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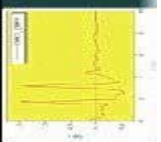

# Reverse Monte Carlo
## and
# Rietveld modelling
## of
# $BaMn(Fe,V)F_7$ glass structures
## from
# neutron data

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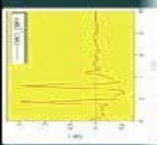

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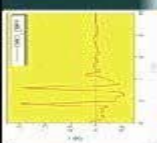
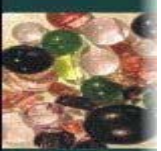




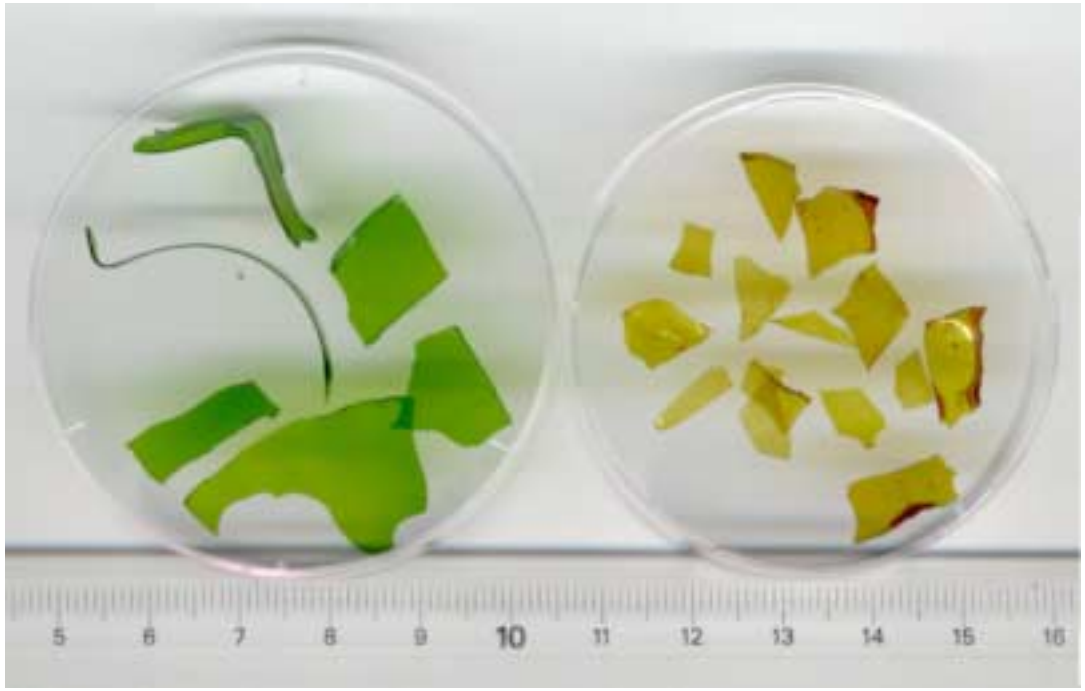
# Introduction

Structure simulations by the reverse Monte Carlo (RMC) method applied to starting models built up from enlarged crystal structures, selected from the quality level of a Rietveld fit of their scattering data, were reported for glassy $SiO_2$, $ZnCl_2$, and $NaPb(Fe,V)_2F_9$.

The Rietveld for disordered materials (RDM) method has previously shown its potentiality to reveal very fast (quite small computing time) if a given crystalline model would be a good starting point for further large-scale modelling by RMC.

This approach is used here for modelling the structure of fluoride glasses for a composition $BaMn(Fe,V)F_7$ selected because it corresponds to the existence of a large number of known different crystal structures, and because of the quasi-isomorphous Fe/V substitution in fluoride materials.

# Experimental

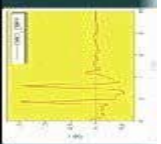


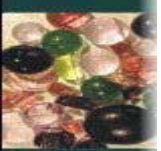

- Neutron data recorded on instrument D4 (ILL –Grenoble)

$$\lambda = 0.497 \text{ Å}$$

- Density number for the two glasses :

$$\rho_0 = 0.0710 \pm 0.0003 \text{ atom.Å}^{-3}$$





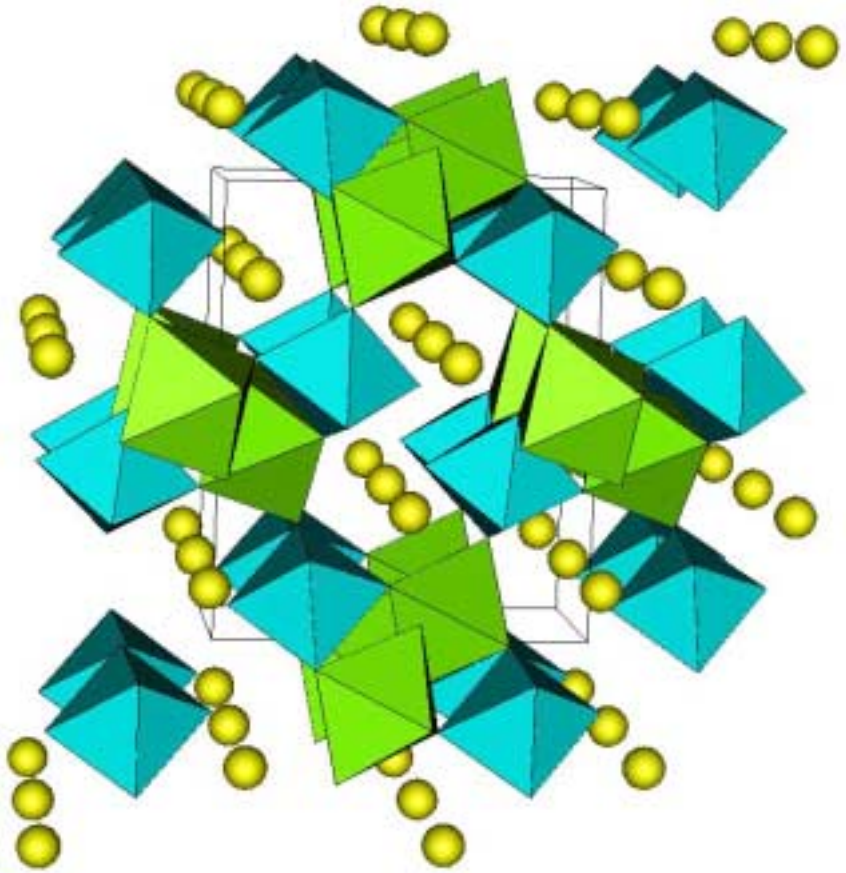
# Models ?

Seven crystal structure-types are known with that composition :

- $BaMnFeF_7$ (I)
- $BaMnGaF_7$ (II)
- $BaZnFeF_7$ (III)
- $BaCaGaF_7$ (IV)
- $BaCuFeF_7$ (V)
- $BaCuInF_7$ (VI)
- $BaNaZrF_7$ (VII)

The $BaMn(Fe,V)F_7$ glasses crystallize in type (II)

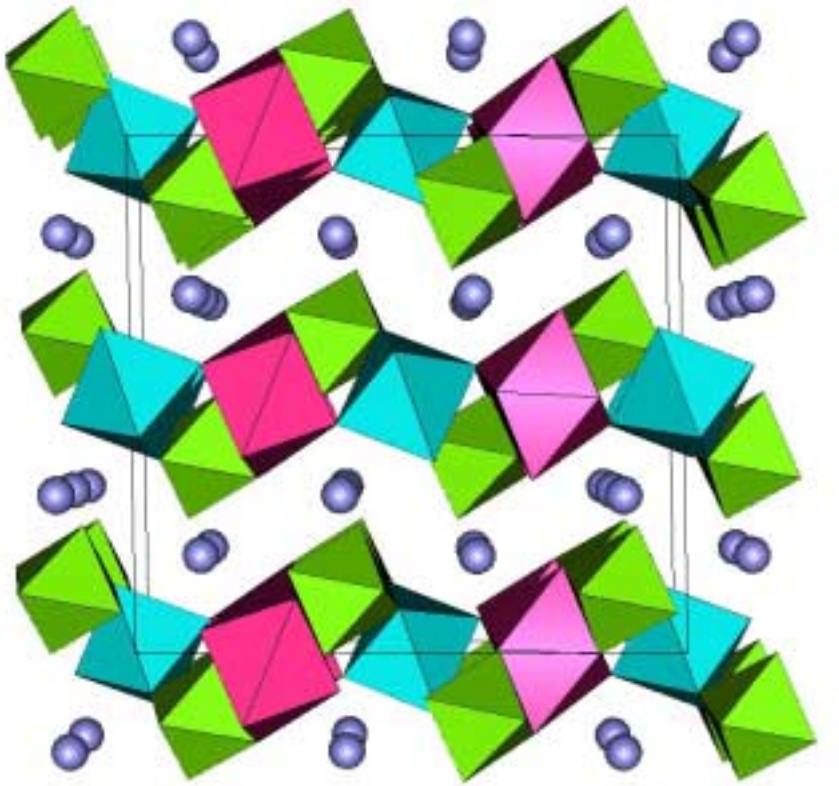
# Model (I) : $BaMnFeF_7$



Three-dimensional octahedral lattice with edge-sharing dinuclear $Mn_2F_{10}$ units (green) linked by corners to $FeF_6$ octahedra (blue).

