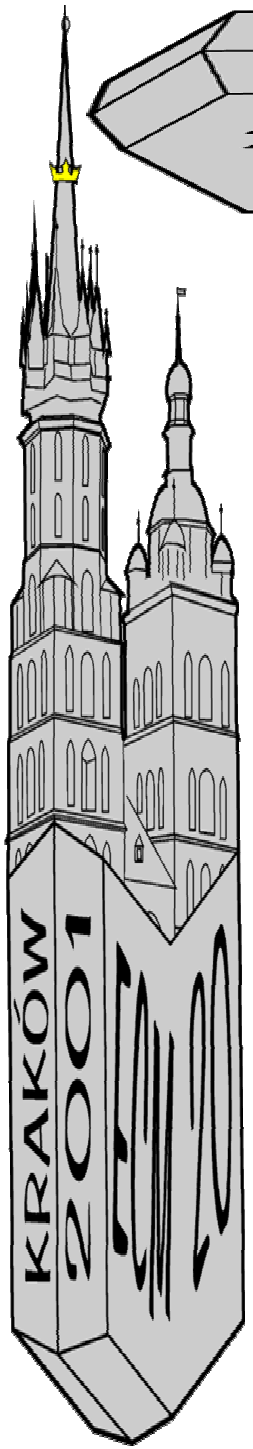


Conditions for building the RMC models from the RDM ones

	$ZnCl_2$	SiO_2	$NaPbM_2F_9$
Initial RDM model	δ -$ZnCl_2$	carnegieite	$NaPbFe_2F_9$
Axes enlarged	ax6, bx4, cx6	ax4, bx4, cx4	ax3, bx2, cx3
Total atom number in RMC modelling	1728	1536	936
RMC constraints	$[ZnCl_4]$	$[SiO_4]$	$[MF_6]$

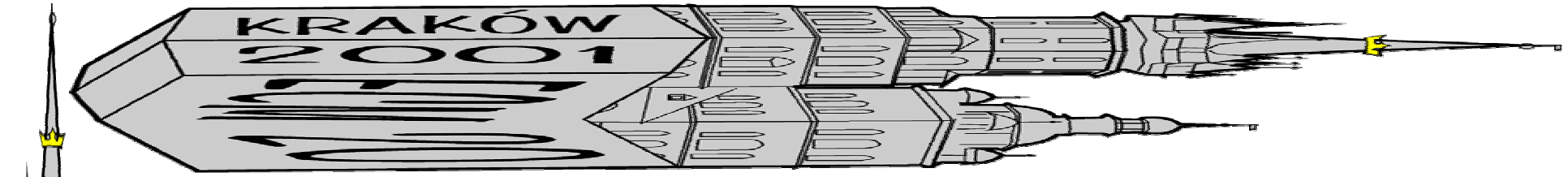
To be noted : the RDM starting models are the phases in which devitrify the glasses, in all cases.

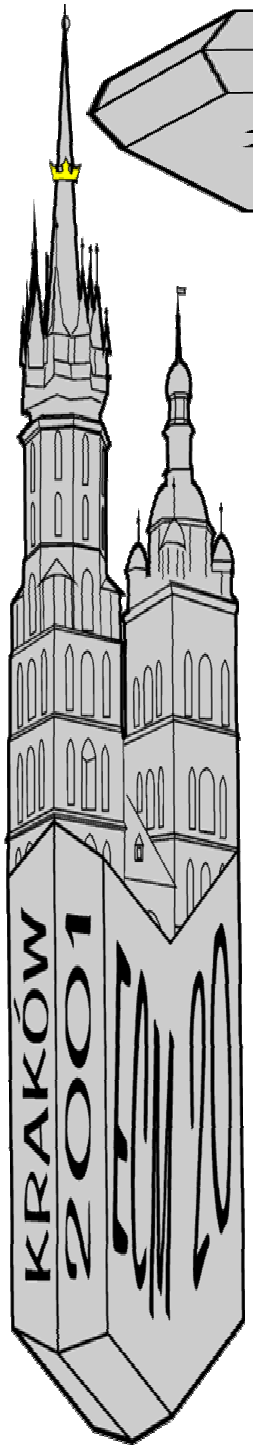


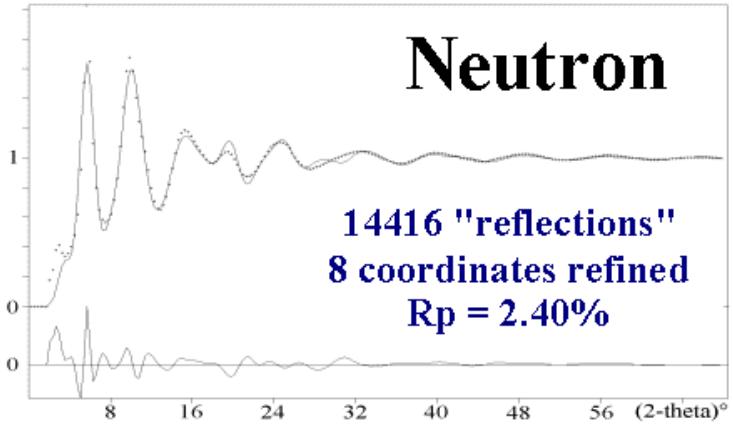


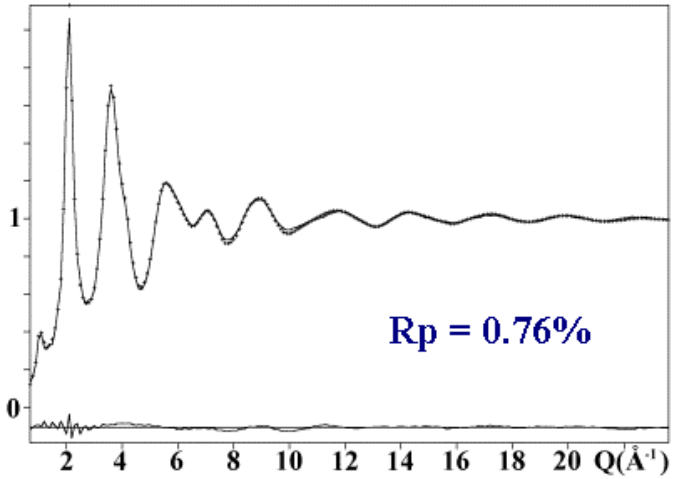
Final reliabilities Rp (%).
N = neutron, X = X-ray ; M = Fe, V.

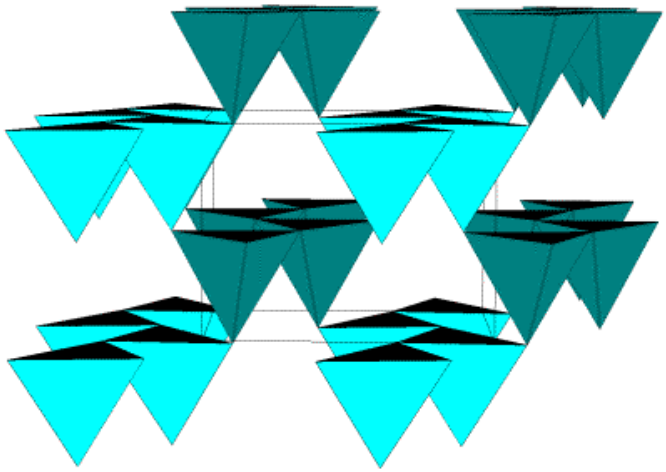
	$ZnCl_2$	SiO_2	$NaPbM_2F_9$
RDM	2.40 (N)	2.45 (N) 2.37 (X)	2.00 (N, Fe) 2.45 (N, V) 5.07 (X, Fe)
RMC - random	0.76 (N)	unavailable D.A. Keen & R.L. McGreevy *Nature* 344 (1990) 423.	0.77 (N, Fe) 1.00 (N, V) 1.14 (X, Fe)
RMC from RDM starting models	1.09 (N)	1.48 (N) 2.00 (N)	0.81 (N, Fe) 1.22 (N, V) 1.75 (X, Fe)


