REFINING STRUCTURAL MODELS FOR GLASSES : IS IT POSSIBLE ?
THE CASE OF "$Pb_2M_2F_9$"

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Résumé – Une méthode permettant la simulation de fonctions d'interférence par affinement des coordonnées atomiques dans un modèle quasi-cristallin est présentée. Le procédé est appliqué aux verres fluorés "$Pb_2M_2F_9$". La structure de $KPbCr_2F_9$ correspond à une bonne description possible de l'organisation locale moyenne dans ces verres.

Abstract - A method allowing the fit of interference functions by a least square refinement of atomic positions in a quasicrystalline starting model is presented. Application is made on "$Pb_2M_2F_9$" fluoride glasses. The crystalline $KPbCr_2F_9$ structure appears to give a good possible description of the mean local organization in these glasses.

I - INTRODUCTION

Structural models for amorphous solids are frequently build in a two steps process : first is made the choice of an initial starting structure based upon available structural information and some chemical intuition ; second, this model is refined using energy minimisation, Monte Carlo or molecular dynamics techniques. Results are then compared with experimental data, mainly interference function $S(Q)$, distribution function $G(R)$ and density. When the comparison is not satisfying, some rearrangements in the starting model or parameter modifications in the second stage may be tested. So modelling remains in fact a trial and error procedure which has produced good results for monatomic or binary compounds ; this is much more difficult to achieve in multicomponent systems. Clearly, in order to obtain the best agreement from a starting model, the atomic positions must be refined according to the experimental diffracted intensities. To do that, a simple mathematical description of the atomic-scale structure of non-periodic solids is necessary. It has been claimed that this is impossible without making doubtfull assumptions. However, diffraction phenomenon gives essentialy a statistical view of solids and thus a statistical representation of the atomic organization must be able to predict the interference function. This is yet achieved in the case of disordered crystalline materials where broadening of diffraction lines are taken into account by a statistical representation of strain /1/ (we would not consider size effect here). A new method /2/ was recently proposed that allows the determination of (size-) strain parameters in a whole pattern fitting technique based on the Rietveld method principles /3-4/ for powder refinement. There is a priori no mathematical or physical reason to assign limits for the application of such a method to any material. The question is in fact : are amorphous structures sufficiently homogeneous to give a statistical organization which could be described in terms of lattice progressively distorted from an arbitrary origin. In this sense, the cell would be an idealized representation of the mean local organization ; distortion of the lattice meaning that there is no periodicity, i.e. no lattice in fact. We report here an attempt to extend the principles of strain analysis of line broadening to amorphous materials. Application is made on fluoride glasses "$Pb_2M^{II}M^{III}F_9$" postulating isomorphous substitution between M^{II} (Mn^{2+}, Zn^{2+}) or M^{III} (Fe^{3+}, V^{3+}) and statistical repartition of M^{II}, M^{III} ions.

II - METHOD

For a gaussian strain distribution (no size effect), the shape of a OOl reflexion in terms of orthorhombic axes (a general treatment leads to the same result) is given by /1/ :

$$P'(2\vartheta) = \frac{KNF^2}{\sin^2\vartheta} \sum_{n=-\infty}^{+\infty} e^{-2\pi^2 l^2 < Z_n^2 >} \cos 2\pi n h_a,$$

where $h_a = 2|a_a| \sin\vartheta/\lambda$ and $|a_a| z_n$ is the distortion between cells separated by n cells. In order to reduce the number of strain parameters $< Z_n^2 >$, the strain variation versus the distance may be approximated by $< Z_n^2 > = n^K < Z_1^2 >$. Then only two strain parameters need to be refined : $< Z_1^2 >$ and K. This was found possible for the powder pattern fitting of imperfectly crystallized materials /2/ but much more difficult in the case of amorphous materials. Consequently K was taken as fixed and results were found more satisfying for K = 2 (corresponding to gaussian peak shape) than for K = 1 (Cauchy-like). Apart this description of line broadening the method uses the principles of the RIETVELD pattern fitting technique /3-4/. Several interference functions for isomorphous or isotopic substitutions must be described by the same structural parameters, only changing the scattering length ; the possibility of refining simultaneously the atomic coordinates from more than one interference function was then included in the algorithm.