A glass with $BaMnFeF_7$ composition does not crystallize in type I.

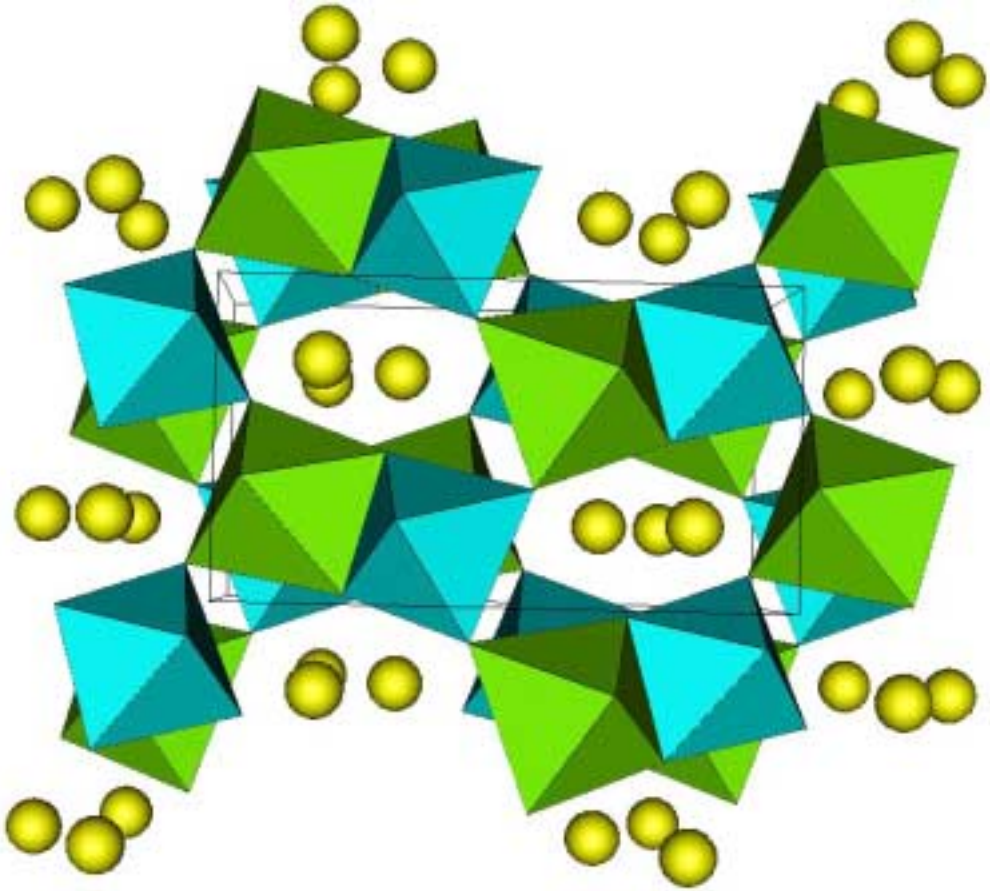
# Model (II) : $BaMnGaF_7$



Edge sharing of $GaF_6$ octahedra (green) and $MnF_8$ (red) polyhedra occur, forming dinuclear $M_2F_{12}$ units interconnected by corners to $MnF_6$ octahedra (blue) and other $M_2F_{12}$ units, building disconnected layers.

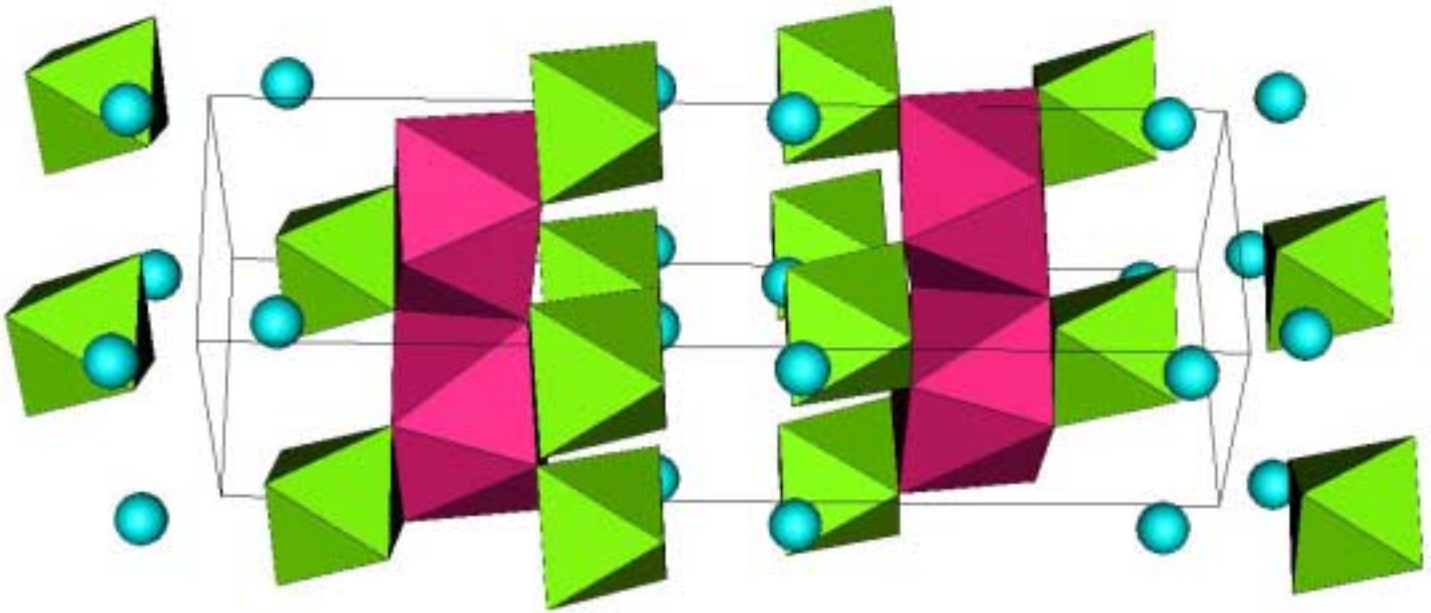
Why glasses prefer to crystallize in this layered structure-type rather than into a 3D network of corner-sharing octahedra ?

# Model (III) : HT-$BaZnFeF_7$



3D structure with edge sharing of $ZnF_6$ and $FeF_6$ octahedra, forming $M_2F_{10}$ groups interlinked by corners, like in type I but differently organized.