KRAKÓW
2001

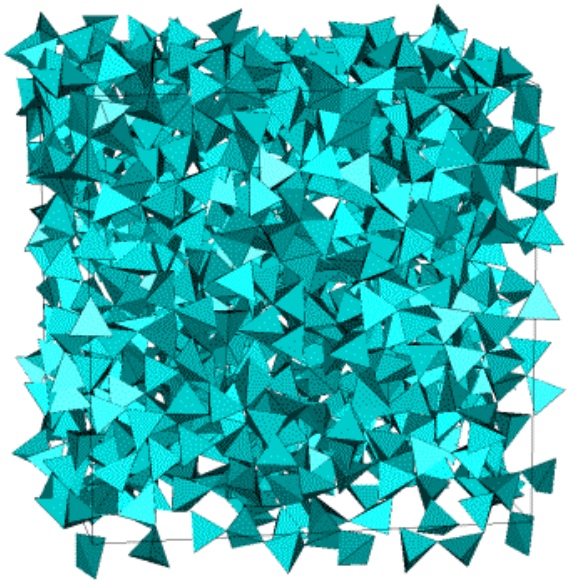

KRAKÓW
2001
ECM 20

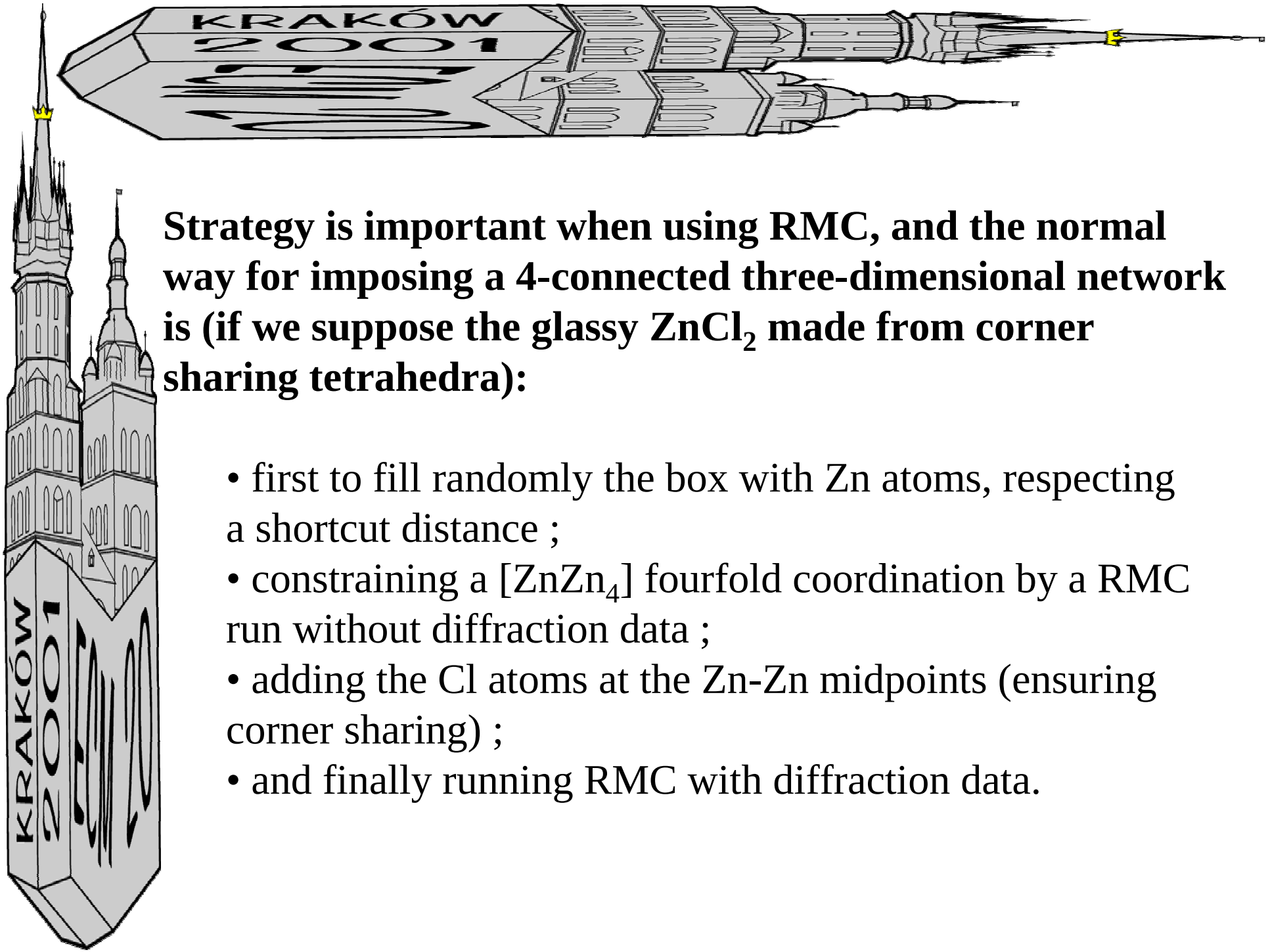

Neutron
14416 "reflections"
8 coordinates refined
Rp = 2.40%
1
0
0
8
16
24
32
40
48
56
(2-theta)°


Rp = 0.76%
1
0
2
4
6
8
10
12
14
16
18
20
Q(Å-1)



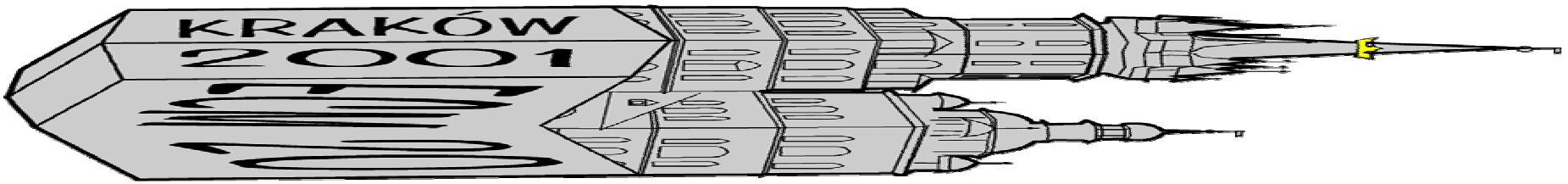
δ-$ZnCl_2$

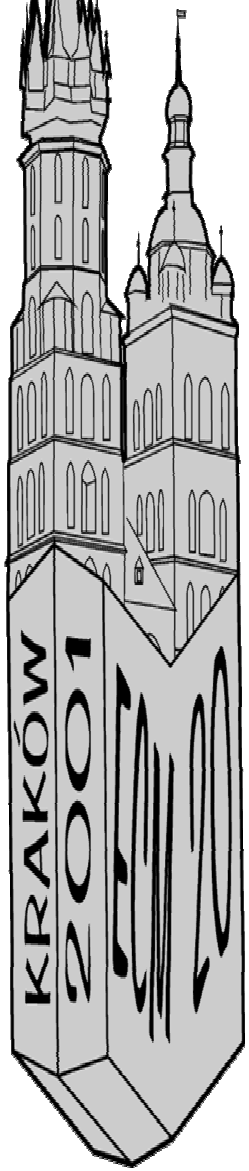




Strategy is important when using RMC, and the normal way for imposing a 4-connected three-dimensional network is (if we suppose the glassy $ZnCl_2$ made from corner sharing tetrahedra):

- first to fill randomly the box with Zn atoms, respecting a shortcut distance ;
- constraining a [$ZnZn_4$] fourfold coordination by a RMC run without diffraction data ;
- adding the Cl atoms at the Zn-Zn midpoints (ensuring corner sharing) ;
- and finally running RMC with diffraction data.





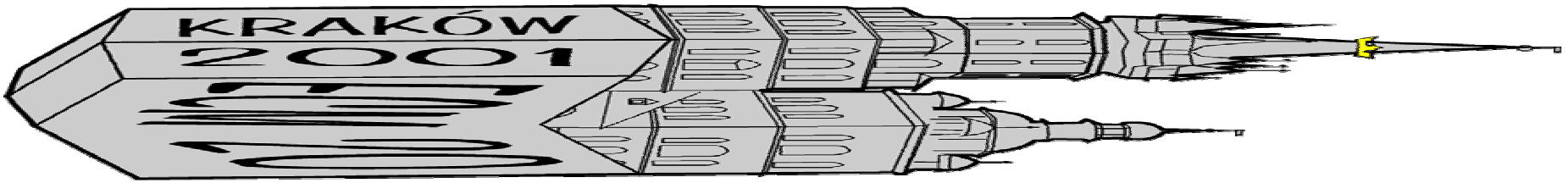
Another approach was deliberately used here, in order to verify if a good fit would be obtained also when edge sharing could occur between [$ZnCl_4$] tetrahedra.

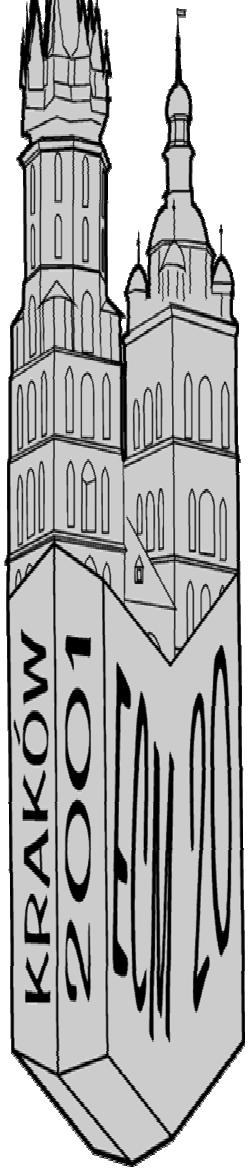
-The model was built up by filling first the box with 650 Zn atoms, at random.

- Then, the chlorine atoms were added at random, with 1.9 Å and 3.0 Å respectively as shortest Zn-Cl and Cl-Cl interatomic distances.

- The RMCA program was then run without diffraction data, adding the constraint that four Cl atoms should be found in the range 2.05-2.65 Å around a Zn atom.

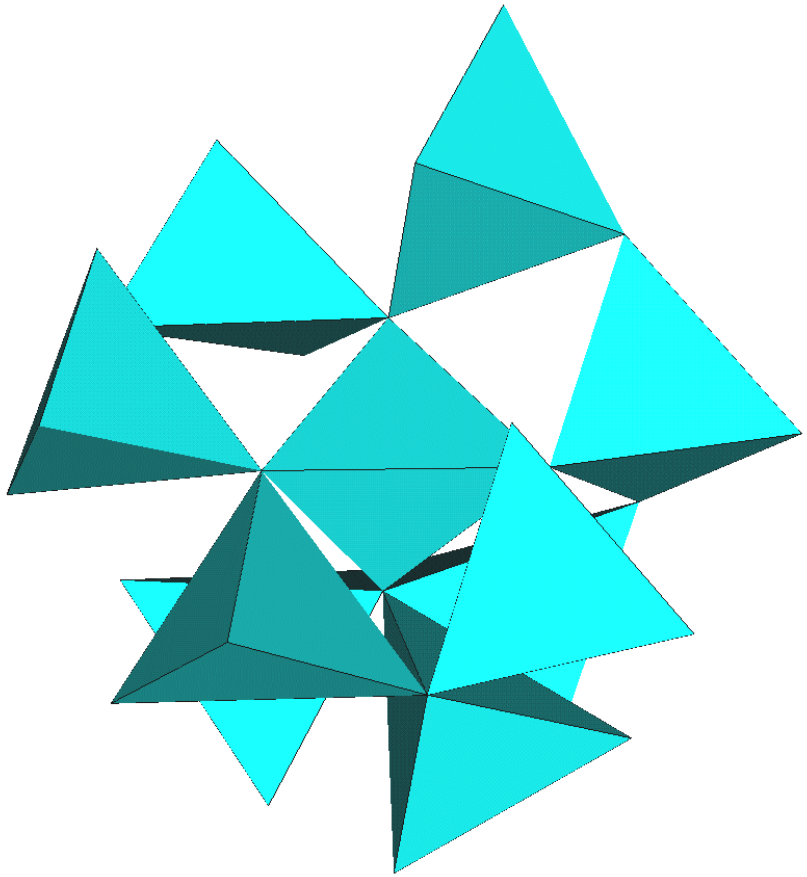
-Then a run was made with diffraction data.