III - "$Pb_2M^{II}M^{III}F_9$" GLASSES - STRUCTURAL BACKGROUND

Structural informations were obtained from EXAFS /5/, Neutron (magnetic /6, 7/, nuclear /8/) and X-ray diffraction. Coordination numbers from EXAFS are typically of low accuracy : we obtain values of the order of 6 ± 1 for M = Mn^{2+}, Zn^{2+}, Fe^{3+} but M-F distances are in good agreement with those commonly observed for such cations octahedrally coordinated in fluoride crystallized compounds. Distribution of distances are consistent with almost regular MF_6 octahedra. The Pb^{2+} environment is largely distorted with an asymetrical distribution of distances (approximately 9F neighbours between 2.3 and 3.1 A). Glasses containing Mn^{2+} and/or Fe^{3+} exhibit spin glass behaviour /9, 10/. The pure neutron magnetic scattering was isolated by substracting data recorded in the paramagnetic domain from those collected below (or near) the spin freezing temperature. With the hypothesis that there is no correlation between the magnetic moment direction and that of the interatomic vector, data were Fourier transformed giving a possible solution for the magnetic correlation function /11/. For various glasses $Pb_2M_2F_9$ with substitution between Mn^{2+}, Fe^{3+} and diamagnetic ions (Zn^{2+}, Ga^{3+}) the correlation is found always antiferromagnetic between first neighbours. The mean M-M distance (M = magnetic ion only) is 3.6 ± 0.1 A in good agreement with an hypothesis of corner linking between MF_6 octahedra. With classical diffraction methods, the situation becomes very complicated because ten partial pair correlation functions contribute to the RDF. In the neutron case the problem is reduced to 6 partials for V-containing glasses and the four partials involving Fe may be separated on the basis of isomorphous substitution between Fe^{3+} and V^{3+} (highly supported by the crystallochemical behaviour of these ions in fluoride compounds). Using these possibilities, neutron results are well consistent with EXAFS ones. In the X-ray case the Pb contribution largely dominates allowing an estimation of the Pb-Pb distance : 4.2 A. At this scale, there is no sensitive descrepancy between glasses and crystallized compounds such as $Pb_5Fe_3F_{19}$ /12/ structurally related to $BaFeF_5$ /13/, or Ba_2CoFeF_9 /14/, $NaBaFe_2F_9$ /15/, $KPbCr_2F_9$ /16/ (the last three showing nearly the same structure). These two models were tested i.e. : I - Ba_2CoFeF_9 and II - $BaFeF_5$; both are built up from corner sharing octahedra.
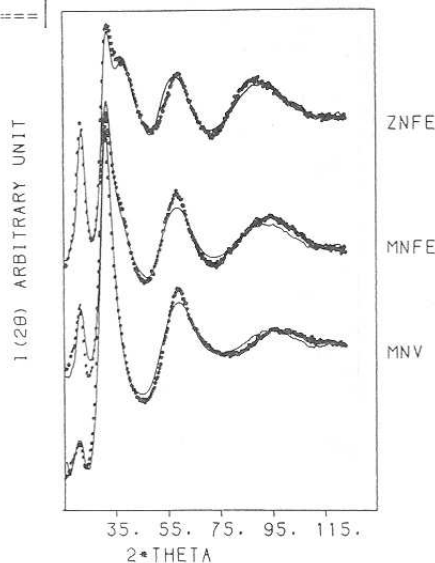
IV - RESULTS OF MODELLING

First, the neutron interference functions (λ = 1.22 A on D2-ILL) of glasses Pb_2ZnFeF_9, Pb_2MnFeF_9 and Pb_2MnVF_9 were together simulated only refining $< Z_1^2 >$ and a scale factor. The two models were able to reproduce relatively well the data with a

statistical repartition of M (Model I was described using the more symetrical space-group Pnma founded for $KPbCr_2F_7$; and model II in the I4cm space-group of $Pb_5Fe_3F_{19}$). Then the atomic coordinates were refined (23 parameters for both models), a clear improvement was obtained (Table 1):

Glass / Model	I	II	I	II
Pb_2ZnFeF_7	7.7	9.0	3.2	5.5
Pb_2MnFeF_7	11.0	12.7	5.2	9.6
Pb_2MnVF_7	12.0	8.4	4.8	8.5
x, y, z	not refined		refined	

Table 1 - R factors as $100*(\Sigma(Iobs-Ical)^2/\Sigma Iobs^2)^{1/2}$ from 12 to 124° 2θ

Reliabilities are in favour of model I, the fit is shown figure 1. Cell parameters were not refined, the average atomic density ρ_o is slightly higher in the final model (0.0703 Atom/A^3) than the mean value for the three glasses (0.066 ± 0.002). Comparison between positional parameters of the starting and refined model I is shown table 2, interatomic distances are in table 3. It may be seen that standard deviations are large and that some distances are out of expected values, particularly Pb(2)-F(1) ; M(1)-F(1) and M(2)-F(2). Mean distances remains however in accordance with EXAFS ones (in the hypothesis of statistical repartition of M) or neutron magnetic for M-M and X-ray for Pb-Pb. View of the structure is shown figure 2, important distortion of MF_6 octahedra is visible. If we assume that these results support our hypothesis (isomorphous substitution and statistical repartition of M), the next step is to separate three sets of partials : (F-F + Pb-F + Pb-Pb) which are constant for the three glasses, (M-F + M-Pb) and (M-M). The weight of the last partial is only 3 %