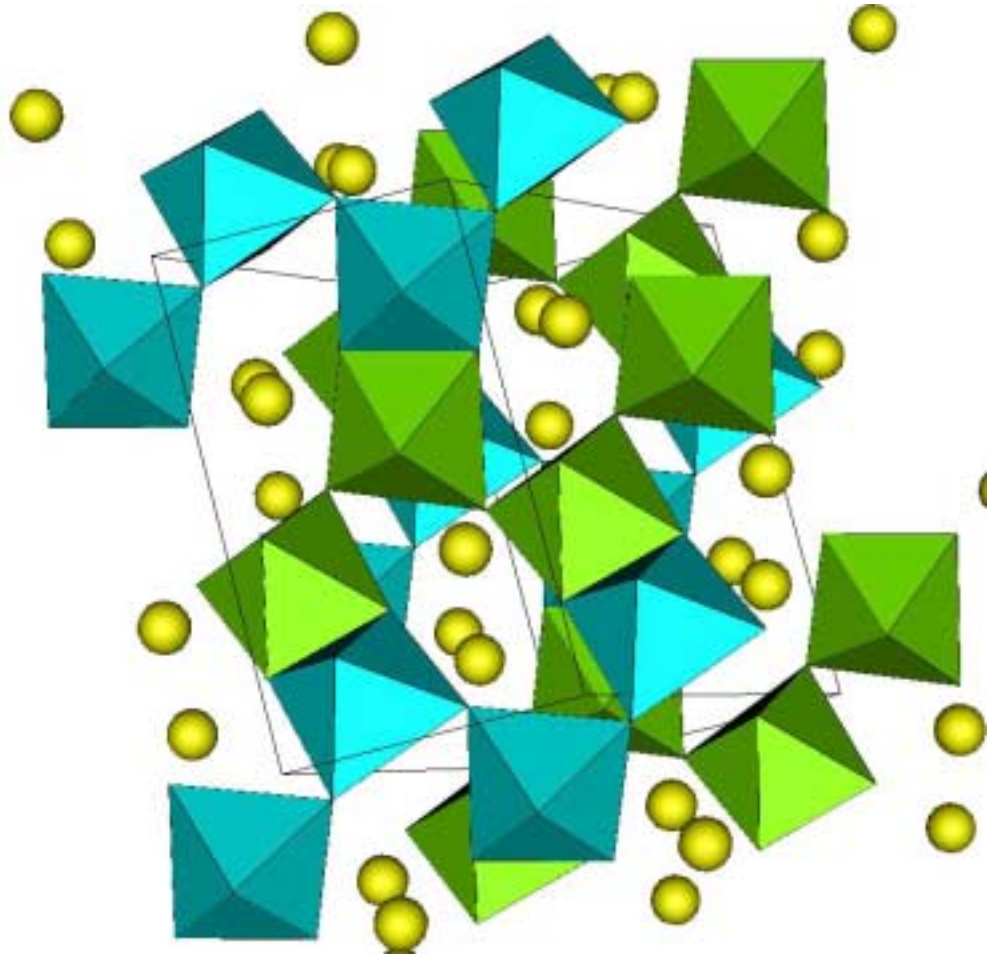
# Model (IV) : $BaCaGaF_7$



$GaF_6$ octahedra (green) and $CaF_8$ square antiprisms (red) are linked by corners and edges forming a two dimensional structure.

$Ga^{3+}$ and $Fe^{3+}$ ionic radii are similar, the difference between $Ca^{2+}$ and $Mn^{2+}$ (smaller) is not a problem since $MnF_8$ square antiprisms are existing in other structures (type II for instance).

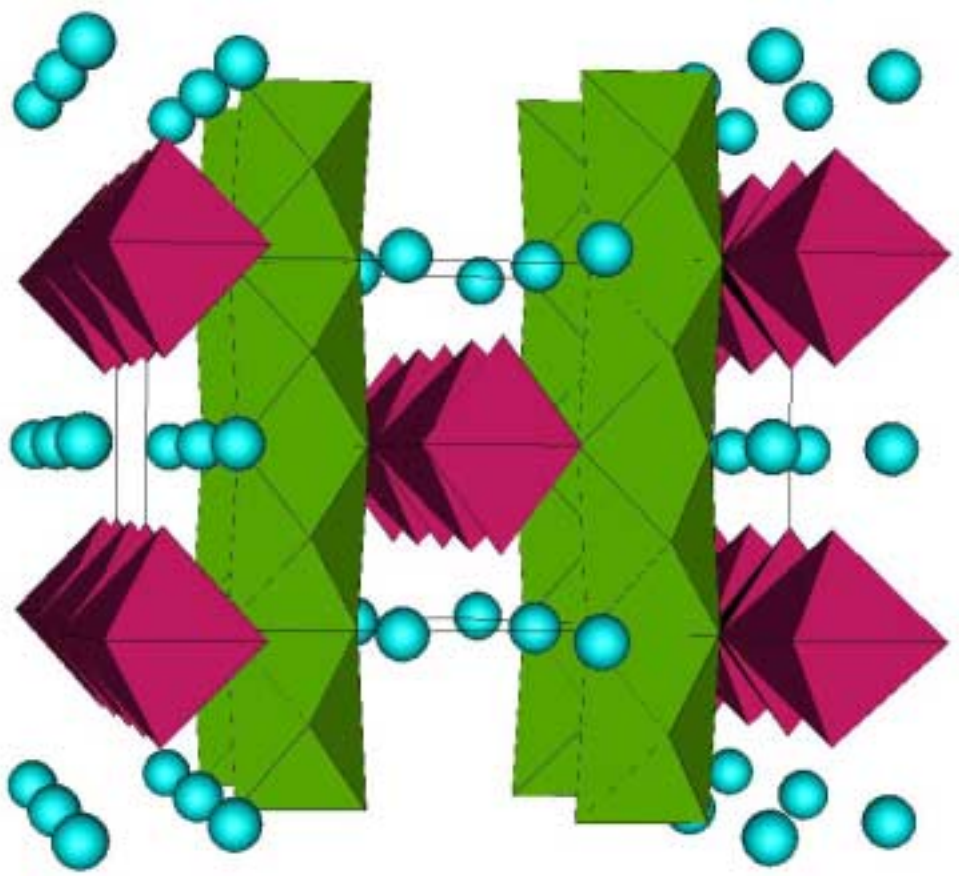
# Model (V) : $BaCuFeF_7$



Edge sharing dioctahedral groups $CuFeF_{10}$ connected by corners in a 3D array, related to HT-BaZnFeF7 (type III).

Partial cationic disorder.

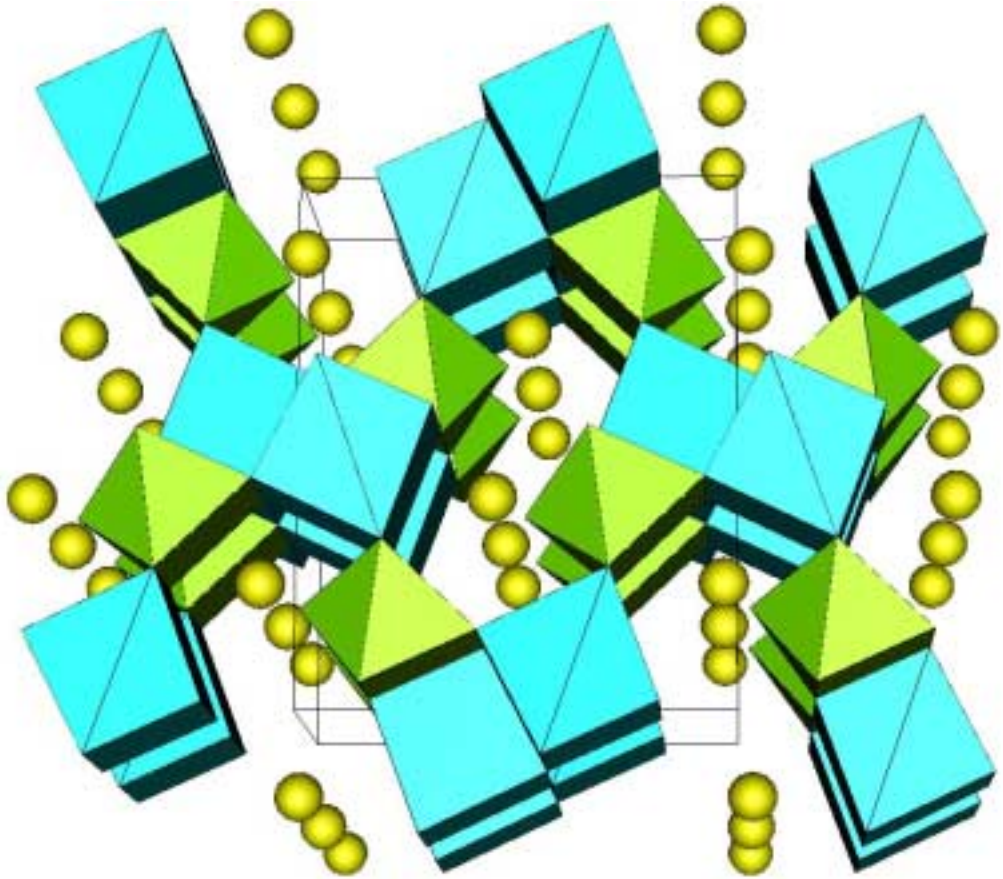
# Model (VI) : $BaCuInF_7$



The 3D structure is built up from infinite rutile-like chains of edge-sharing octahedra, interconnected by octahedra corners.

Cu and In are disordered.

# Model (VII) : $BaNaZrF_7$



3D structure build up from infinite zig-zag cis-chains of edge sharing $NaF_8$ cubes (blue) linked together by $ZrF_7$ monocapped trigonal prism (green).

Systematic microtwinning.

