

## NEUTRON MAGNETIC DIFFRACTION STUDY OF FLUORIDE “ $\text{Pb}_2\text{MnFeF}_9$ ” SPIN GLASS DILUTED BY DIAMAGNETIC IONS

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The effect of dilution by diamagnetic ions on the short range magnetic ordering of fluoride “ $\text{Pb}_2\text{MnFeF}_9$ ” spin glass has been examined by neutron diffraction. Partial spin correlation functions for pairs Mn–Mn, Fe–Fe and Mn–Fe show that first neighbours of the same type exist with antiferromagnetic interaction but are more numerous for Mn–Mn than Fe–Fe, the Mn–Fe contribution being predominant for second neighbours (ferromagnetic interaction). A difference of  $18^\circ$  between the mean angles Fe–F–Fe and Mn–F–Mn could explain the large differences in  $|\theta p|$  for two series of glasses where  $\text{Mn}^{2+}$  is substituted by  $\text{Zn}^{2+}$  or  $\text{Fe}^{3+}$  by  $\text{Ga}^{3+}$ . The structure is described in terms of corner sharing  $\text{MF}_6$  octahedra, M–M distances and spin correlations present some analogies with those of a  $\text{ReO}_3$ -type lattice for which half of cationic sites would be occupied.

### 1. Introduction

The fluoride glasses “ $\text{Pb}_2\text{M}_t^{\text{II}}\text{M}_t^{\text{III}}\text{F}_9$ ” ( $\text{M}_t^{\text{II}} = \text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ;  $\text{M}_t^{\text{III}} = \text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ) belong to a new glass family [1–2] with interesting optical and magnetic properties [2–4] which justify a structural approach. Fluoride 3d transition metal chemistry shows prevailing octahedral coordination in crystallized compounds; previous EXAFS [5] and UV visible [2] studies confirm this fact for this glass family.

Neutron diffraction measurements on “ $\text{Pb}_2\text{MnFeF}_9$ ” and “ $\text{PbMnFeF}_7$ ” glasses which show spin glass behaviour [3–4] have lead to the short range magnetic ordering for  $\text{M}_t$ – $\text{M}_t$  pairs without any distinction between  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ : the glassy network is built on corner shared octahedra [6].  $^{19}\text{F}$  NMR study of “ $\text{Pb}_2\text{MnFe}_{1-x}\text{Ga}_x\text{F}_9$ ” and “ $\text{Pb}_2\text{Mn}_{1-x}\text{Zn}_x\text{FeF}_9$ ” [7] glasses seems to indicate that  $\text{M}_t^{\text{III}}$  and  $\text{M}_t^{\text{II}}$  ions tend to alternate along octahedral chains. These two kinds of substituted glasses showed some systematic differences for magnetic constants: Curie–Weiss  $|\theta p|$  and spin freezing  $T_g$  temperatures [7–8]. The aim of this work was to determine if the magnetic behaviour could be related to some different structural ordering for  $\text{M}_t^{\text{II}}$  and  $\text{M}_t^{\text{III}}$  ions by studying their magnetic contribution from  $x = 0$  to  $x = 1$  (for  $x = 1$ , only  $\text{M}_t^{\text{II}}$ – $\text{M}_t^{\text{II}}$  or  $\text{M}_t^{\text{III}}$ – $\text{M}_t^{\text{III}}$  paramagnetic ions pairs contribute).

The 3d transition metal crystallochemistry (sixfold coordination, ionic radii)

justify isomorphous substitution hypothesis; our present results give additional arguments in this way.

## 2. Experiment and data analysis

Glasses were prepared by heating the anhydrous fluoride mixtures in a covered platinum crucible under inert atmosphere. The melt is cast and rolled in a bronze mould heated at 200°C.