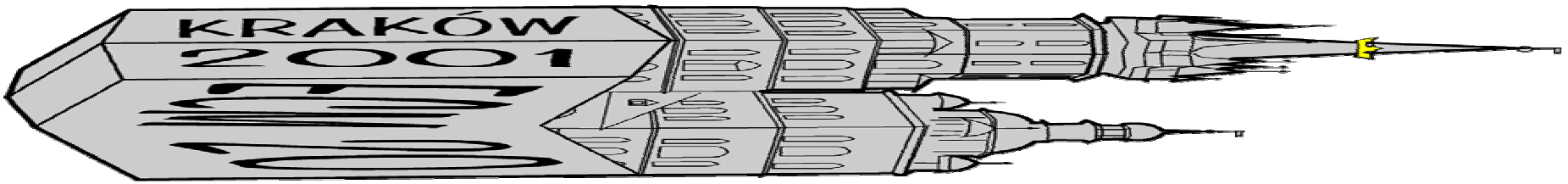


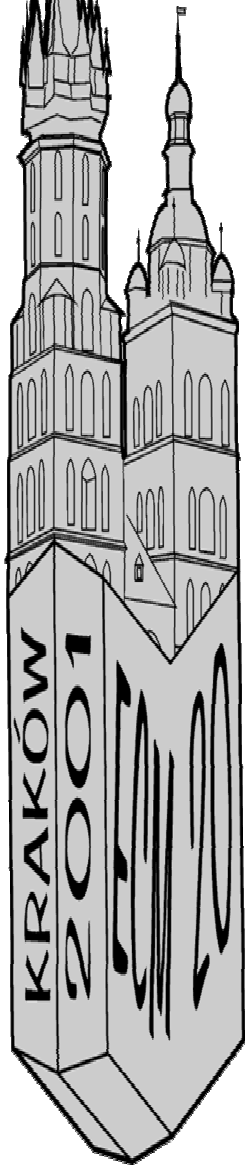


One tetrahedron among 650 is isolated and clusters were built, of which the biggest are 5 tetrahedra sharing each of their Cl atoms with 2 other tetrahedra (8 neighbours).

One tetrahedron has even 9 other tetrahedra as next neighbours :





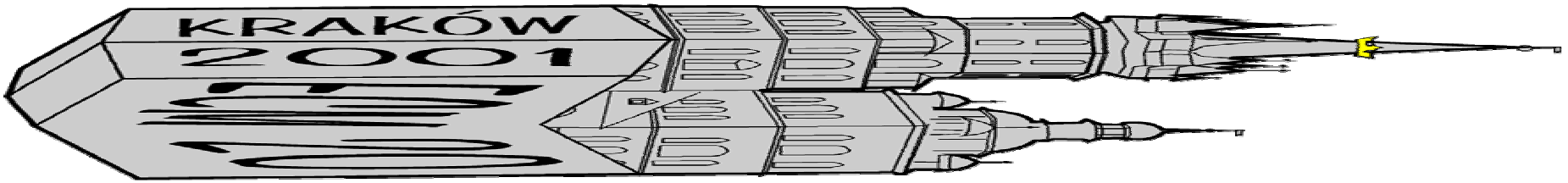


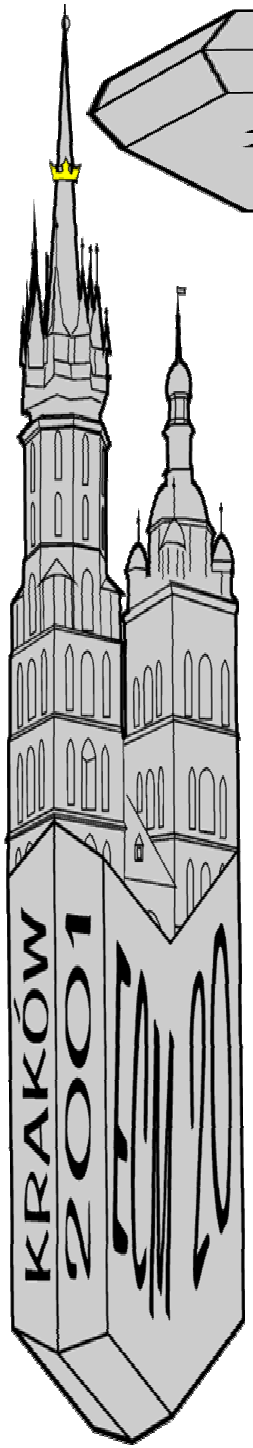
A total of 37 tetrahedra share one edge and 2 tetrahedra share 2 edges.

So that, the building conditions were unable to ensure the corner sharing exclusivity, if we expected it.

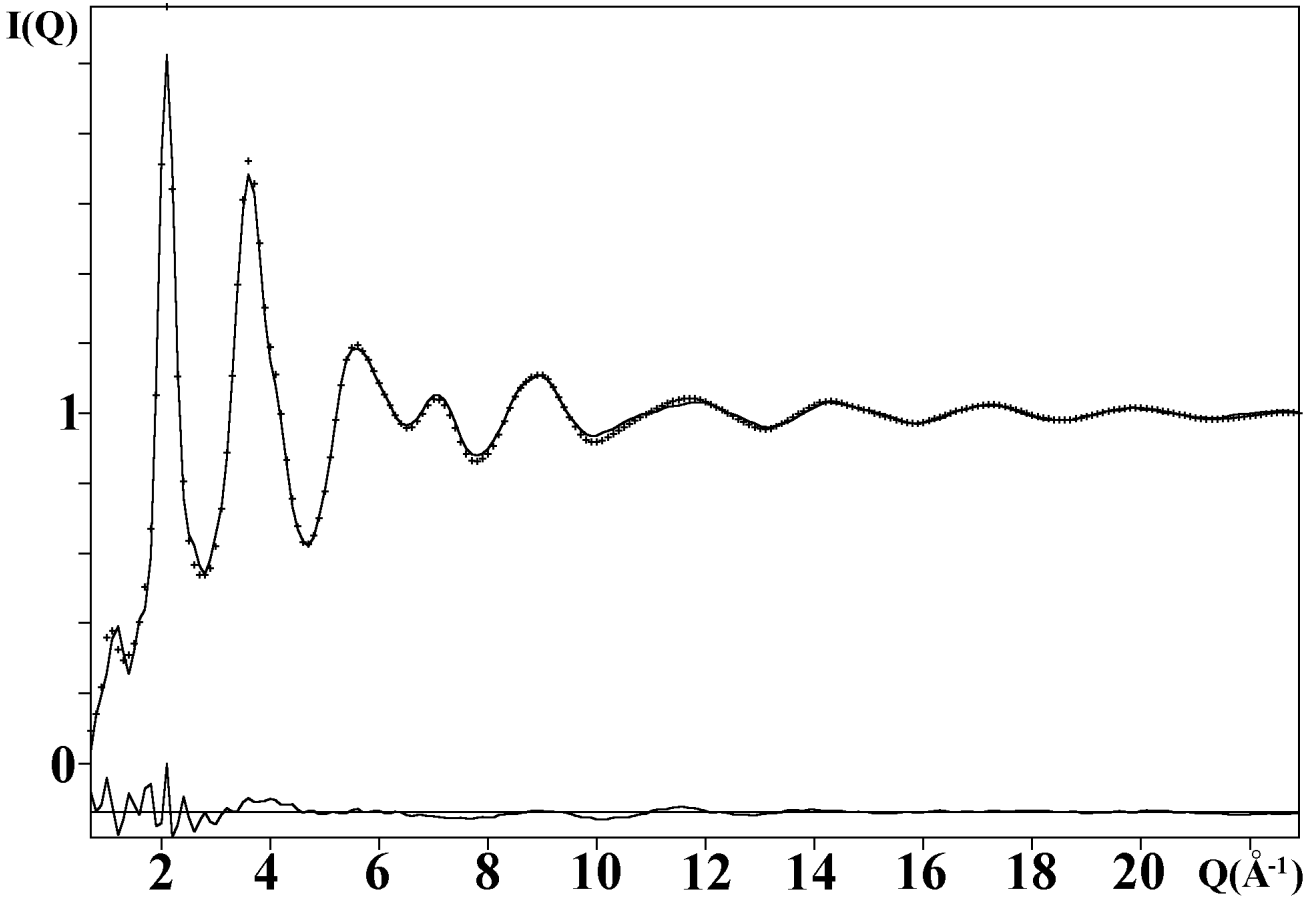
Nevertheless, the fit is almost perfect. As perfect as the published RMC fit with exclusive corner sharing.

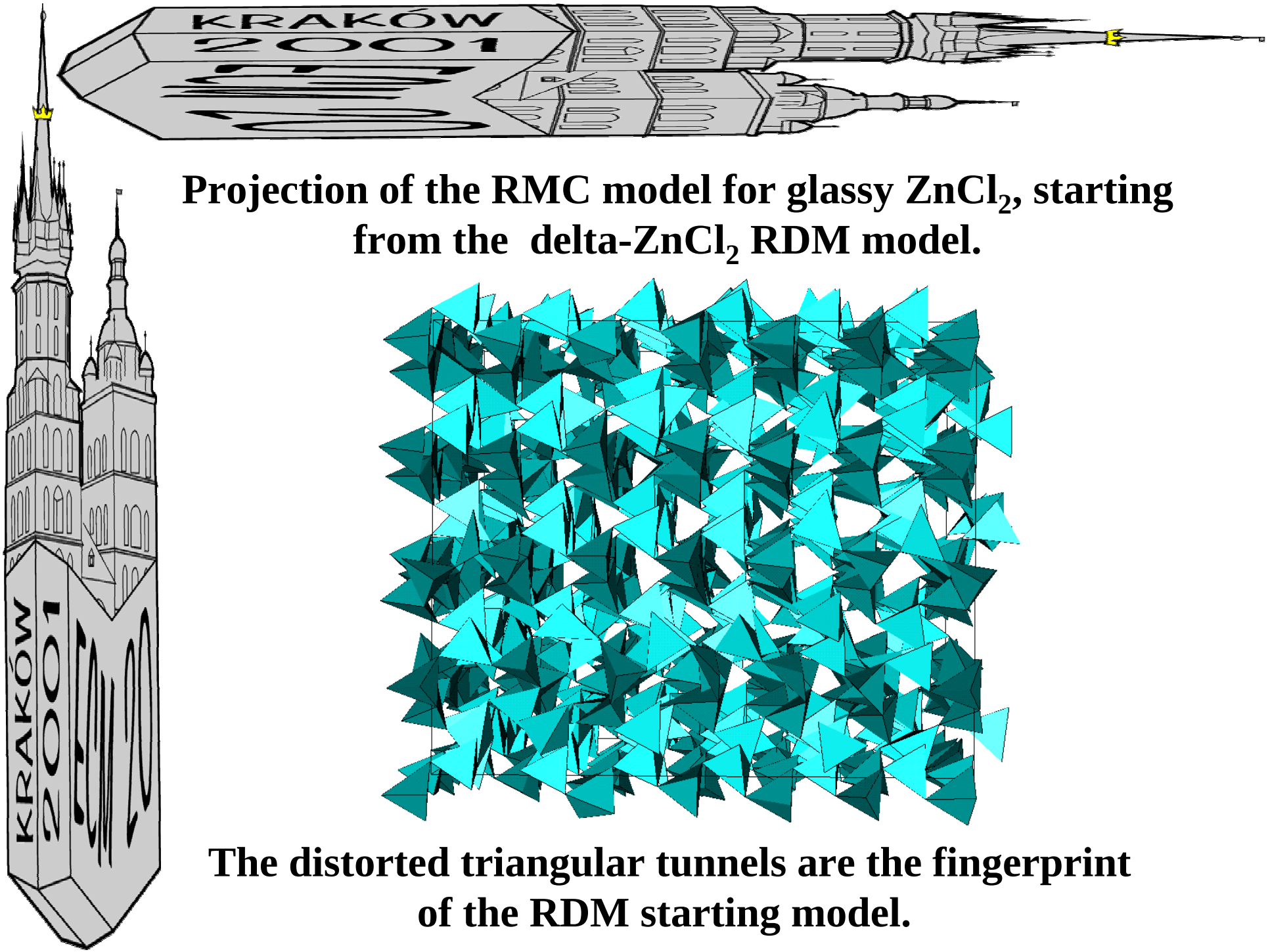
On the other hand, the $ZnCl_2$ RDM model (Rp = 2.40 %), built up from the delta-$ZnCl_2$ structure, corresponds to a perfect 4-connected three-dimensional network.