# Fe/V Isomorphous substitution

As a rule, when a $Fe^{3+}$-based crystalline fluoride exists, the isostructural equivalent $V^{3+}$ material can be prepared too, with generally no more than 1% variation in cell dimensions.

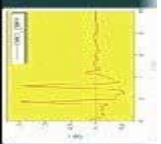
| Compounds | *a* | *b* | *c* | *β* | *S.G.* | *V* | $\rho_0$ | *Ref.* |
|---|---|---|---|---|---|---|---|---|
| $BaCdFeF_7$ | 13.852 | 5.390 | 15.023 | 91.27 | C2/c | 1121.4 | 0.07134 | [9] |
| $BaCdVF_7$ | 13.853 | 5.400 | 15.043 | 91.50 | C2/c | 1124.9 | 0.07112 | |
| $BaMnFeF_7$ | 13.797 | 5.343 | 14.764 | 90.83 | C2/c | 1088.3 | 0.07351 | this work |
| $BaMnVF_7$ | 13.764 | 5.355 | 14.778 | 90.94 | C2/c | 1089.1 | 0.07345 | |

Neutron Fermi scattering lengths :

Fe : 0.954

V : -0.038

The substitution ensures a quite large contrast



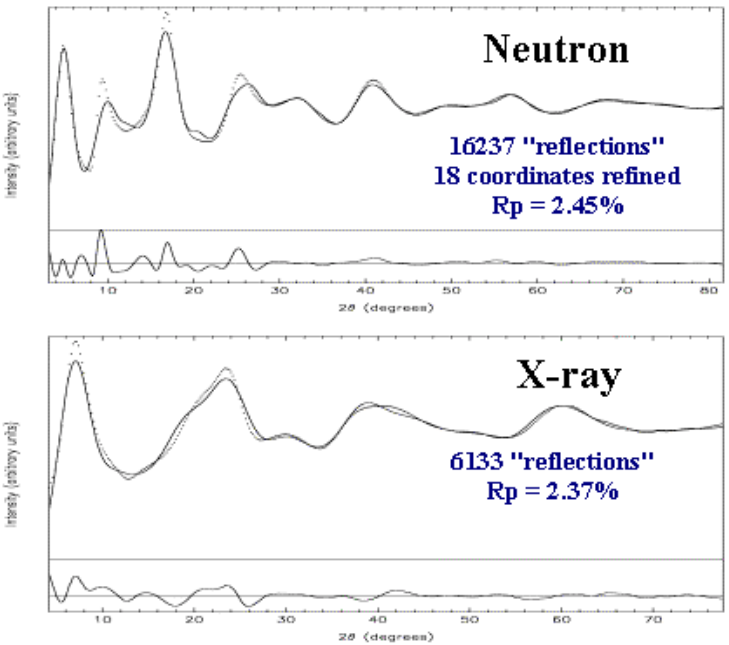
# RDM modelling – What is it ?

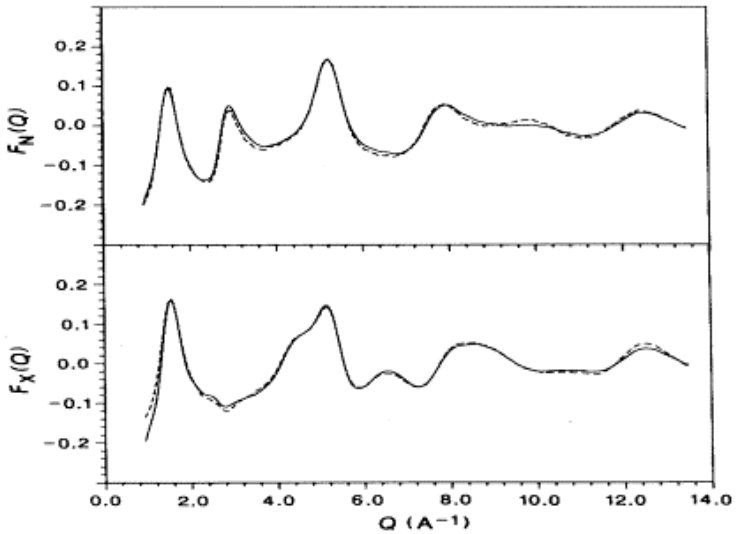
**Done by using the ARITVE software which is simply a Rietveld method program allowing :**

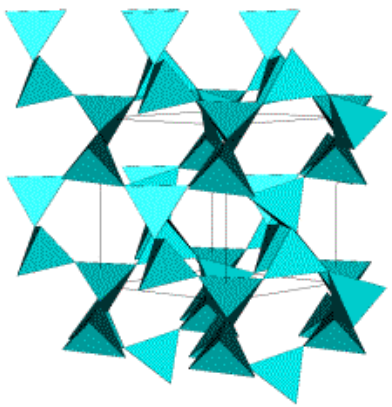
- **a huge limit of reflection number (60000 on each pattern)**
- **3 interference functions maximum fitted simultaneously**
- **a huge limit of reflections overlapping at the same angle (20000)**
- **a small number of parameters to be refined (max = 75)**
- **only Gaussian peak shape**
- **line broadening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

**= RDM : Rietveld for Disordered Materials**

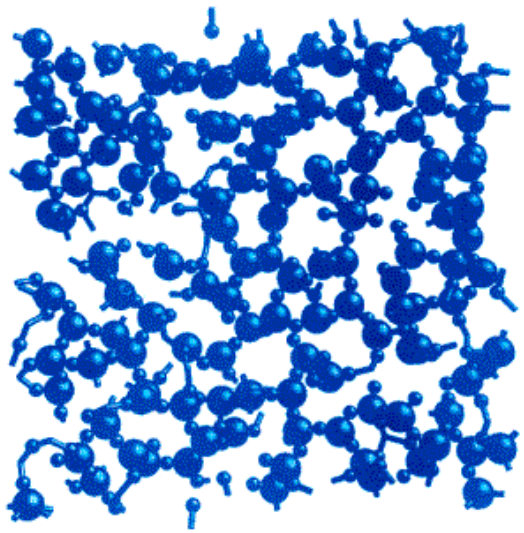
# RDM performance compared to RMC ?



α-carnegieite



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

# RDM results on $BaMn(Fe/V)F_7$ glasses

The fit quality by the Rietveld method is characterized by a profile reliability factor :

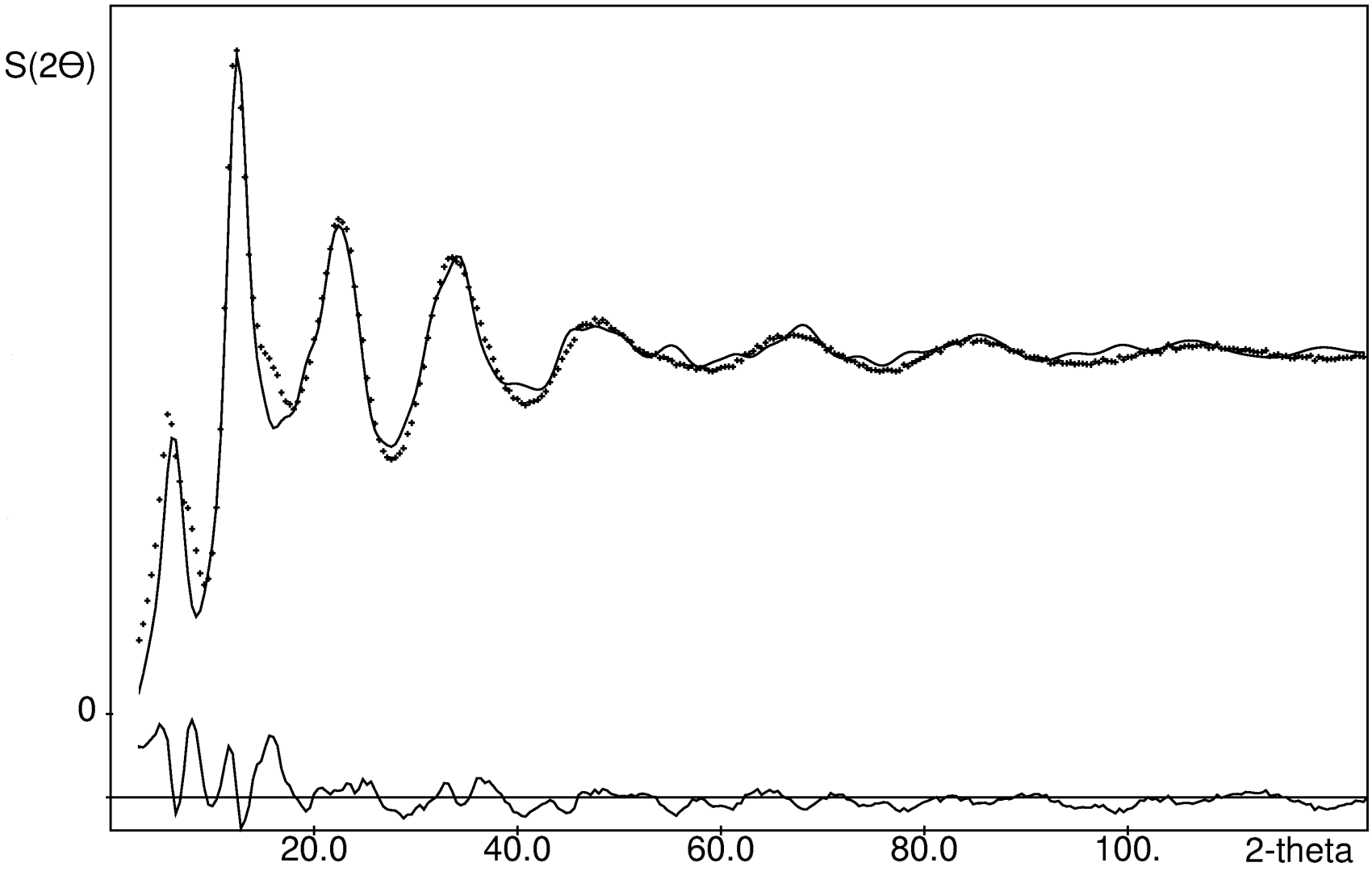
$$Rp = 100*\Sigma|I_{obs}-kI_{calc}|/\Sigma|I_{obs}| \ (\%)$$