Experiment was performed on powdered samples with the D2 diffractometer (ILL, Grenoble) in the range of momentum transfer  $Q = 0.4\text{--}9.1 \text{ \AA}^{-1}$  ( $4\pi \sin \theta/\lambda$ ) with a wavelength  $\lambda = 1.22 \text{ \AA}$ . A well-established method to isolate the magnetic scattering  $I_m(Q)$  when using unpolarized neutron beams is to subtract intensity data recorded above and below the magnetic ordering temperature; so intensity data were collected in the paramagnetic range (290 K) and at 4 K for each glass. This last temperature is below the spin freezing temperature  $T_g$  of "Pb<sub>2</sub>MnFeF<sub>9</sub>" but slightly above  $T_g$  for the other glasses (table 1) for which the ac susceptibility cusp is progressively displaced and less sharp when the dilution by diamagnetic ions increases [7]. Previous study of short-range magnetic ordering in "PbMnFeF<sub>7</sub>" and "Pb<sub>2</sub>MnFeF<sub>9</sub>" glasses has shown that the phenomenon remains nearly the same in a large range of temperature: a detectable decreasing in the magnitude of ordering occurs only 20 K above  $T_g$  and extends to more than 150 K [6]. The same behaviour is expected to apply here. Intensities for both the surroundings and the empty cylindrical vanadium cell (5 cm height and 0.4 cm radius) were measured for background correction. In order to obtain normalized magnetic contribution, difference spectra were made between low and high temperature data, corrected for background and absorption, and normalized with the aid of a scaling factor evaluated by a fit between the sum of the calculated various parts (coherent, incoherent, paramagnetic, multiple and inelastic scattering) and a curve obtained by a complete smoothing of intensities for  $Q > 6 \text{ \AA}^{-1}$ . The paramagnetic contribution was computed using the analytical constants describing the magnetic form factor of Lisher and Forsyth [9] and values of magnetic moments on the transition metal ions obtained from magnetic measurements ( $\mu_{\text{Fe}^{3+}} = 5.9 \mu\text{B} = \mu_{\text{Mn}^{2+}}$ ); the magnetic moment is assumed to be

Table 1  
Curie-Weiss ( $|\theta p|$ ) and spin freezing temperatures ( $T_g$ )

	$ \theta p $ (K)	$T_g$ (K)
Pb <sub>2</sub> MnGaF <sub>9</sub>	36	0.35
Pb <sub>2</sub> MnFe <sub>0.4</sub> Ga <sub>0.6</sub> F <sub>9</sub>	76	1.65
Pb <sub>2</sub> MnFeF <sub>9</sub>	135	5.26
Pb <sub>2</sub> Mn <sub>0.4</sub> Zn <sub>0.6</sub> FeF <sub>9</sub>	119	2.37
Pb <sub>2</sub> ZnFeF <sub>9</sub>	100	0.73

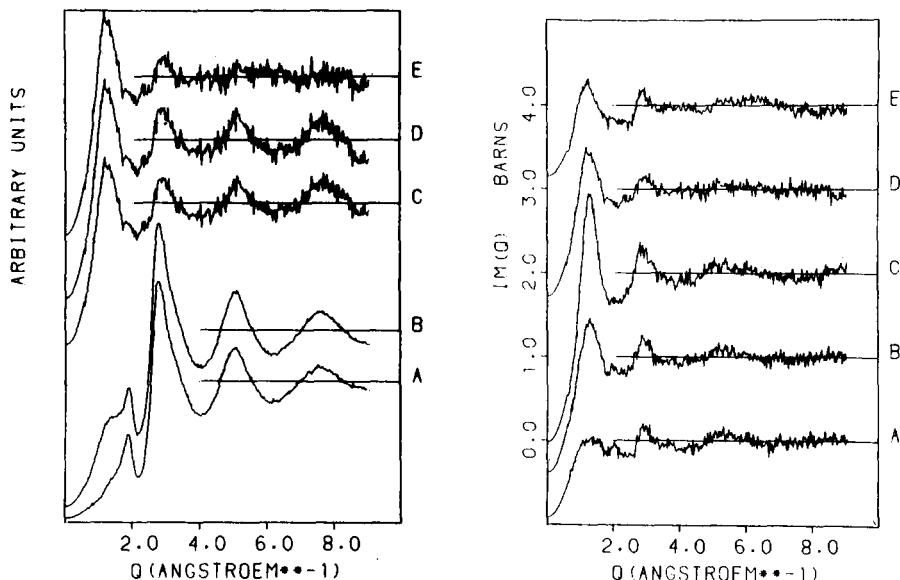


Fig. 1. “ $\text{Pb}_2\text{MnGa}_{0.6}\text{Fe}_{0.4}\text{F}_9$ ” normalized total diffraction spectra (290 K (A); 4 K (B)) and difference spectra (4 K–290 K) between: no corrected total spectra (C), normalized (D), corrected for thermal motions (E).

Fig. 2. Magnetic difference spectra corrected for thermal motions for “ $\text{Pb}_2\text{M}_1^{\text{II}}\text{M}_1^{\text{III}}\text{F}_9$ ” with  $\text{M}_1^{\text{II}}\text{M}_1^{\text{III}} = \text{ZnFe}$  (A);  $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}$  (B);  $\text{MnFe}$  (C);  $\text{MnFe}_{0.4}\text{Ga}_{0.6}$  (D);  $\text{MnGa}$  (E).

the same at the two temperatures. Multiple scattering was estimated from the expressions due to Blech and Averbach [10] and the inelastic correction terms were computed following the method of Yarnell [11]. Finally, intensities were extrapolated from  $0.4 \text{ \AA}^{-1}$  to the origin.