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Fig. 1 - Observed (...) and simulated (——) diffracted intensities of "$Pb_2M^{II}M^{III}F_7$" glasses

in the most favourable case and was very noisy in the experimental but the two others show well agreement with the simulated ones. The reduced distribution functions are shown figure 3 and 4 for the best model I ; R factors are respectively 11.1 and 22.7 % from 0 to 12 A (22.8 and 29.0 for model II). It may be noticed that the best agreement is obtained for partials containing pairs F-F which largely dominate in weight, so the best accuracy in the refinement is expected on the F positional parameters.

V - DISCUSSION

The success of the RIETVELD method is due to its ability to work even for severe overlapping between reflexions, we are in such a case (1 800 hkl for each spectrum in figure 1) and the refinement was convergent only with the three associated spectra. The complexity of our glasses was reduced by some hypothesis which correspond to large approximations. Particularly M^{II}-F and M^{III}-F distances are not equivalent (EXAFS results /5/) and isomorphism substitution is not strict. However, owing to the difficulties, results may be considered as not so bad. Clearly, such a method can work only if glasses are constructed from statistically significant structural "building blocks". The final model represents, in our opinion, the best mean organization available in the limits of the starting model. We have shown that two different models, with the same number of refined parameters, may be differenciated by their final reliabilities. However the model II could be considered also as almost satisfying. In fact, the radial organization in the two

Atoms		Site	x	y	z
Glass	Model				
Pb(1)		4c	0.294(2)	3/4	0.310(2)
	K		0.2703(4)	3/4	0.2975(2)
Pb(2)		4c	0.396(3)	1/4	0.082(3)
	Pb		0.4449(5)	1/4	0.1105(4)
M(1)		4c	0.066(4)	1/4	0.164(3)
	Cr(1)		0.0669(2)	1/4	0.1559(1)
M(2)		4c	0.157(4)	3/4	-0.016(3)
	Cr(2)		0.2307(2)	3/4	0.0076(1)
F(1)		4c	0.292(5)	1/4	0.182(3)
	F(1)		0.2440(7)	1/4	0.2086(7)
F(2)		4c	0.164(6)	1/4	0.611(4)
	F(2)		0.1513(7)	1/4	0.6122(8)
F(3)		8d	0.010(2)	0.505(4)	0.271(2)
	F(3)		0.0142(6)	0.486(1)	0.2469(5)
F(4)		8d	0.181(3)	0.432(3)	0.445(2)
	F(4)		0.1575(7)	0.492(1)	0.4492(5)
F(5)		4c	0.394(5)	1/4	0.358(4)
	F(5)		0.3850(8)	1/4	0.3963(6)
F(6)		8d	0.132(4)	0.551(5)	0.112(2)
	F(6)		0.1213(7)	0.499(2)	0.0659(5)

Table 2- Positional parameters in the final model and $KPbCr_2F_9$
(a=9.81, b=5.412, c=13.93 A), S.D. in parenthesis.

M(1) ; Cr(1) environment

2 M(1) - F(3)	2.11(4)		2 Cr(1) - F(3)	1.872(7)
2 M(1) - F(6)	1.89(4)		2 Cr(1) - F(6)	1.917(7)
M(1) - F(1)	2.22(7)		Cr(1) - F(1)	1.887(5)
M(1) - F(5)	1.72(6)		Cr(1) - F(5)	1.927(5)
< M(1) - F >	1.99		< Cr(1) - F >	1.899

M(2) ; Cr(2) environment

2 M(2) - F(6)	2.10(4)		2 Cr(2) - F(6)	1.912(7)
2 M(2) - F(4)	1.95(4)		2 Cr(2) - F(4)	1.890(6)
M(2) - F(2)	2.49(7)		Cr(2) - F(2)	1.862(7)
M(2) - F(5)	1.83(6)		Cr(2) - F(5)	1.922(5)
< M(2) - F >	2.07		< Cr(2) - F >	1.898