The reliability factors were calculated for two fit ranges, full range ($Rp_1$), and low angle-limited range ($Rp_2$), because the full range includes large-angle data which are rather smooth, tending to produce small *Rp* values whatever the fit is good or not.

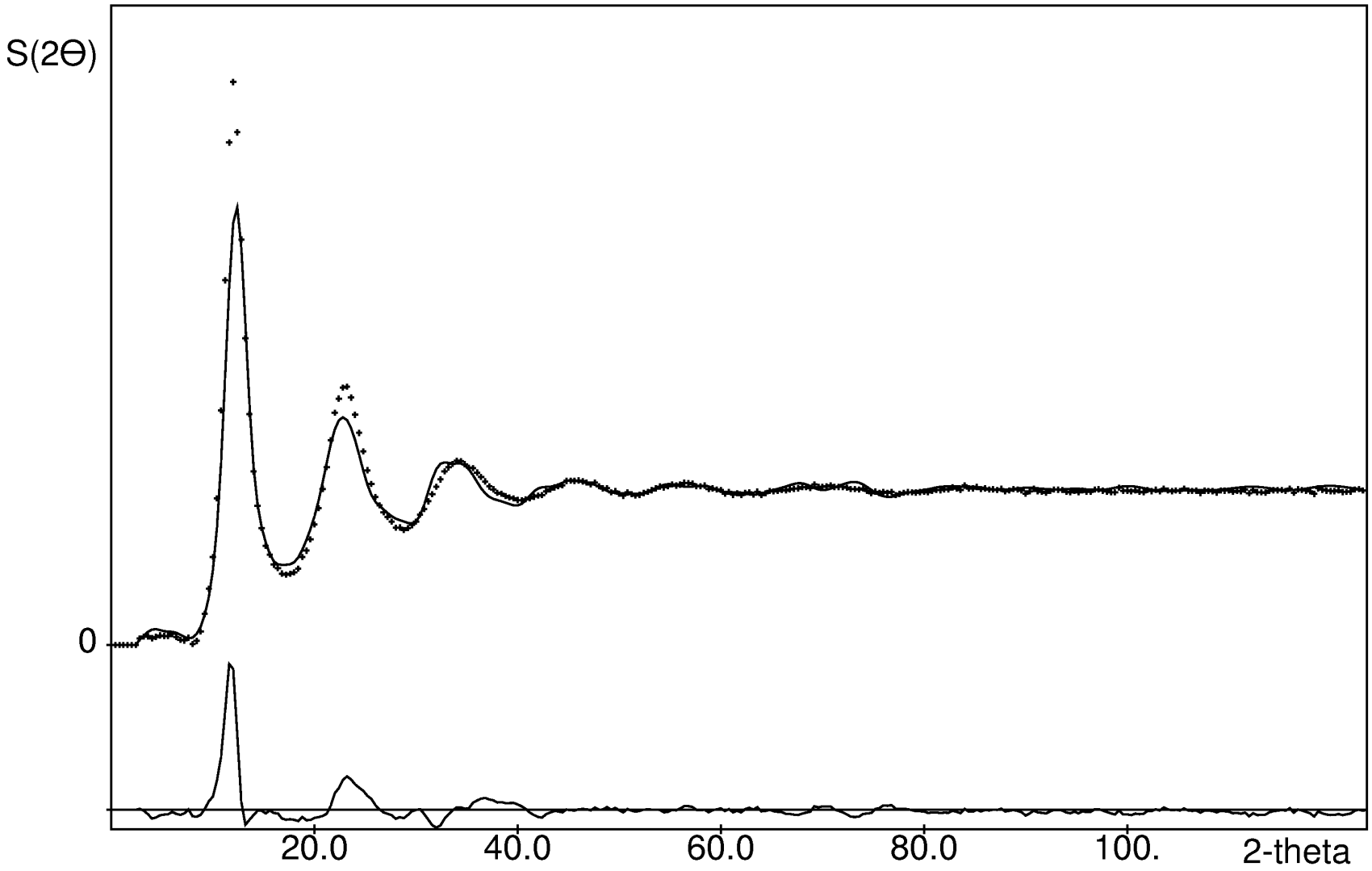
| | I $BaMnFeF_7$ | II $BaMnGaF_7$ | III $BaZnFeF_7$ | IV $BaCaGaF_7$ | V $BaCuFeF_7$ | VI $BaCuInF_7$ | VII $BaNaZrF_7$ |
|---|---|---|---|---|---|---|---|
| $Rp_1$ (Fe - V) | 2.97 - 3.78 | 3.30 - 3.61 | 3.51 - 4.37 | 3.36 - 4.09 | 3.14 - 4.74 | 6.87 - 6.50 | 3.81 - 5.41 |
| $Rp_2$ (Fe - V) | 5.90 - 8.62 | 7.15 - 8.86 | 6.99 - 10.36 | 6.89 - 9.24 | 6.55 - 11.30 | 21.2 - 14.7 | 7.41 - 12.14 |

**Models I and II provide the smallest Σ *Rp* values**

# Example of RDM fits for model I : Fe



# Example of RDM fits for model I : V



# RMC modelling from enlarged RDM models

Constraints on coordinations and interatomic distance ranges are applied in order to not destroy the Mn and (Fe,V) polyhedra and their connectivity. Calculations took several days on fast PCs (processor > 2 GHz).