An example of normalized total diffraction spectra  $I(Q)$  for high and low temperature is given in fig. 1 together with difference spectra obtained in various ways. The main difference between C and D of fig. 1 is due to the Placzek correction; a comparison with the total spectra shows high correlation between the last three peaks of the difference spectra and those of the total. It must be remembered that the magnetic form factor decreases very quickly as  $Q$  increases: for instance, at  $Q = 6 \text{ \AA}^{-1}$  the value of the  $\text{Fe}^{3+}$  squared magnetic form factor represents only 3% of its value at the origin. The conclusion is that the two last peaks near  $5$  and  $7.5 \text{ \AA}^{-1}$  on the difference spectra are more probably due to thermal motion variation on nuclear intensities upon which depend inelastic terms but also the interference function. In the quasi-static approximation of neutron total scattering, the coherent differential scattering cross section for the nuclear part can be written as follows:

$$\frac{d\sigma}{d\Omega_T} \approx \sum_j \{ c_j b_j^2 [1 + P_j(Q, T)] \} + \langle b \rangle^2 [I(Q) - 1] e^{-2W(T)}$$

where  $P(Q, T)$  represents the Placzek (inelastic) correction terms at temperature  $T$  and  $e^{-2W(T)}$  the Debye–Waller factor [12]. In fact, each atom type must have its own factor but we have no other possibility here that to consider a general factor and only the difference  $B(T_1) - B(T_2)$  ( $W(T) = B(T) \sin^2\theta/\lambda^2$ ) can be found using the ratio of the reduced interference functions for the two temperatures. An empirical correction was made assuming that  $B(4 \text{ K}) = 0.0$  and searching a value of  $B(290 \text{ K})$  which minimizes the sum of the squared difference spectra intensities between 5 and 9  $\text{\AA}^{-1}$ . The result of this correction is shown in fig. 1E: the second peak intensity near 3  $\text{\AA}^{-1}$  is greatly reduced but can be considered with confidence to be of magnetic origin. Fig. 2 shows all the magnetic difference spectra obtained in this way, corresponding  $B$  values lying between 0.62 and 0.71  $\text{\AA}^2$ . The correction is not perfect but the magnetic reality of the peak near 3  $\text{\AA}^{-1}$  is confirmed if we consider that it is the most intense for “ $\text{Pb}_2\text{MnFeF}_9$ ” although, for the nuclear scattering only, the most intense peak at this position is for “ $\text{Pb}_2\text{MnGaF}_9$ ”.

The reduced magnetic correlation function was calculated by the sine-Fourier transformation previously described [6]:

$$d_m(R) = 4\pi R [\rho_m(R) - \rho_m^0] = \frac{3}{\pi} \int_0^{Q_{\max}} \frac{Q \operatorname{Im}(Q)}{\langle P(Q) \rangle^2} M(Q) \sin QR \, dQ, \quad (2)$$

where

$$\langle P(Q) \rangle^2 = \left[ \frac{e^2\gamma}{2mc^2} \right]^2 S(S+1) \langle f(Q) \rangle^2. \quad (3)$$

$\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  are in the same  ${}^6\text{S}$  ground state and this authorizes the use of a mean magnetic form factor  $\langle f(Q) \rangle$ ; others terms in expression (3) having their usual meaning. The numerical integration of (2) was performed for  $Q_{\max} = 4.5 \text{ \AA}^{-1}$  and the modification function  $M(Q)$  due to Lorich [13] was used in order to remove truncation effects. The magnetic density function  $\rho_m(R)$  corresponds to the product of two terms:  $\rho(R)$ , the magnetic atoms number per unit volume at distance  $R$  of an arbitrary atom origin and  $\langle \mathbf{S}_0 \cdot \mathbf{S}_R \rangle / S(S+1)$ , the spin average correlation. For an antiferromagnetic material,  $\rho_m^0$  is zero and positive or negative peaks on  $\rho_m(R)$  mean respectively magnetic ions with parallel or antiparallel spins to that of the origin.