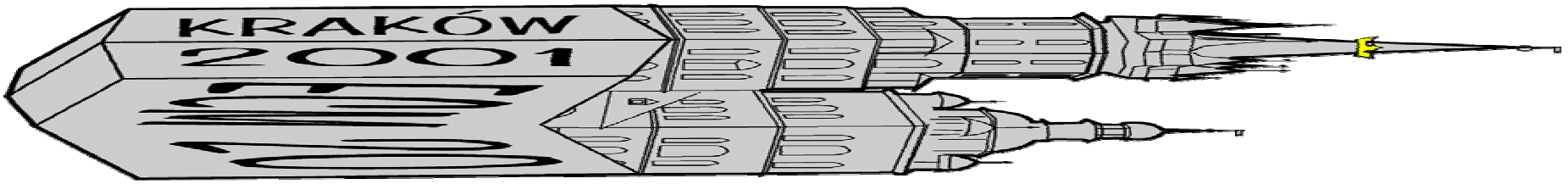
That RDM model was expanded to 1728 atoms, before to realize the RMC approach, obtaining finally the low reliability value Rp = 1.09 %.

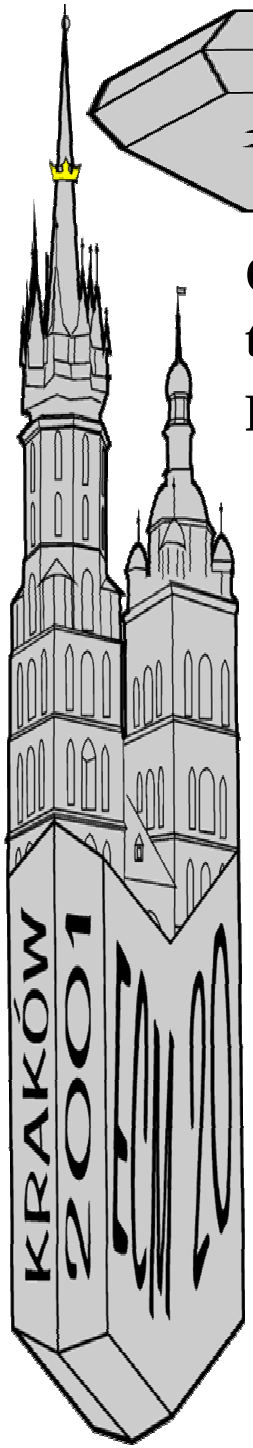




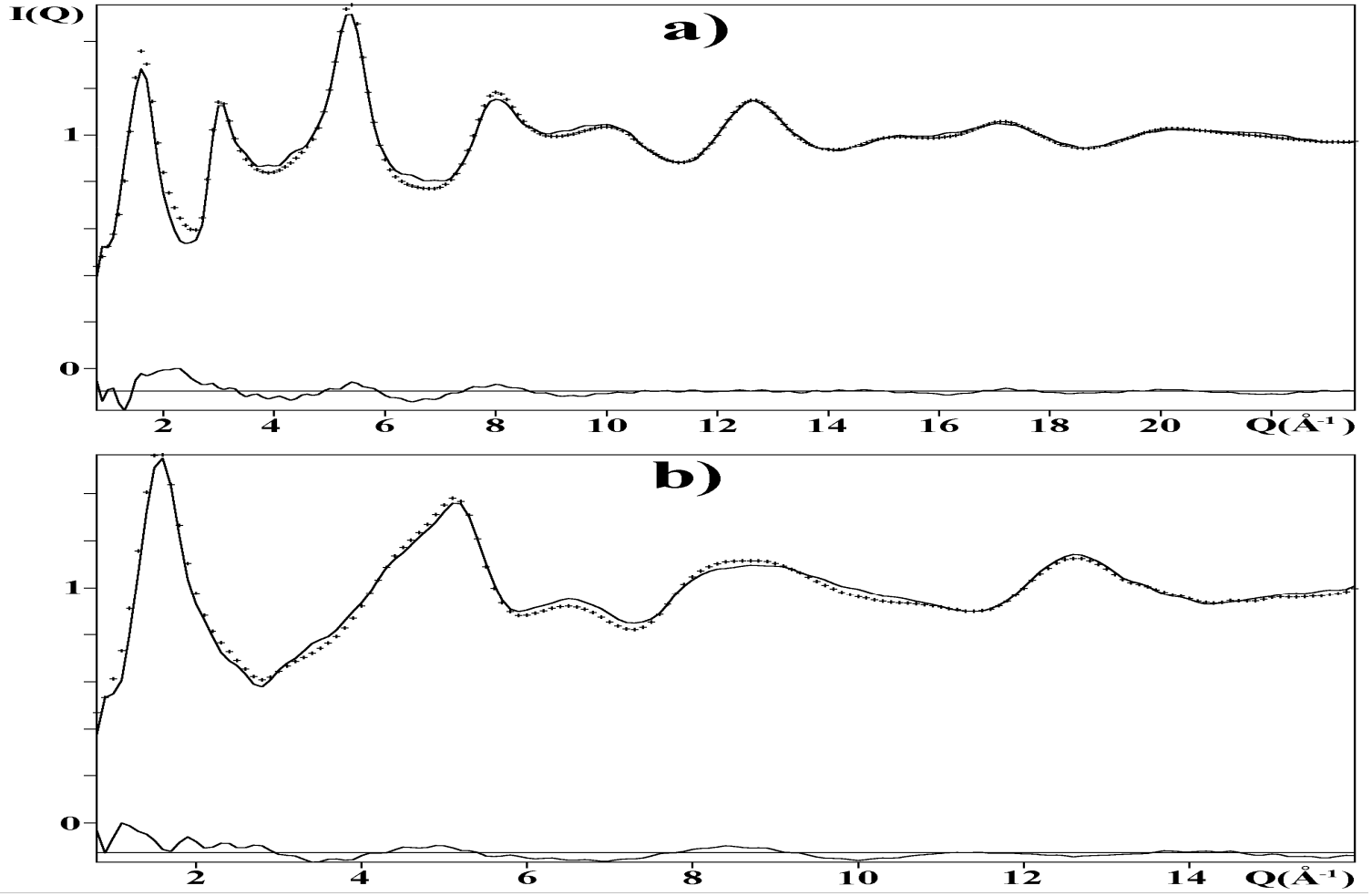
Projection of the RMC model for glassy $ZnCl_2$, starting from the delta-$ZnCl_2$ RDM model.

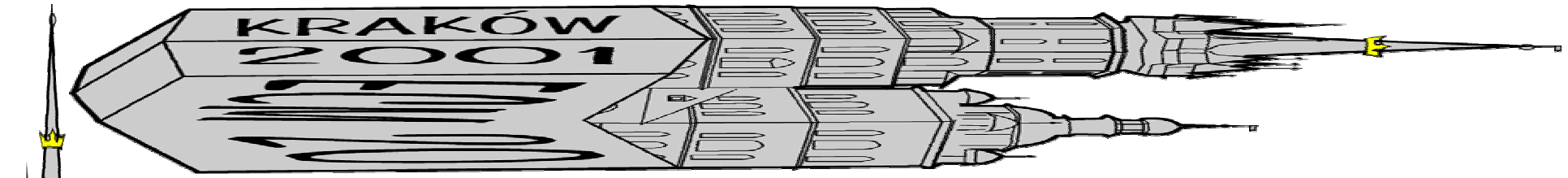
The distorted triangular tunnels are the fingerprint of the RDM starting model.