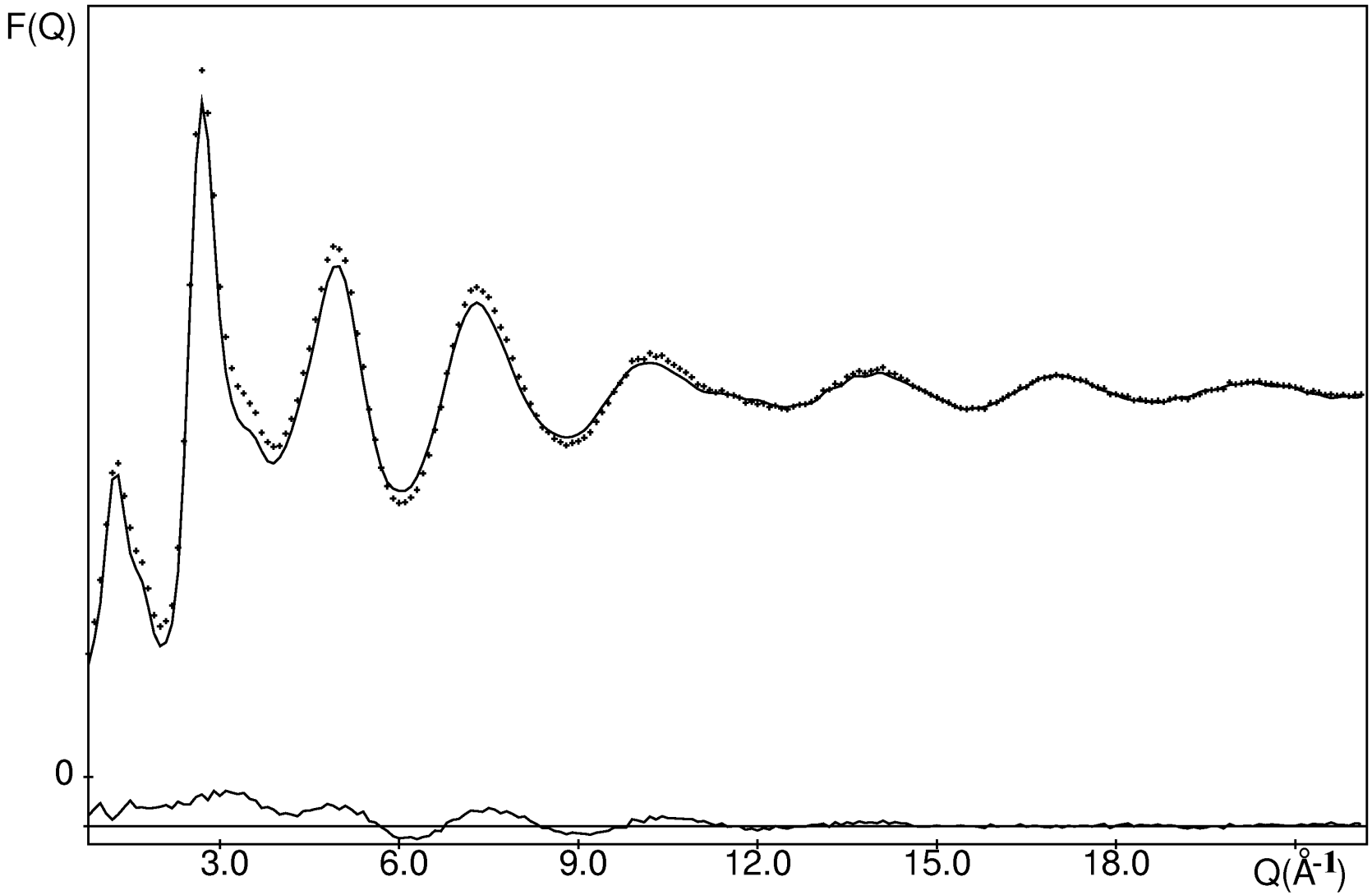
$Rp_1$ (%) for the 0.8-22.2 Q range (Å$^{-1}$) (Fe and V) and $Rp_2$ for 0.8-9 Å$^{-1}$.

| | I $BaMnFeF_7$ | II $BaMnGaF_7$ | III $BaZnFeF_7$ | IV $BaCaGaF_7$ | V $BaCuFeF_7$ | VI $BaCuInF_7$ | VII $BaNaZrF_7$ |
|---|---|---|---|---|---|---|---|
| ***a*** x by | 7 | 3 | 7 | 8 | 4 | 6 | 4 |
| ***b*** x by | 4 | 6 | 4 | 7 | 4 | 6 | 7 |
| ***c*** x by | 4 | 3 | 4 | 2 | 7 | 3 | 4 |
| ***N atoms*** | 4480 | 4320 | 4480 | 4480 | 4320 | 4320 | 4480 |
| $Rp_1$ (Fe - V) | 2.10 - 2.50 | 1.91 - 2.57 | 1.97 - 2.57 | 2.21 - 2.67 | 2.12 - 2.50 | 2.14 - 2.63 | 2.06 - 2.57 |
| $Rp_2$ (Fe - V) | 4.39 - 5.50 | 4.02 - 5.46 | 4.13 - 5.46 | 4.52 - 5.78 | 4.38 - 5.51 | 4.41 - 5.59 | 4.27 - 5.48 |

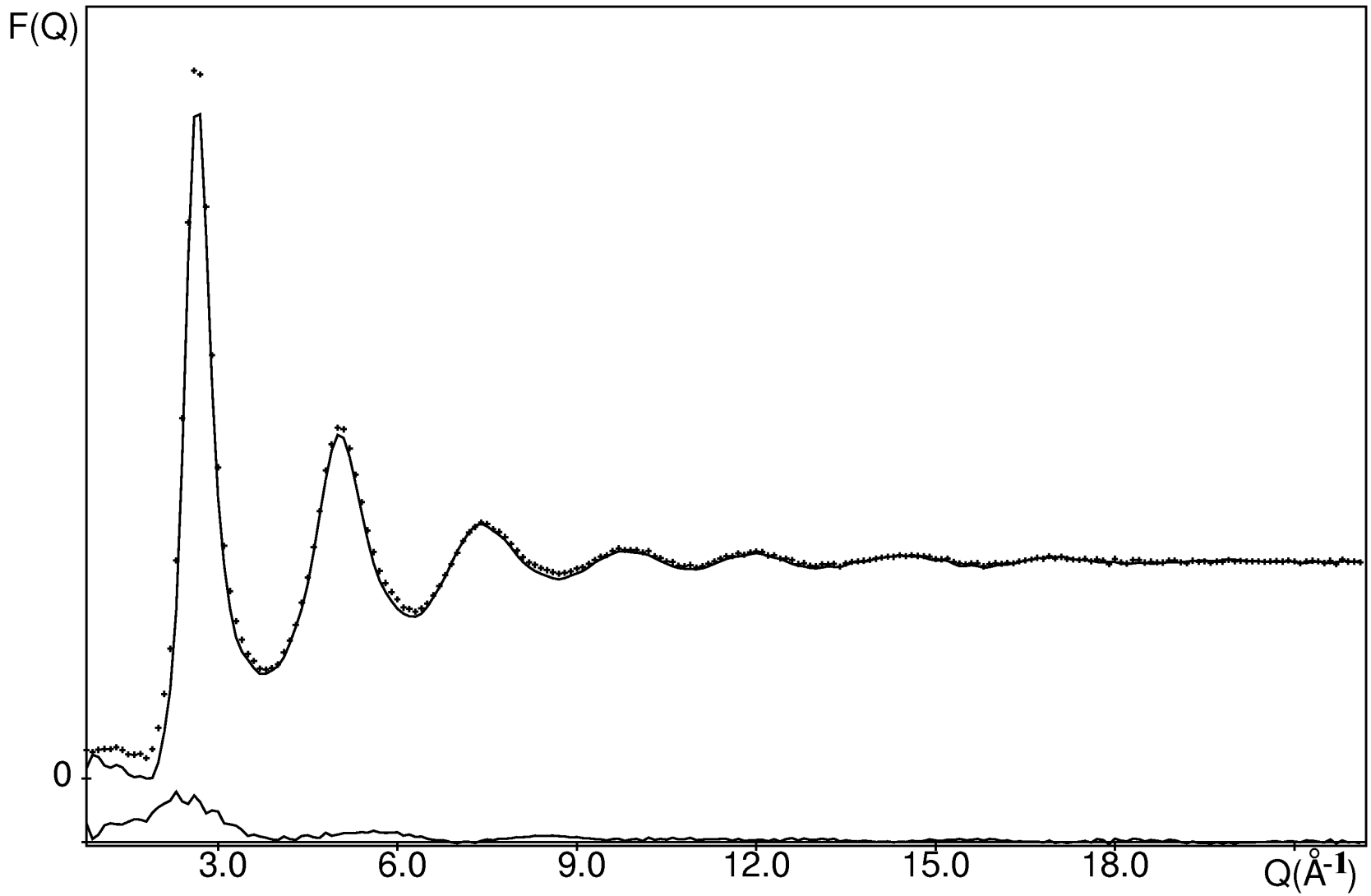
**$1.91 < Rp_1 < 2.21$ % for the Fe-based glass**
**$2.50 < Rp_1 < 2.67$ % for the V-based glass**

