

SHORT RANGE ANTIFERROMAGNETIC ORDERING IN FLUORIDE GLASSES  
 "PbMnFeF<sub>7</sub>" AND "Pb<sub>2</sub>MnFeF<sub>9</sub>"

A. Le Bail, C. Jacoboni and R. De Pape

*Laboratoire des Fluorures et Oxyfluorures Ioniques, ERA 609, Université  
 du Maine, 72017 Le Mans Cedex, France*

**Résumé.** - L'ordre magnétique moyen des premiers voisins M-M (M = Mn<sup>2+</sup>, Fe<sup>3+</sup>) ainsi que l'environnement local de ces ions ont été abordés par diffraction de neutron et EXAFS pour les verres fluorés "PbMnFeF<sub>7</sub>" et "Pb<sub>2</sub>MnFeF<sub>9</sub>". Les fonctions de corrélation magnétique mettent en évidence, pour les deux verres, une forte interaction antiferromagnétique à 3,6 Å et des interactions ferromagnétiques à 5,4 et 6,7 Å. Les résultats EXAFS confirment la coordination octaédrique de Mn<sup>2+</sup> et Fe<sup>3+</sup>. La structure de ces verres est interprétée selon un modèle de chaînes interconnectées d'octaèdres MF<sub>6</sub> liés par des sommets avec Pb<sup>2+</sup> en position interstitielle.

**Abstract.** - Neutron diffraction and EXAFS experiments have been made on fluoride glasses "PbMnFeF<sub>7</sub>" and "Pb<sub>2</sub>MnFeF<sub>9</sub>" to provide informations about the magnetic short range order of pairs M-M (M = Mn<sup>2+</sup>, Fe<sup>3+</sup>) and the local environment of Mn<sup>2+</sup> and Fe<sup>3+</sup>. The magnetic correlation function shows in both glasses prevailing strong antiferromagnetic first neighbour interaction at 3.6 Å and two ferromagnetic interactions at 5.4 and 6.7 Å. EXAFS results confirm the expected sixfold coordination of Mn<sup>2+</sup> and Fe<sup>3+</sup>. The structure of these glasses is described in term of randomly linked corner shared MF<sub>6</sub> octahedra chains with Pb<sup>2+</sup> in interstitial sites.

1. **Introduction.** - New transition metal fluoride glasses in PbF<sub>2</sub>-M<sup>II</sup>F<sub>2</sub>-M<sup>III</sup>F<sub>3</sub> systems authorize large extent of vitreous area and various associations of magnetic ions (1,2). Magnetic studies on "PbMnFeF<sub>7</sub>" and "Pb<sub>2</sub>MnFeF<sub>9</sub>" have clearly shown the existence of strong antiferromagnetic interactions between magnetic ions (Mn<sup>2+</sup>, Fe<sup>3+</sup>) (effective Curie-Weiss temperature are respectively -190K and -135K), and established spin glass behaviour with relatively high freezing temperature : 11.77 and 5.35K respectively (3-6). The sixfold coordination is well established for 3d transition ions in crystallized fluorides and absorption spectra in the visible range confirm this fact for Ni<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup> or V<sup>3+</sup> based glasses but this demonstration is not possible for Mn<sup>2+</sup> and Fe<sup>3+</sup>. We report here a study of Mn<sup>2+</sup> and Fe<sup>3+</sup> local environment and magnetic ordering in "PbMnFeF<sub>7</sub>" and "Pb<sub>2</sub>MnFeF<sub>9</sub>" glasses by means of EXAFS and magnetic neutron scattering. Results are discussed in order to propound a structural model for these glasses.