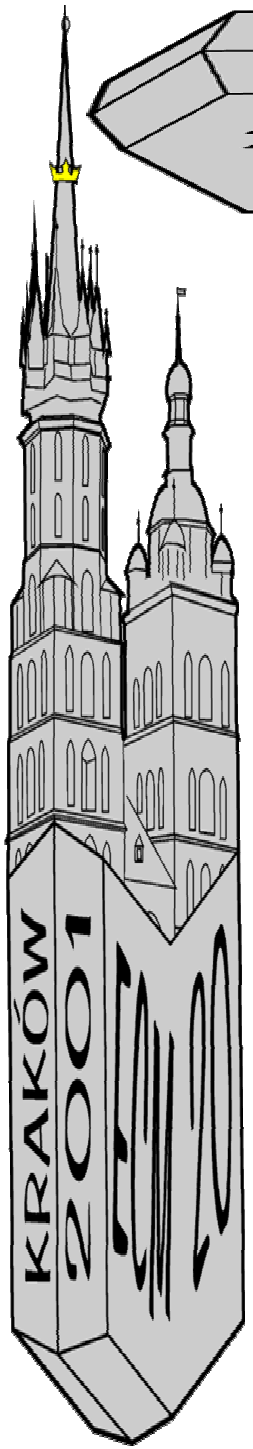




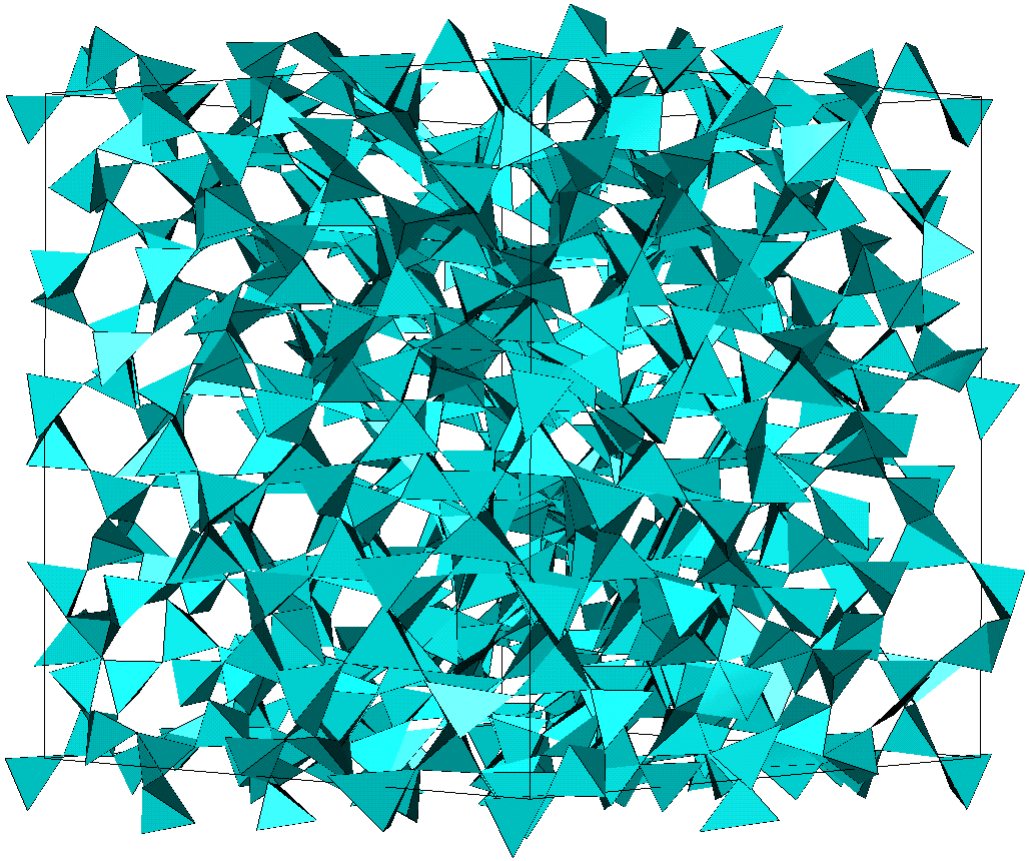
Observed (+++) and calculated interference functions corresponding to the RMC modelling of glassy SiO_2, starting from the alpha-carnegieite RDM model. a) Neutrons, Rp = 1.48 % ;b) X-ray,Rp = 2.00 %.



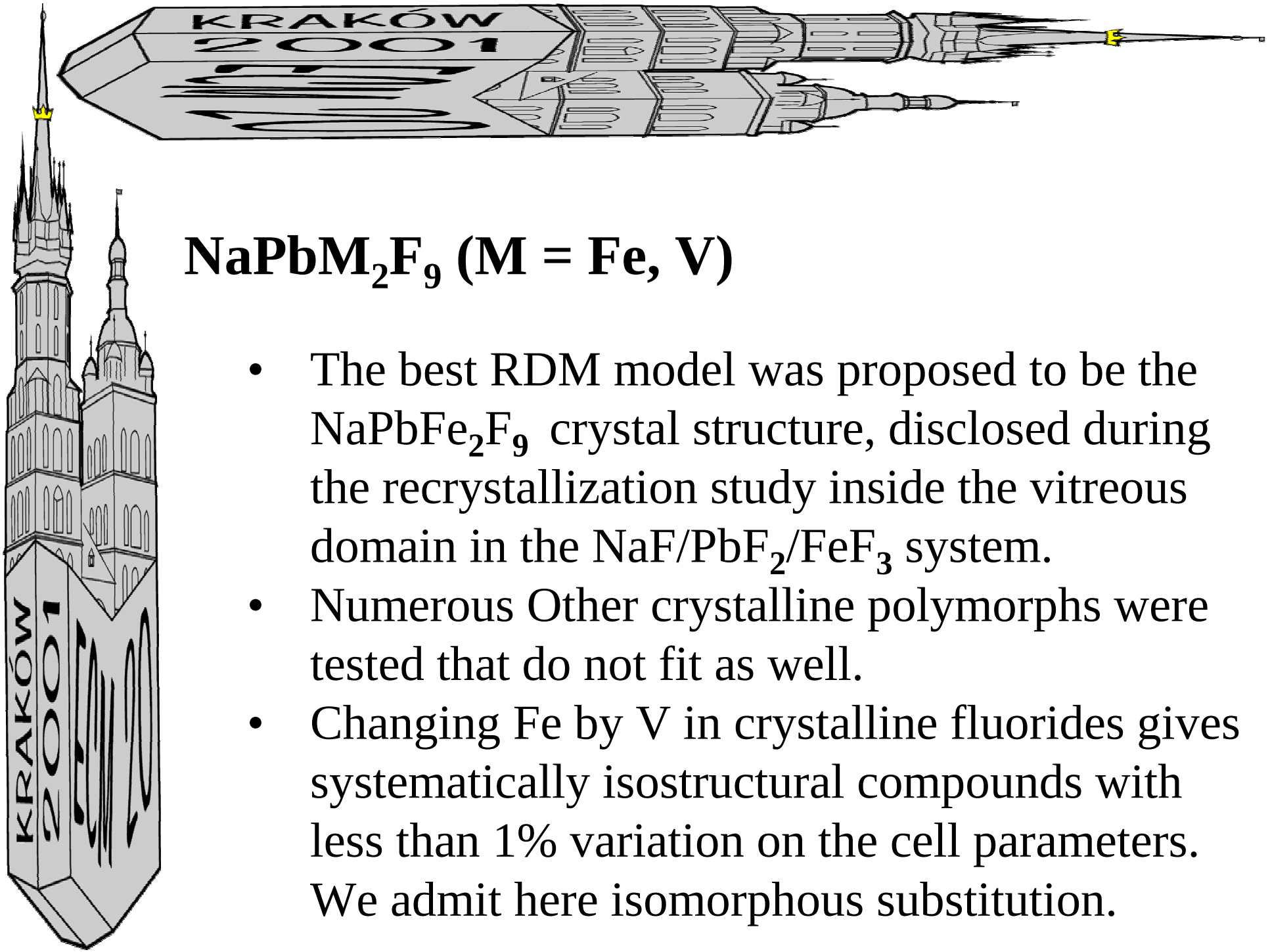




Projection of the RMC model for glassy SiO_2, starting from the alpha-carnegieite RDM model.