Pb(1) ; K environment

2 Pb(1) - F(3)	2.74(3)		2 K - F(3)	2.859(7)
2 Pb(1) - F(3)	3.13(3)		2 K - F(3)	2.975(7)
2 Pb(1) - F(5)	2.95(2)		2 K - F(1)	2.987(6)
2 Pb(1) - F(4)	2.79(3)		2 K - F(4)	2.766(7)
Pb(1) - F(2)	2.79(6)		K - F(2)	2.693(7)
< Pb(1) - F >	2.89		< K - F >	2.873

Pb(2) ; Pb environment

2 Pb(2) - F(3)	2.71(4)		2 Pb - F(3)	2.457(7)
Pb(2) - F(1)	1.73(5)		Pb - F(1)	2.398(5)
2 Pb(2) - F(4)	2.67(4)		2 Pb - F(4)	2.599(7)
2 Pb(2) - F(4)	2.99(4)		2 Pb - F(4)	2.833(7)
2 Pb(2) - F(2)	2.80(2)		2 Pb - F(2)	2.866(7)
< Pb(2) - F >	2.67		< Pb - F >	2.656

Other mean distances

3 < M - M > 3.53 ; 6 < M - Pb > 3.93 ; 4 < Pb - Pb > 4.22

Table 3 - Distances (A) in the final model and in $KPbCr_2F_9$
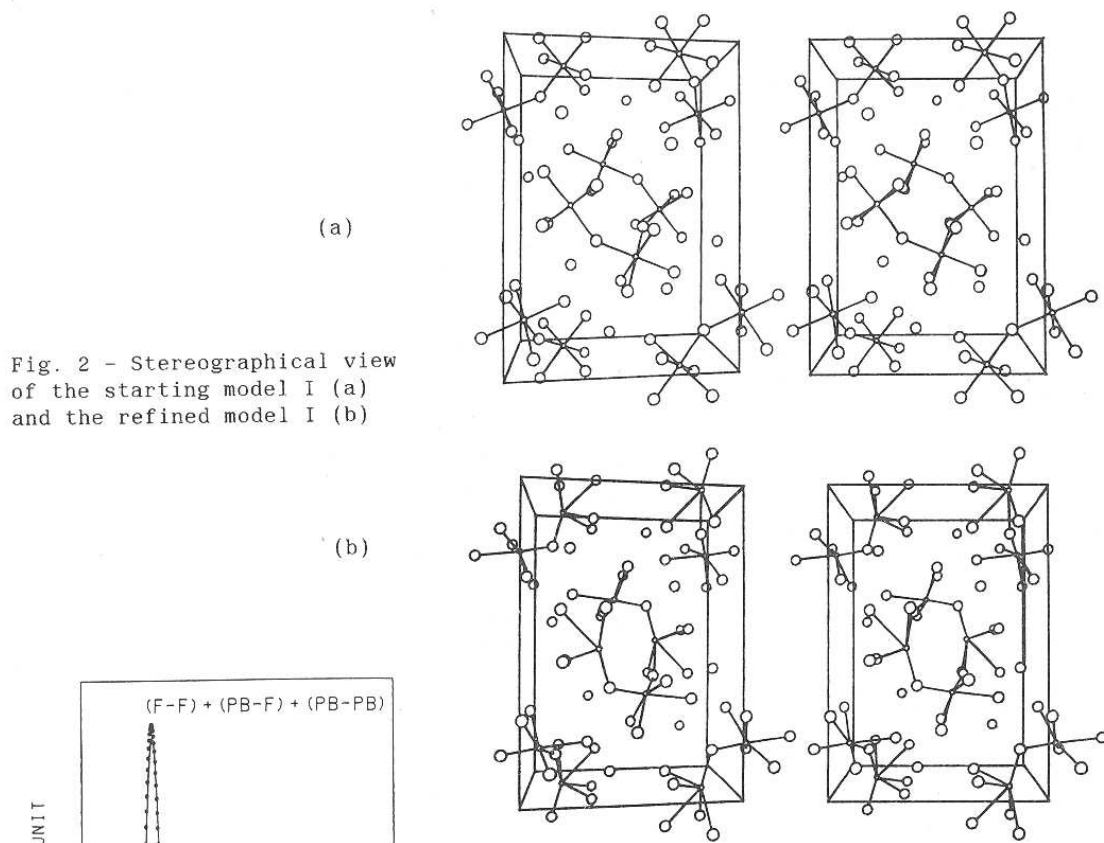(S.D. in parenthesis)