## ANY MODEL IS OK ??

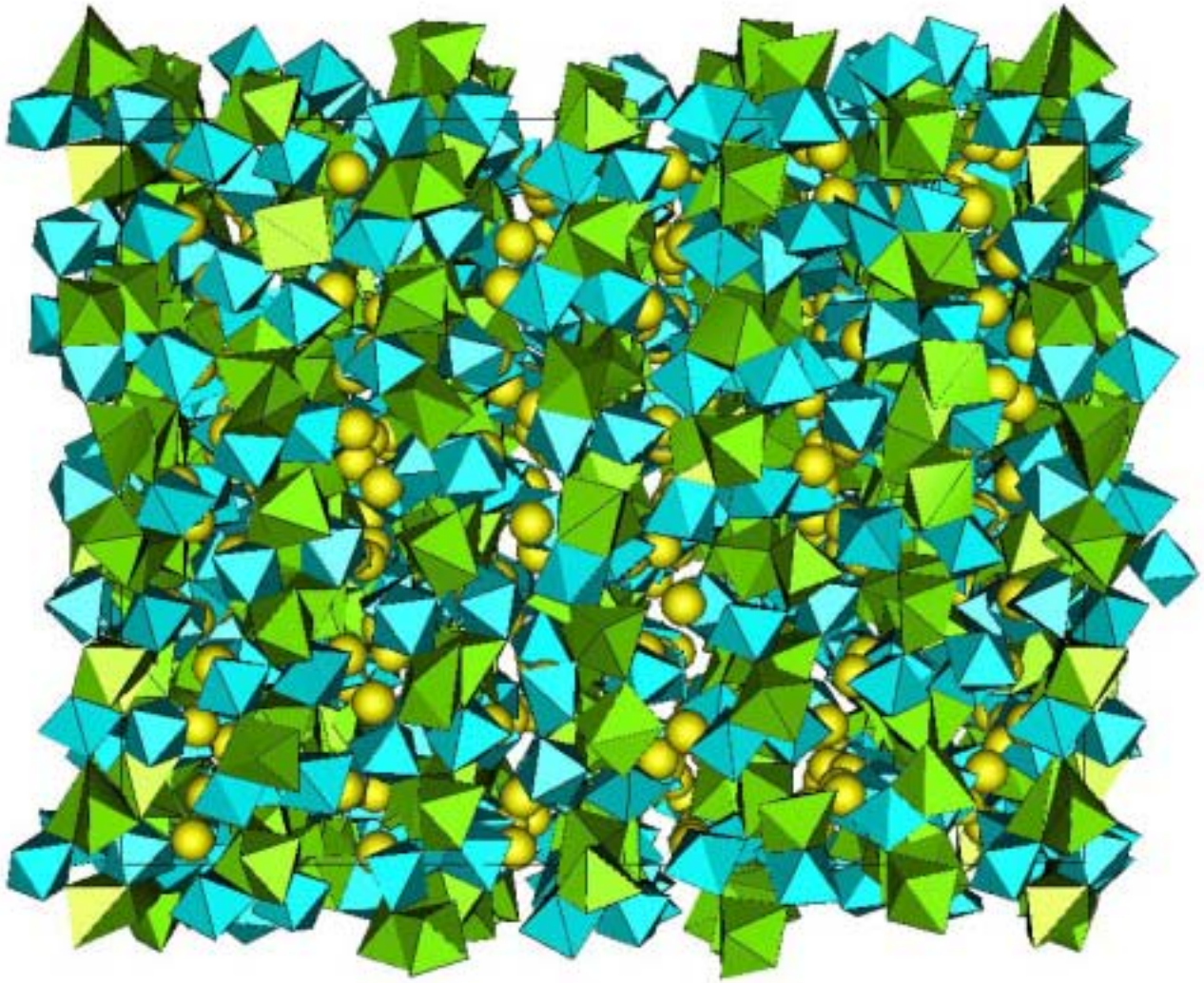
# Example of RMC+RDM fits for model II : Fe



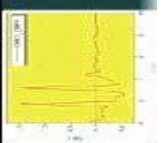
# Example of RMC+RDM fits for model II : V

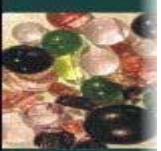


# The 4320 atoms in the box – Model II



Green $MnF_6$ polyhedra, blue $(Fe,V)F_6$ polyhedra, Ba atoms as yellow spheres.





# RMC modelling from random starting models

Cubic box of 5000 atoms (cubic edge L = 41.2956 Å).

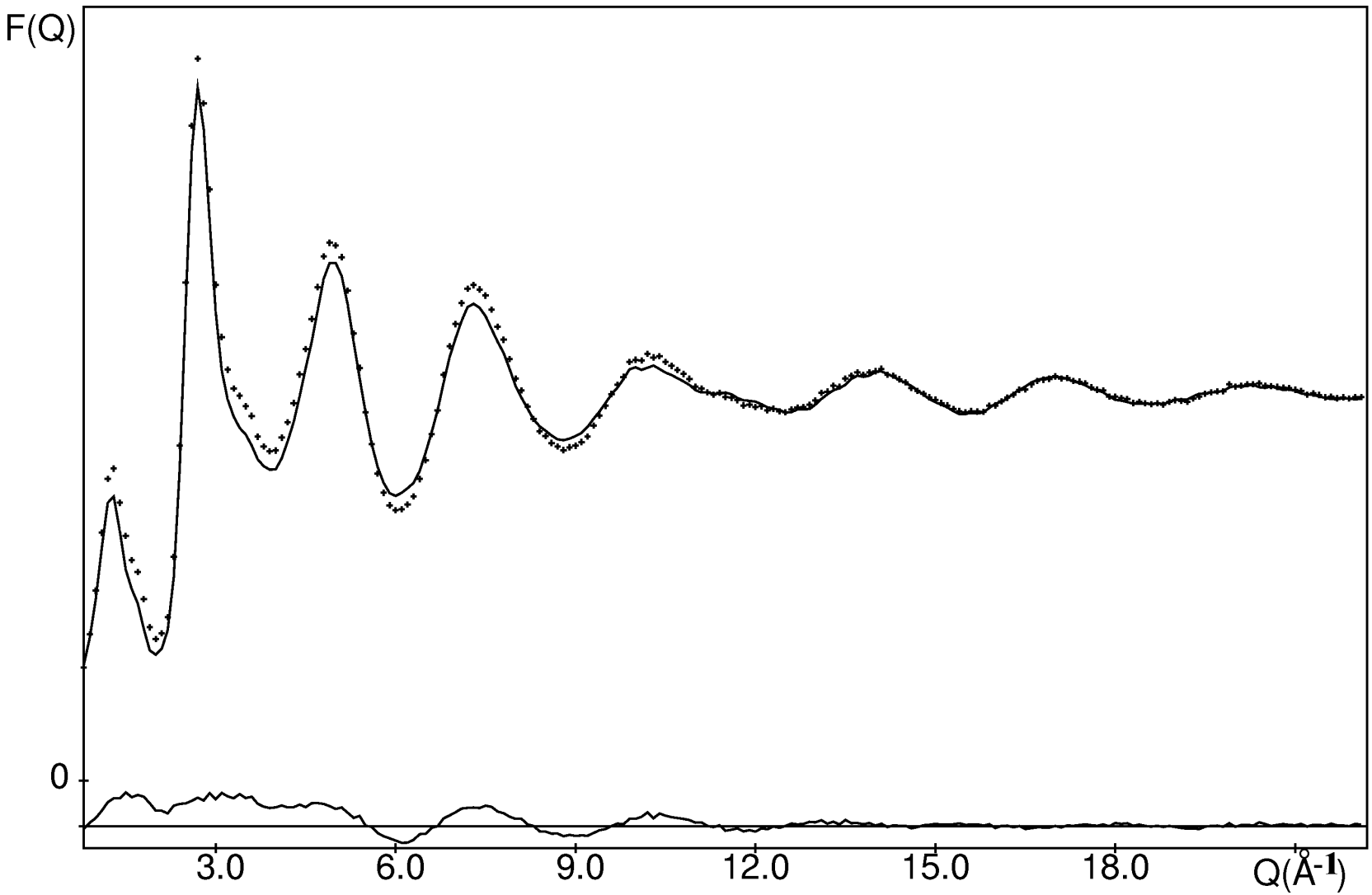
Very long runs were needed up to obtain the expected sixfold fluorine coordination around the 3d elements.

The "best" of three independent modellings provided
$Rp_1$ = 2.11 % (Fe); $Rp_1$ = 2.59 % (V);
$Rp_2$ = 4.36 % (Fe); $Rp_2$ = 5.54 % (V).

**NOT BETTER THAN THE RMC+RDM MODELS**

As previously observed when modelling $NaPbFe_2F_9$ glasses, the sixfold polyhedra show all possibilities between octahedra and trigonal prisms.