2. **Neutron.** - The neutron experiments were performed at an incident wavelength of 2.522 Å using the D1B diffractometer on the high flux beam reactor at the Institut Laue-Langevin, Grenoble. A well established method for isolating the magnetic scattering Im(Q) when using unpolarized neutron beams is to subtract intensity data recorded above and below the magnetic ordering temperature : so intensity data were recorded in the paramagnetic range (250K) and below the spin freezing temperature for both glasses. Assuming that there is no correlation between the magnetic moments directions and that of the radius vector  $\vec{r}$  between two magnetic ions, the magnetic correlation function dm(r) is of the form (7) :

$$dm(r) \propto \int_0^Q \frac{\max Q \operatorname{Im}(Q)}{\langle f(Q) \rangle^2} M(Q) \sin rQ \, dQ,$$

where  $Q = 4\pi \sin \theta/\lambda$ ;  $M(Q)$  is a modification function to reduce the effects of the termination of the Fourier integral at a finite value  $Q_{\max}$  (8),  $\langle f(Q) \rangle$  is the mean magnetic form factor for  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ . Such a simplification is possible only because the two magnetic species are in the same  $^6S$  ground state and  $dm(r)$  will represent the magnetic correlation function between M-M pairs ( $M = \text{Mn}^{2+}, \text{Fe}^{3+}$ ). Difference spectra  $\text{Im}(Q)$  for " $\text{PbMnFe}_7$ " and " $\text{Pb}_2\text{MnFe}_9$ " are shown figure 1 and the corresponding  $dm(r)$  are represented figure 2 in arbitrary units. It was found necessary to apply a Placzek correction in order to remove a strong negative error ripple near  $r = 0$  on  $dm(r)$ ; the magnitude of the correction was determined using the zero ripple technique (8,9); we present only the corrected  $dm(r)$  on figure 2. For a material containing short range antiferromagnetic ordering, positive and negative peaks in  $dm(r)$  indicate respectively magnetic ions with their spin parallel and antiparallel to that of the origin. The two glasses exhibit essentially the same  $dm(r)$  with a strong negative peak at 3.6 Å, two ferromagnetic interactions at 5.4 and 6.7 Å and an antiferromagnetic one at 8.4 Å.

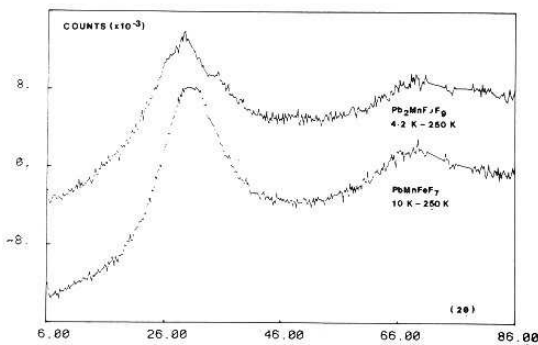


Fig. 1 : Difference of the neutron diffraction spectra.

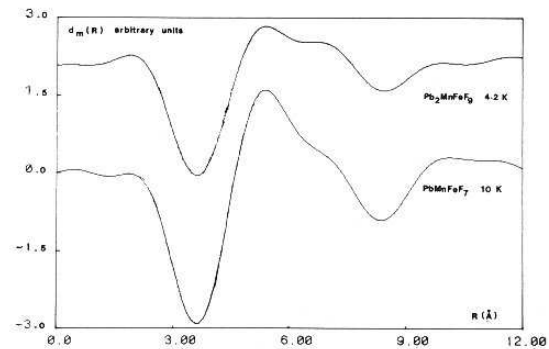


Fig. 2 : Neutron magnetic correlation functions.

3. EXAFS. - X-ray absorption spectra were recorded at the "Laboratoire pour l'Utilisation du Rayonnement Electromagnétique", using radiation from the D.C.I. storage ring, at Orsay and a Si(220) channel cut monochromator under vacuum. The EXAFS spectra were analyzed following standard techniques of background subtraction and normalization (10,11) in order to extract the absorption coefficient modulations  $X(k)$  on the iron and manganese K-edge (respectively 7111 and 6537 e.V.). The Fourier transform of  $X(k)$  exhibits only one peak for both glasses at the two K-edge. This peak, after filtering and backtransforming, restitutes the modulation  $X_1(k)$  of the first shell which was fitted by using the well-known formula (12) :

$$X_1(k) = N_1 F_1(k) \frac{S_0^2(k)}{kR_1^2} e^{-2\sigma_1^2 k^2} \sin \left[ 2kR_1 + \phi_1(k) \right]$$