Fig. 2 - Stereographical view
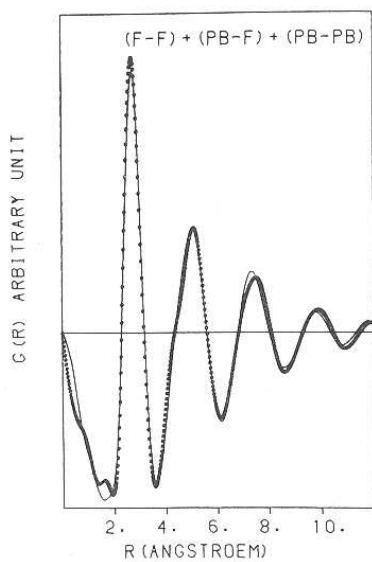of the starting model I (a)
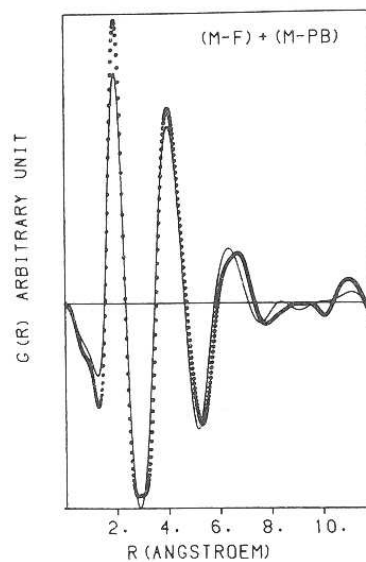and the refined model I (b)

(a)

(b)

Fig. 3

Fig. 4

Experimental (ᵒᵒᵒ) and simulated (---) partial reduced atomic distribution function
of "$Pb_2M_2F_9$" glasses, weighted as: 53.5 FF + 39.2 PbF + 7.3 PbPb (Fig. 3)
and 73 MF + 27 MPb (Fig. 4). (Neutrons, Q_{max} = 9.2 A^{-1})

models is not very different because they have in common the same main structural aspects (corner sharing octahedra and dense packing of F^- and large cations), so the inherent ambiguity of amorphous structures cannot be overcome. More application is needed in order to be convinced ; satisfying results have been yet obtained on amorphous FeF_3, $_x HF$ /17/, vapour deposited amorphous FeF_3 and a $BaCuFeF_7$ glass. A good test would be to work on very accurate partial pair distribution functions (for instance $Ni_{81}B_{19}$ /18/ which has been yet modelized by several techniques), this is a call for data.

REFERENCES

/1/ Warren, B.E., Prog. Metal Phys. 8 (1959) 147.
/2/ Le Bail, A., Proc. 10th Colloque Rayons X - Siemens - Grenoble (1985) in press.
/3/ Rietveld, H.M., J. Appl. Cryst. 2 (1969) 65.
/4/ Hewat, A.W., Harwell Report AERE-R7350 (1973).
/5/ Le Bail, A., Jacoboni, C., De Pape, R., J. Solid State chem. 52 (1984) 32.
/6/ Le Bail, A., Jacoboni, C., De Pape, R., J. Solid State chem. 48 (1983) 168.
/7/ Le Bail, A., Jacoboni, C., De Pape, R., J. Non-Cryst. Solids, in press.
/8/ Le Bail, A., Jacoboni, C., De Pape, R., J. Non-Cryst. Solids, in press.
/9/ Renard, J.P., Miranday, J.P., Varret, F., Solid State Comm. 35 (1980) 41.
/10/ Dupas, C., Le Dang, K., Renard, J.P., Veillet, P., Miranday, J.P., Jacoboni, C., J. physique 42 (1981) 1345.
/11/ Bertaut, E.F., Burlet, P., Solid State Comm. 5 (1967) 279.
     Wright, A.C., J. Non Cryst. Solids 40 (1980) 325.
/12/ Jacoboni, C., Le Bail, A., De Pape, R. and Renard, J.P., Studies in Inorganic Chemistry - Elsevier 3 (1983) 687.
/13/ Von Der Muhl, R., Galy, J., Anderson, S., C.R. Acad. Sci. C267 (1968) 569.
/14/ De Kozak, A., Leblanc, M., Samouël, M., Ferey, G. and De Pape, R., Rev. Chim. Miner. 18 (1981) 659.
/15/ Ferey, G., Leblanc, M., De Kozak, A., Samouël, M., Pannetier, J., J. of Solid State Chem. 56 (1985) 288.
/16/ Vlasse, M., Chaminade, J.P., Dance, J.M., Saux, M. and Hagenmuller, P., J. Solid State Chem. 41 (1982) 272.
/17/ Leblanc, M., Ferey, G., Greneche, J.M., Le Bail, A., Varret, F., De Pape, R., Pannetier, J. This congress - A21.
/18/ Lamparter, P., Sperl, W., Steeb, S., Bletry, J., Z. Naturforschung 37a (1982) 1223.