### 3. Results and discussion

The general form of magnetic difference spectra in fig. 2 is very similar, this holds also for the magnetic radial distribution functions  $4\pi R^2 \rho_m(R) \langle \mathbf{S}_0 \cdot \mathbf{S}_R \rangle$  shown in fig. 3 for which distances and magnetic interaction type are summarized in table 2. All the curves show (fig. 3) an antiferromagnetic interaction near 3.6  $\text{\AA}$  and two ferromagnetic ones at 5 and 6.9  $\text{\AA}$ ; the main modification with dilution of magnetic species by diamagnetic ones is a variation in

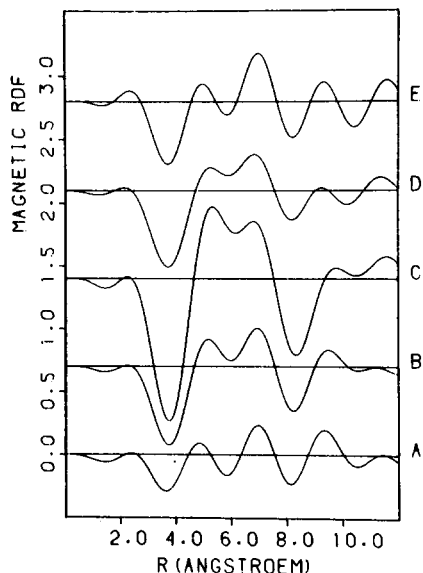


Fig. 3. Magnetic radial distribution functions  $4\pi R^2\rho(R)\langle S_0 \cdot S_R \rangle$ : “ $\text{Pb}_2\text{M}_I^{\text{II}}\text{M}_I^{\text{III}}\text{F}_9$ ” with  $\text{M}_I^{\text{II}}\text{M}_I^{\text{III}} = \text{ZnFe}$  (A);  $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{Fe}$  (B);  $\text{MnFe}$  (C);  $\text{MnFe}_{0.4}\text{Ga}_{0.6}$  (D);  $\text{MnGa}$  (E).

magnitude. According to the first  $\text{M}_I\text{--M}_I$  distance,  $\text{M}_I\text{F}_6$  octahedra (coordination established by EXAFS measurements [5]) are only corner-shared.

In the case of “ $\text{Pb}_2\text{ZnFeF}_9$ ” and “ $\text{Pb}_2\text{MnGaF}_9$ ”, where only pairs  $\text{Fe}\text{--Fe}$  and  $\text{Mn}\text{--Mn}$  respectively participate to the phenomenon, it is evident that first neighbours of the same type exist (figs. 3A, 3E). This result does not confirm previous hypothesis that  $\text{M}_I^{3+}$  and  $\text{M}_I^{2+}$  ions tend to alternate along chained  $\text{M}_I\text{F}_6$  octahedra as suggested by  $^{19}\text{F}$  NMR measurements [7]; such a model had the advantage to explain the strong decrease of paramagnetic Curie temperature  $|\theta_p|$  with Ga concentration (table 1). A higher value of  $\text{Fe}^{3+}\text{--Fe}^{3+}$  exchange interaction if compared to  $\text{Mn}^{2+}\text{--Mn}^{2+}$  interaction, because of the higher covalence of the former, was involved to explain the rather smoothly

Table 2  
Shell distances and interaction type (AF = antiferromagnetic, F = ferromagnetic)

	$R_1$ (Å)	$R_2$ (Å)	$R_3$ (Å)	$R_4$ (Å)	$R_5$ (Å)
$\text{Pb}_2\text{MnGaF}_9$	3.60	4.95	5.87	6.98	8.23
$\text{Pb}_2\text{MnGa}_{0.6}\text{Fe}_{0.4}\text{F}_9$	3.63	5.18	(5.88)	6.77	8.16
$\text{Pb}_2\text{MnFeF}_9$	3.65	5.28	(6.20)	6.75	8.30
$\text{Pb}_2\text{Mn}_{0.4}\text{Zn}_{0.6}\text{FeF}_9$	3.65	5.14	(5.98)	6.91	8.21
$\text{Pb}_2\text{ZnFeF}_9$	3.57	4.84	5.82	6.95	8.13
Interaction type	AF	F	AF	F	AF
Distances for cubic lattice	3.62	5.12	6.27	7.24	8.09
	( $a$ )	( $a\sqrt{2}$ )	( $a\sqrt{3}$ )	( $2a$ )	( $a\sqrt{5}$ )