# The best pure random RMC model : Fe



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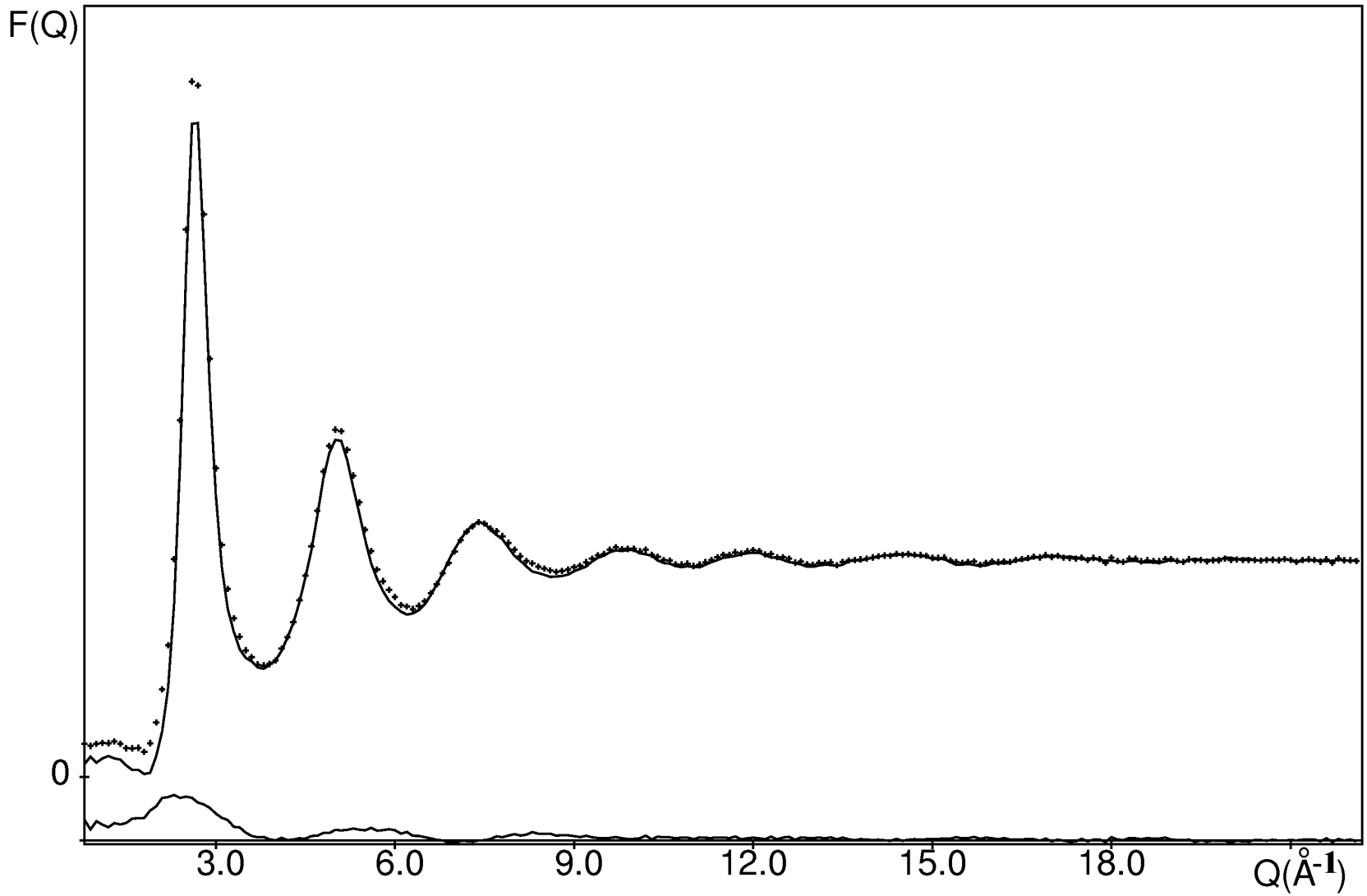
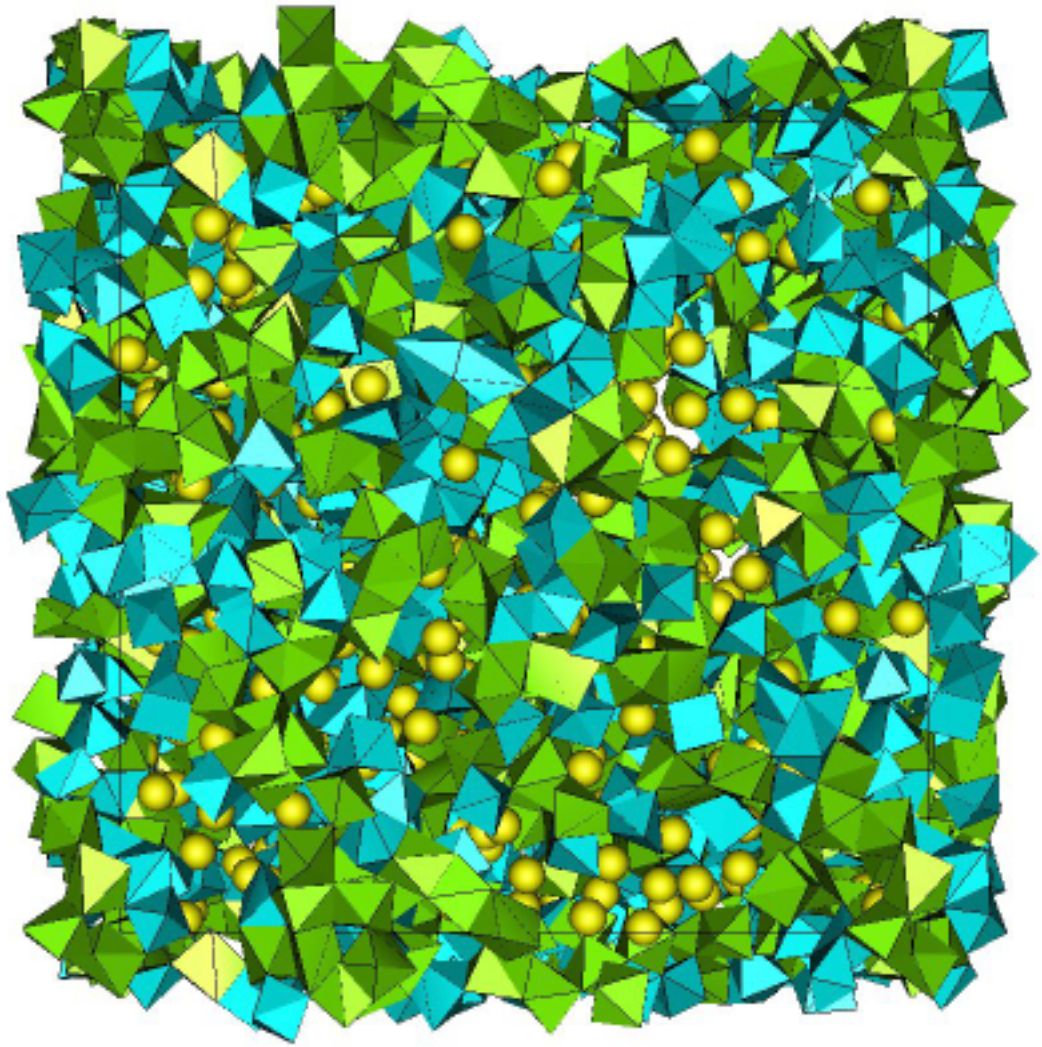
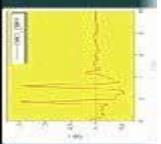
# The best pure random RMC model : V



# The 5000 atoms in the cubic box



Green $MnF_6$ polyhedra, blue $(Fe,V)F_6$ polyhedra, Ba atoms as yellow spheres.

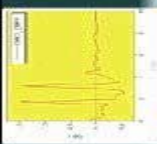


# Conclusions on $BaMn(Fe/V)F_7$ glasses

Several previous consecutive RDM-RMC modelling have shown that the starting crystalline model leading to the most satisfying structure simulation of a glass is generally that of its crystallization product, when it is a unique phase.

The conclusion of the present study is again favouring a generalization of this observation since the structure-type II is found to represent the most satisfying model which can be built by RMC among the types I-VII. Even the fully random models built by RMC cannot produce a better agreement between the observed and calculated neutron interference functions.

However, there is not a so clear gap in fit quality between model II and some others which would allow to claim having elucidated these fluoride glass structures. As usual, the frustrating conclusion is moderated. And the preference of the glass for crystallizing into the structure-type II rather than into the type I is not well understood.

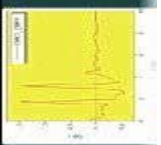


# Why not more differences between models ?

This may mean that the availability of only two interference functions for a four-elements glass (for which ten interference functions would have to be known) gives rise to an undetermined problem, in spite of the coordination and distance constraints.

It may also signify that the average orders at short and medium-range which characterizes all these models are finally very similar, in spite of their obvious differences in connectivity and three- or two-dimensionality.

The RDM method operates with a considerably smaller number of degrees of freedom (a few atomic coordinates), and thus produces more clear differences in the fits from various models.



# The ARITVE software for RDM can be downloaded at :

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