Where  $N_1$  is the number of atoms in the first scattering shell at the distance  $R_1$  from the absorbing atom. We have used the atom phase shifts  $\phi(k)$  and the backscattering amplitudes  $F(k)$  calculated by Teo and Lee (13).  $\sigma_1$  is the relative mean-square displacement between the scattering atom and the central atom,  $S_0^2$  is the many electron overlap factor. The crystallized compounds  $\alpha\text{-LiMnFeF}_6$  and  $\text{Pb}_5\text{Fe}_3\text{F}_{19}$  were used in order to calculate the  $S_0^2$  factor (considered to be a constant in approximation) using the known values of  $N_1$  (6 in all cases); the others parameters  $\sigma_1$ ,  $R_1$  and the energy threshold  $E_0$  were considered as adjustables. To compensate for the rapidly attenuating backscattering amplitude of fluorine, the fit was made using the weighting scheme of  $k^3 X(k)$  in the range of  $k = 2 - 4.5$  (atomic units) and the parameters  $\sigma_1$ ,  $R_1$ ,  $N_1$  and  $E_0$  for the glasses were calculated using the value of  $S_0^2$  previously determined. The magnitude  $F(R)$  of the  $k^3 X(k)$  Fourier transforms are shown figure 3 for the two glasses " $\text{PbMnFe}_7$ " and " $\text{Pb}_2\text{MnFe}_9$ ". Figure 4 shows typical fits for

Fourier filtered first shell signals  $k^3X_1(k)$  in the "PbMnFeF<sub>7</sub>" case. The best neighbor parameters for glasses and crystallized compounds are shown in table 1.

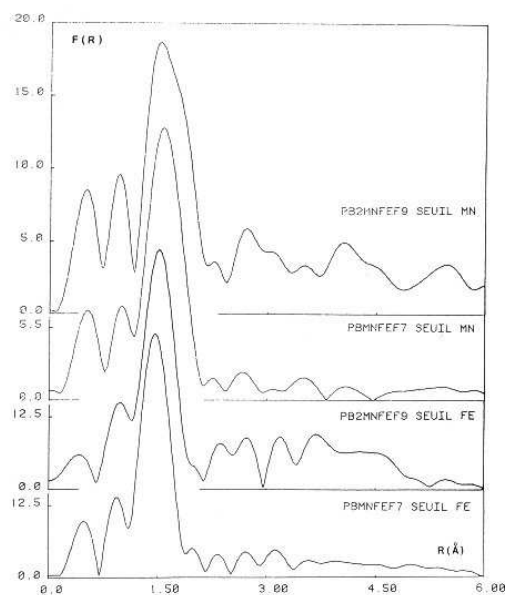


Fig. 3 : Amplitude of the Fourier transform of  $k^3X(k)$  on Fe and Mn K edges for "PbMnFeF<sub>7</sub>" and "Pb<sub>2</sub>MnFeF<sub>9</sub>".

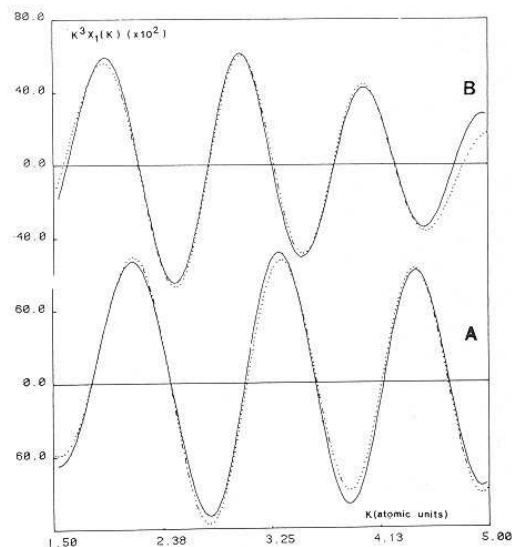


Fig. 4 :  $k^3X_1(k)$  filtered experimental spectra (dots) and the corresponding theoretical fit (solid line) for "PbMnFeF<sub>7</sub>". A : Fe edge, B : Mn edge.