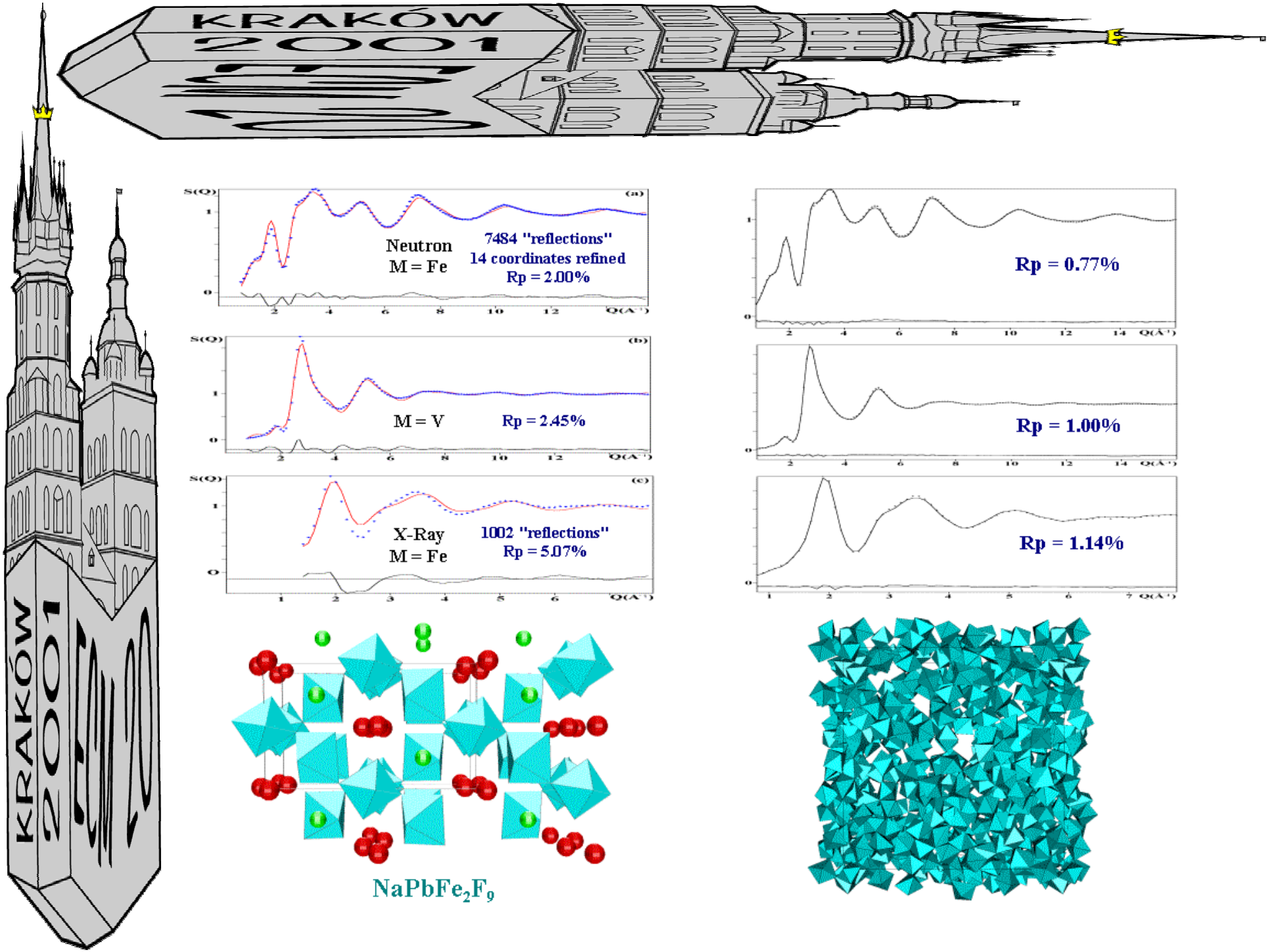


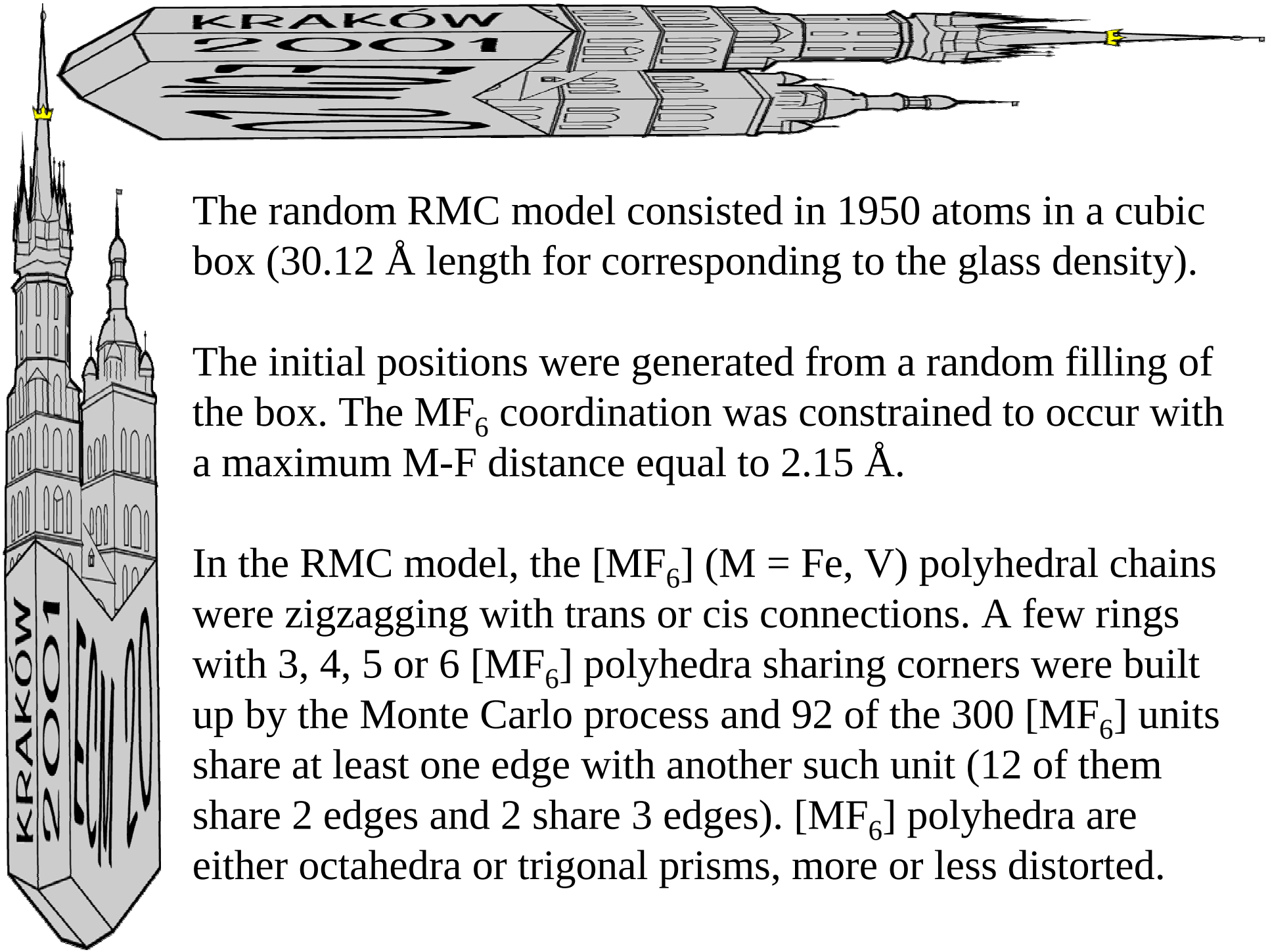
The distorted hexagonal tunnels are the fingerprint of the starting high-cristobalite-like model



$NaPbM_2F_9$ (M = Fe, V)

- The best RDM model was proposed to be the $NaPbFe_2F_9$ crystal structure, disclosed during the recrystallization study inside the vitreous domain in the $NaF/PbF_2/FeF_3$ system.
- Numerous Other crystalline polymorphs were tested that do not fit as well.
- Changing Fe by V in crystalline fluorides gives systematically isostructural compounds with less than 1% variation on the cell parameters. We admit here isomorphous substitution.

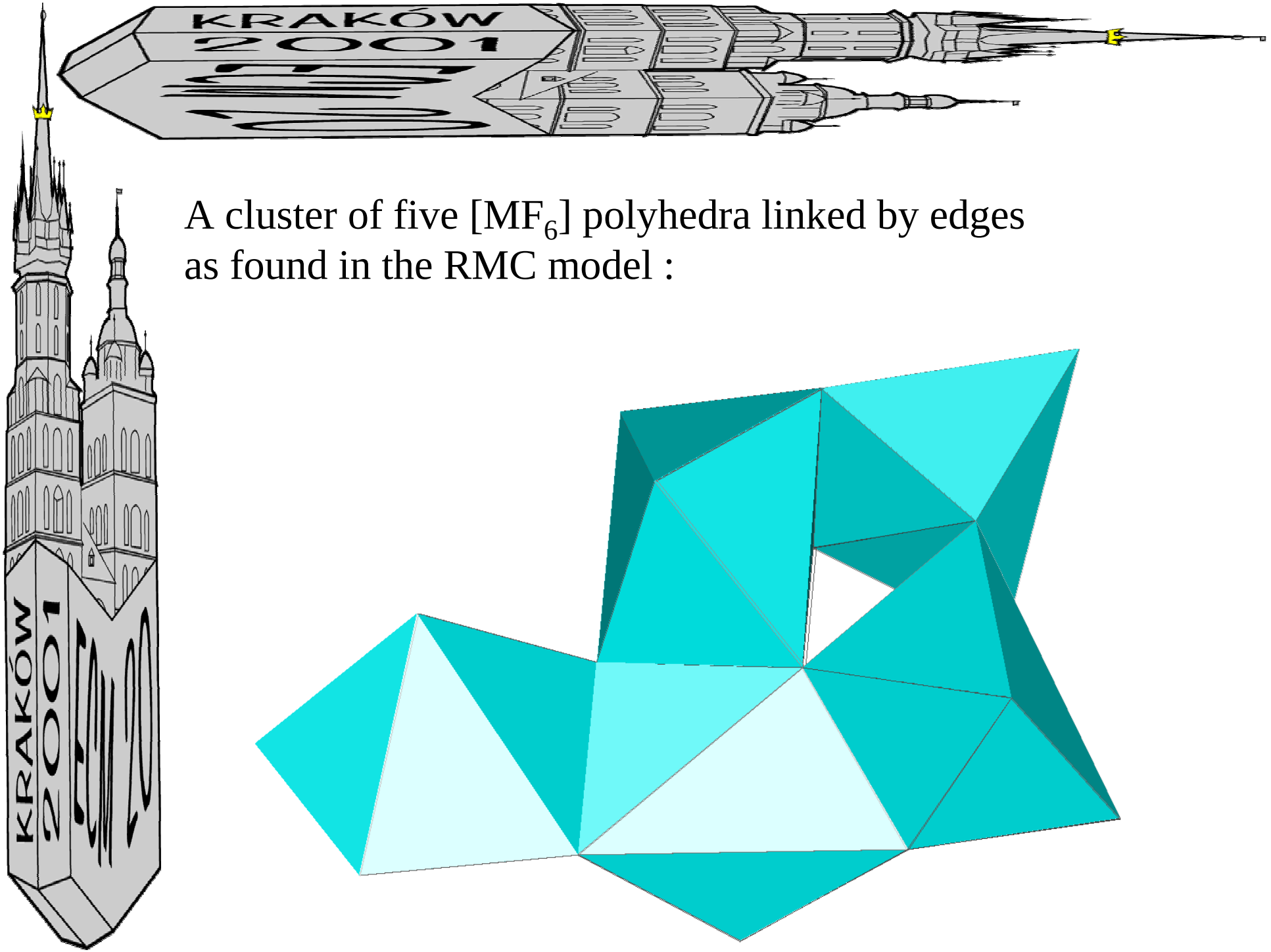

KRAKÓW
2001
KRAKÓW
2001
ECM 20
S(Q)
(a)
Neutron
M = Fe
7484 "reflections"
14 coordinates refined
Rp = 2.00%
Q(Å⁻¹)
(b)
M = V
Rp = 2.45%
(c)
X-Ray
M = Fe
1002 "reflections"
Rp = 5.07%
Rp = 0.77%
Rp = 1.00%
Rp = 1.14%
NaPbFe2F9



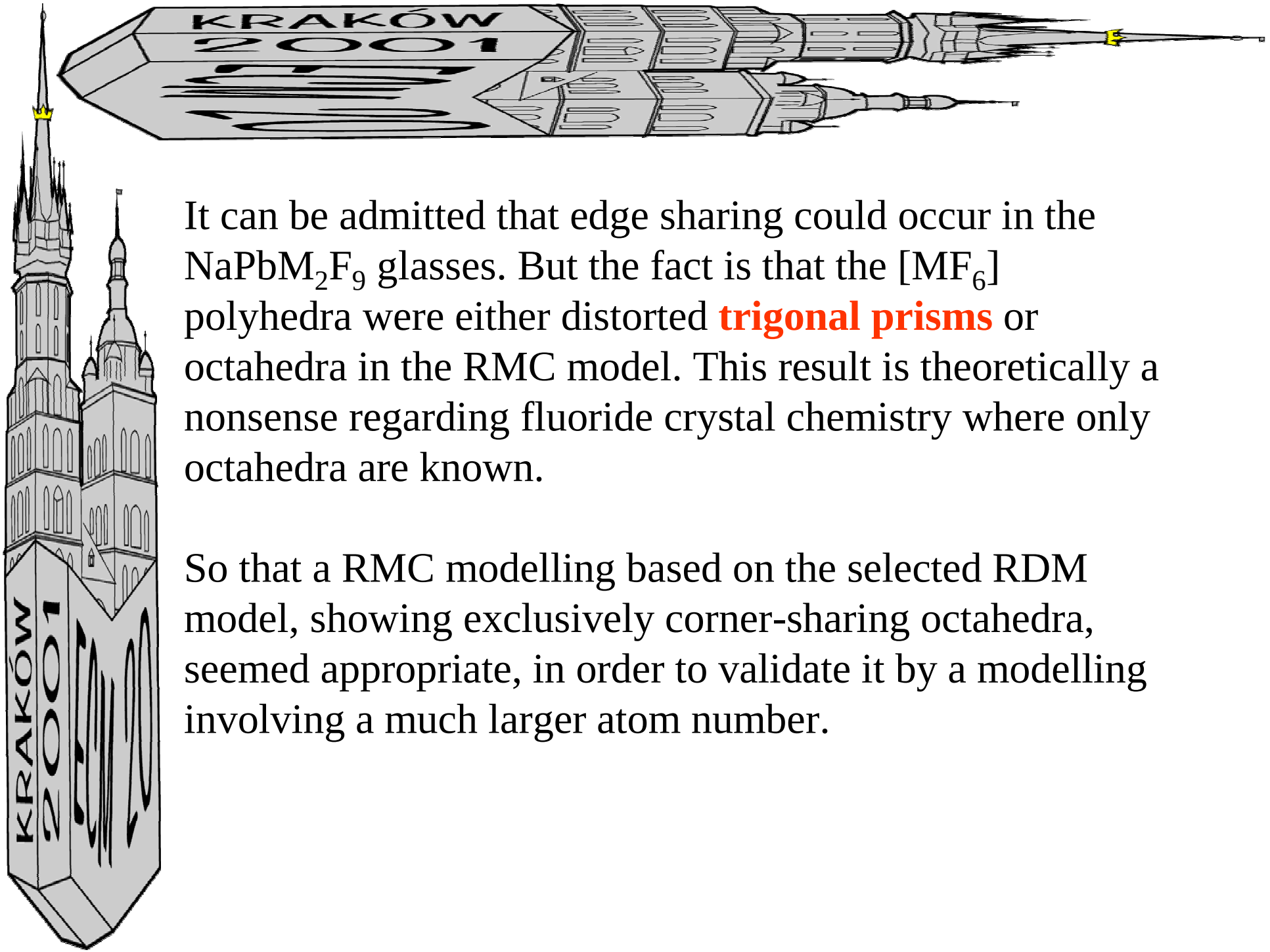
The random RMC model consisted in 1950 atoms in a cubic box (30.12 Å length for corresponding to the glass density).

The initial positions were generated from a random filling of the box. The MF_6 coordination was constrained to occur with a maximum M-F distance equal to 2.15 Å.

In the RMC model, the [MF_6] (M = Fe, V) polyhedral chains were zigzagging with trans or cis connections. A few rings with 3, 4, 5 or 6 [MF_6] polyhedra sharing corners were built up by the Monte Carlo process and 92 of the 300 [MF_6] units share at least one edge with another such unit (12 of them share 2 edges and 2 share 3 edges). [MF_6] polyhedra are either octahedra or trigonal prisms, more or less distorted.

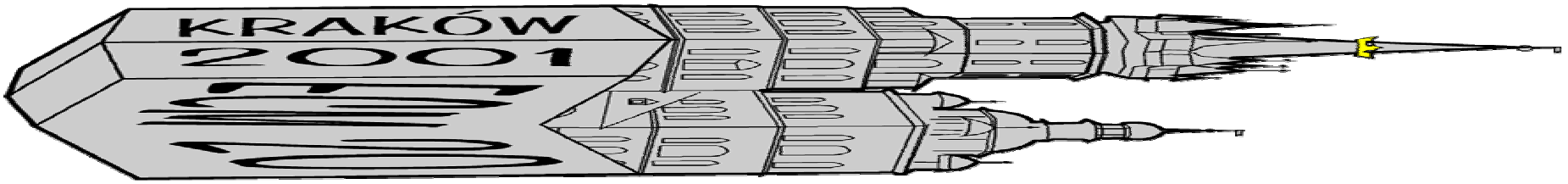


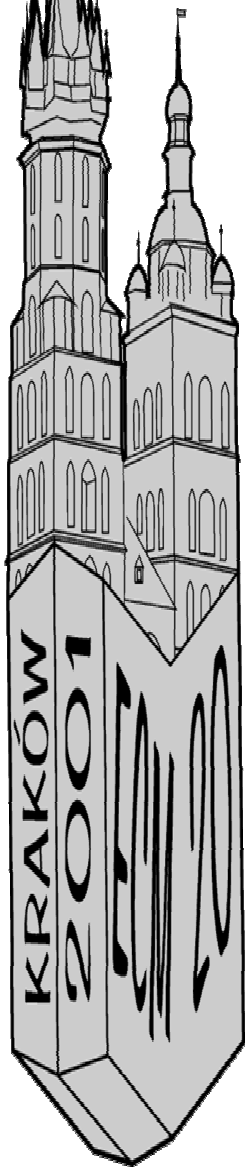
A cluster of five [MF_6] polyhedra linked by edges as found in the RMC model :



It can be admitted that edge sharing could occur in the $NaPbM_2F_9$ glasses. But the fact is that the $[MF_6]$ polyhedra were either distorted **trigonal prisms** or octahedra in the RMC model. This result is theoretically a nonsense regarding fluoride crystal chemistry where only octahedra are known.

So that a RMC modelling based on the selected RDM model, showing exclusively corner-sharing octahedra, seemed appropriate, in order to validate it by a modelling involving a much larger atom number.



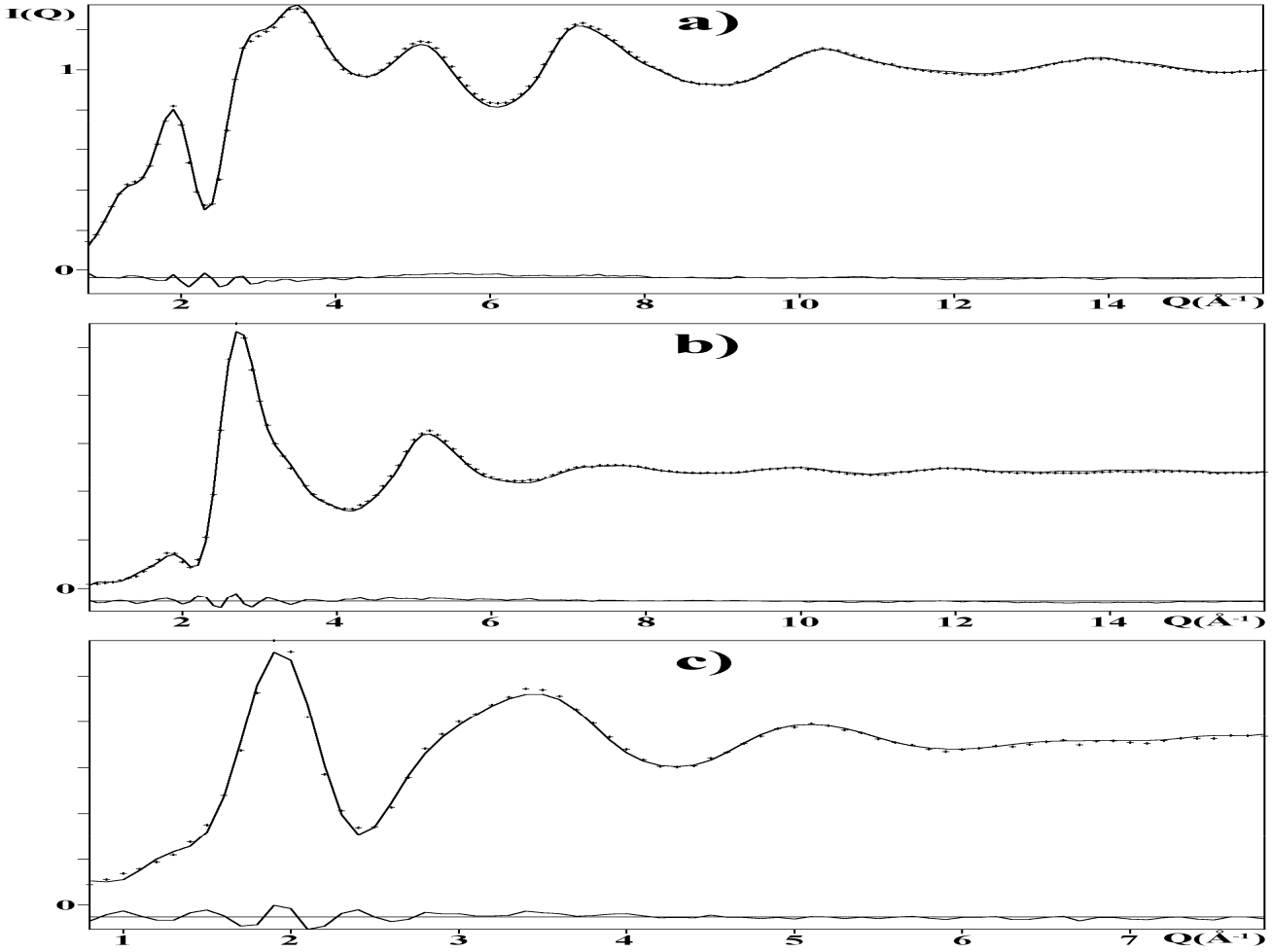


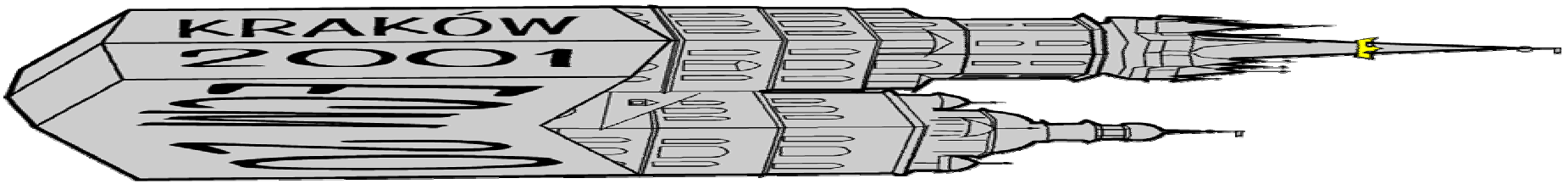
The RDM model was extended to 936 atoms, and the RMC application produced soon acceptable Rp values.