		"PbMnFeF <sub>7</sub> "	"Pb <sub>2</sub> MnFeF <sub>9</sub> "	$\alpha$ -LiMnFeF <sub>6</sub>	Pb <sub>5</sub> Fe <sub>3</sub> F <sub>19</sub>
R(Å)	Fe-F	1.93	1.94	1.937 (1.935)	1.94 (1.96)
	Mn-F	2.11	2.12	2.123 (2.126)	-
N	Fe-F	5.7	5.3	(6.00)	(6.00)
	Mn-F	5.3	5.2	(6.00)	
So <sup>2</sup>	Fe	0.45	0.45	0.46	0.44
	Mn	0.42	0.42	0.42	
$\sigma$ (Å)	Fe-F	0.033	0.029	0.036	0.031
	Mn-F	0.075	0.073	0.063	
E <sub>o</sub> (eV)	Fe	7130	7130	7130	7128
	Mn	6551	6552	6552	

Table 1 : Neighbor parameters for glasses and standards (under parenthesis : the known X-ray values).

4. Results and Discussion. - EXAFS results for crystallized compounds show distances M-F ( $M = \text{Mn}^{2+}, \text{Fe}^{3+}$ ) in good agreement with X-ray data and we can estimate their accuracy to be  $\Delta R \approx 0.02 \text{ \AA}$  also for the glasses. On the other hand, if we compare the  $S_0^2$  values with known ones (for example 0.68 for Mn in  $\text{MnCl}_2$  and 0.69 for Fe in  $\text{FeCl}_2$  (12)), they appear very weak. We cannot actually exclude the possibility of amplitude reduction caused by contamination of x-ray beam with harmonics or by inhomogeneity of the sample before carefully verifying the effect of sample thickness; so we do not expect the N values to be more accurate than  $\Delta N \approx 1.5$ . However the observed values of N are in agreement with the expected value of 6 and the M-F distances are closely related to Mn-F, Fe-F distances for such sixfold coordinated transition metal in crystallized fluoride compounds. With the distances Mn-F and Fe-F of EXAFS, one can calculate a mean distance M-F of  $2.025 \text{ \AA}$  so that we can conclude with the M-M Neutron distances that  $\text{MF}_6$  octahedra are only corner-shared: indeed, if octahedra are linked by edge, this leads to a maximum M-M distance of  $2.9 \text{ \AA}$  which is inconsistent with our result of  $3.6 \text{ \AA}$ . The mean angle M-F-M calculated for the glasses is  $126^\circ$ , in good agreement with superexchange angles observed in antiferromagnetic fluoride crystals with corner shared octahedra.

The magnetic functions correlation for the two glasses are very close (figure 2), indicating that  $\text{Pb}^{2+}$  do not modify the octahedral framework over a distance of about  $9 \text{ \AA}$  for large concentration variations. These results are consistent with a glassy network model of distorted connected chains build up from corner sharing octahedra with  $\text{Pb}^{2+}$  in interstitial sites. In this hypothesis the observed distance of  $6.7 \text{ \AA}$  could correspond to second neighbors M-M in the same chain and that of  $5.4 \text{ \AA}$  to second neighbors of two connected chains. The frequency of connections between chains is probably greater for " $\text{PbMnFeF}_7$ " compared to " $\text{Pb}_2\text{MnFeF}_9$ " as suggested by the intensity of the peak at  $5.4 \text{ \AA}$ , with regard to the  $6.7 \text{ \AA}$  one, clearly more important in the case of " $\text{PbMnFeF}_7$ " (figure 2).

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