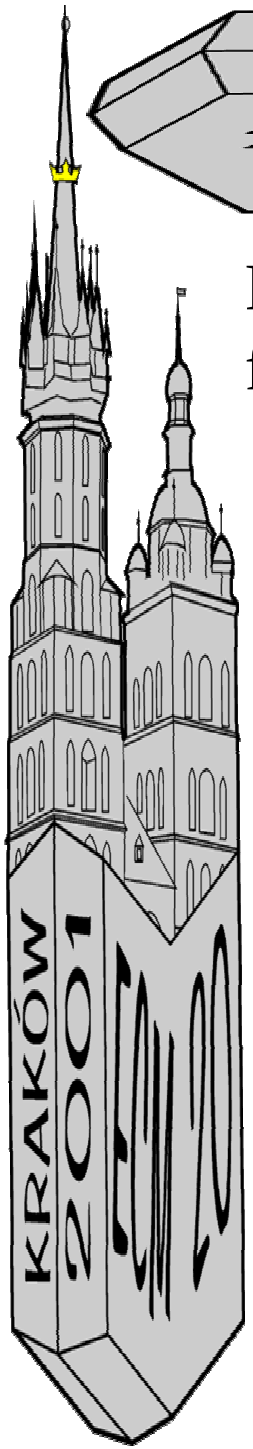
a) Neutron,
M = Fe
Rp = 0.81 %

b) Neutron,
M = V and
Rp = 1.22 %

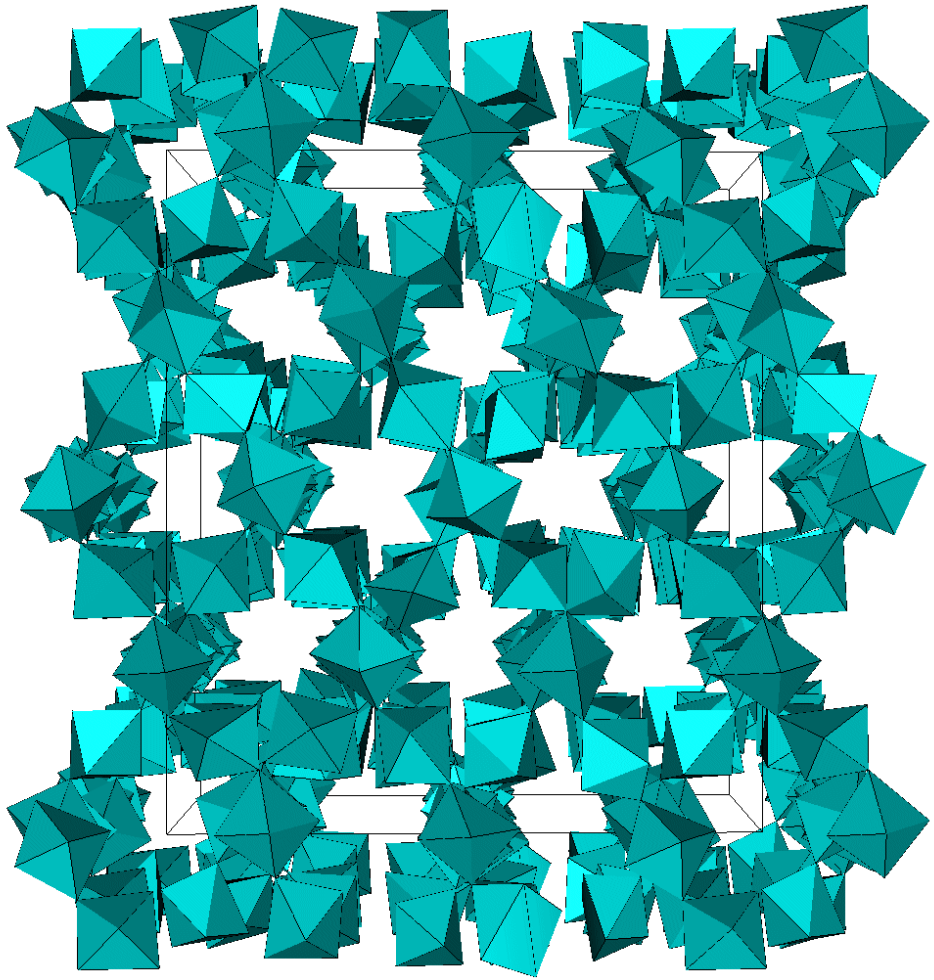
c) X-ray,
M = Fe and
Rp = 1.75 %



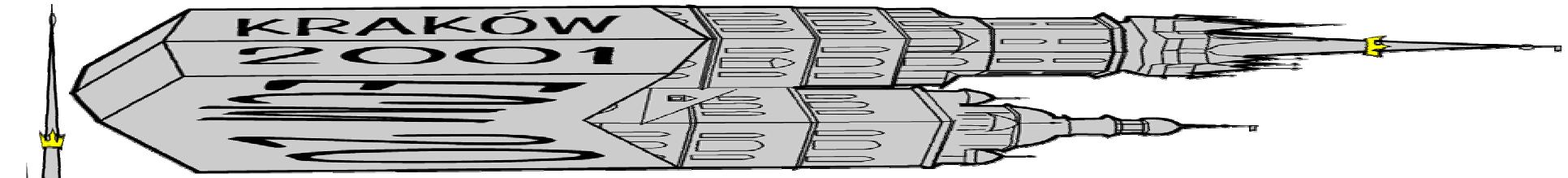


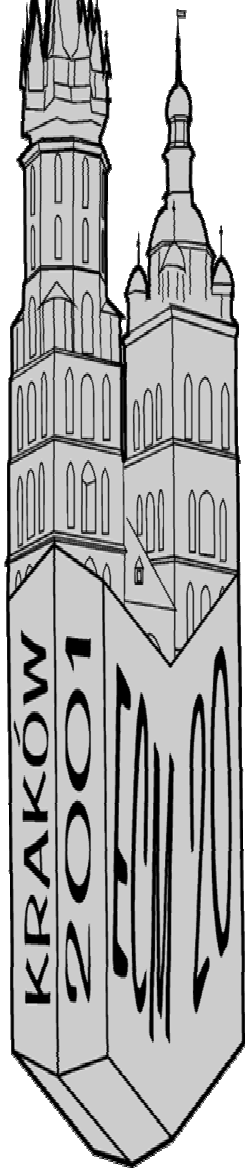


Projection of the RMC model for $NaPbM_2F_9$ (M = Fe, V) fluoride glasses, starting from the $NaPbFe_2F_9$ RDM model.



The distorted intercrossed chains of $[MF_6]$ octahedra are the fingerprint of the starting model.

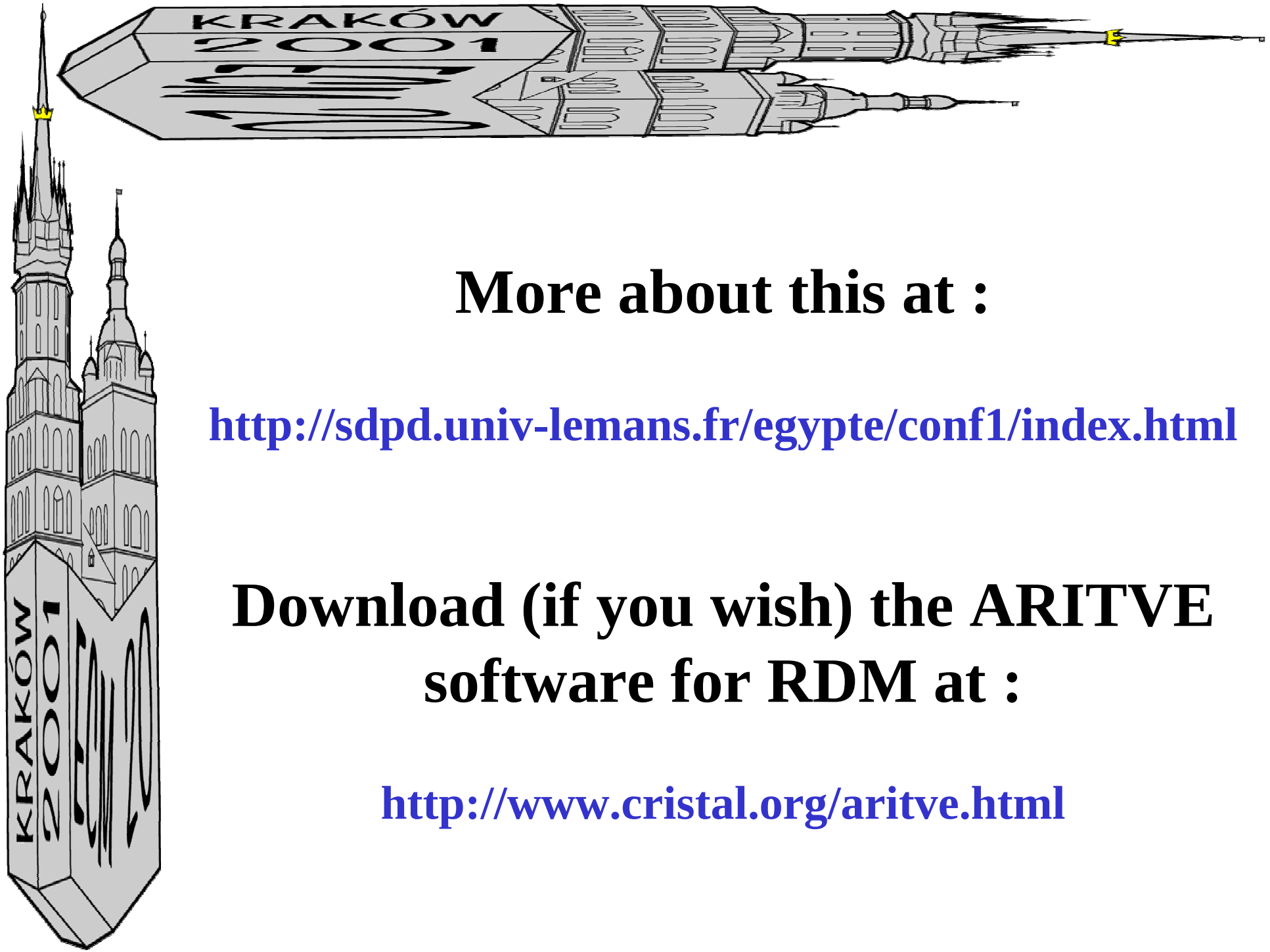




Very brief conclusion :

• It has been shown that a satisfying RDM model may constitute a starting model for a successful RMC simulation with constraints.
• In other words, the RDM best models were structures in the group of possible RMC solutions.

Old-style modelling can bring starting models for new-style modelling. But you have first to find the good RDM model…



More about this at :

http://sdpd.univ-lemans.fr/egypte/conf1/index.html

Download (if you wish) the ARITVE software for RDM at :

http://www.cristal.org/aritve.html