decreasing of  $|\theta p|$  with the Zn substitution. These ideas clearly must be modified to interpret our present results. On the point of view of the superexchange mechanisms, the large difference observed on  $|\theta p|$  for the same degree of substitution between  $\text{Mn}^{2+}\text{-Zn}^{2+}$  and between  $\text{Fe}^{3+}\text{-Ga}^{3+}$  can be explained principally by considerations on  $\text{M}_i\text{-F-M}_i$  angles. The combination of neutron results distances Fe-Fe (3.57 Å) and Mn-Mn (3.60 Å) with EXAFS results [5] Fe-F (1.93 Å) and Mn-F (2.10 Å) leads to angles Fe-F-Fe = 135° and Mn-F-Mn = 117°:  $\text{Fe}^{3+}\text{-Fe}^{3+}$  interaction is consequently expected to be much larger than  $\text{Mn}^{2+}\text{-Mn}^{2+}$  interaction. Evolution in area of the first negative peak ( $\text{M}_i\text{-M}_i$  antiferromagnetic interaction) in fig. 3, taking "Pb<sub>2</sub>MnFeF<sub>9</sub>" as a reference, shows a large decrease when paramagnetic ions are substituted by diamagnetic ones; this area remain very similar for paramagnetic ion concentration Mn<sub>0.4</sub>Fe or Fe<sub>0.4</sub>Mn but is very much lower for Fe alone (fig. 3A) than for Mn (fig. 3E). This seems to be incompatible with a larger Fe-Fe interaction if a higher exchange integral implies more ordering but these areas depend also on the pairs number so that we must conclude to a very low number of Fe-Fe neighbours at 3.6 Å in "Pb<sub>2</sub>ZnFeF<sub>9</sub>" compared to the Mn-Mn neighbours number in "Pb<sub>2</sub>MnGaF<sub>9</sub>" for this distance.

The other evident evolution of magnetic RDF with substitution is an intensity inversion between the two ferromagnetic peaks near 5.3 and 6.8 Å: the latter becomes more important with increasing substitution by diamagnetic ions, and an antiferromagnetic correlation is seen near 5.9 Å for the total change of  $\text{Mn}^{2+}$  by  $\text{Zn}^{2+}$  or  $\text{Fe}^{3+}$  by  $\text{Ga}^{3+}$ . This suggest a special ordering of pairs Mn-Mn and Fe-Fe if compared to the total contribution of magnetic pairs in "Pb<sub>2</sub>MnFeF<sub>9</sub>" and predominant Mn-Fe pairs contribution would be for the second nearest neighbours ferromagnetic ones at 5.3 Å: the partial contribution of Mn-Fe pair was isolated by a simple difference between the

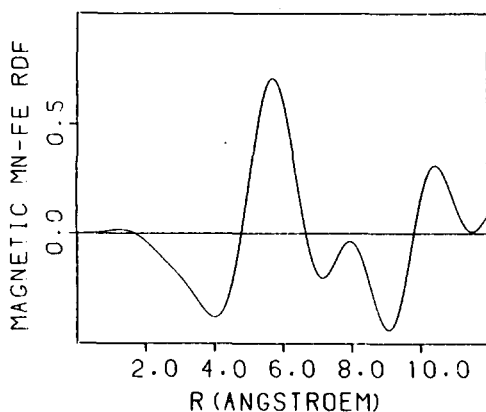


Fig. 4. Partial magnetic radial distribution function for Mn-Fe pairs.

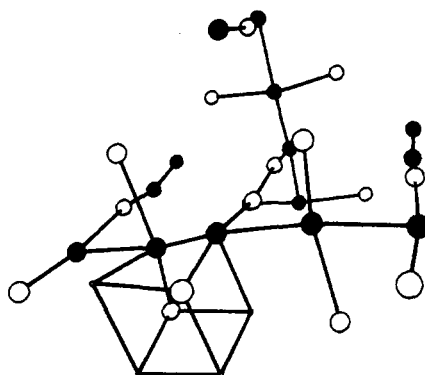


Fig. 5. Structural model for  $\text{M}_i\text{-M}_i$  network; ●:  $\text{Mn}^{2+}$ , ○:  $\text{Fe}^{3+}$ .

normalized magnetic RDF (“Pb<sub>2</sub>MnFeF<sub>7</sub>”–“Pb<sub>2</sub>ZnFeF<sub>9</sub>”–“Pb<sub>2</sub>MnGaF<sub>9</sub>”) and the results is shown in fig. 4. Such a separation supposes perfect isomorphism substitution but also that the magnetic ordering remains not only the same in the type of correlation (which appears to be the case) but also in magnitude, which is less evident.

A simple tridimensional model can be proposed which well explains these facts: the five first distances of table 2 are in nearly accordance with the distances of a simple cubic lattice i.e.:  $a$ ,  $a\sqrt{2}$ ,  $a\sqrt{3}$ ,  $2a$ ,  $a\sqrt{5}$  giving for a mean value of the first neighbours distances 3.62; 5.12; 6.27; 7.24; and 8.09 Å. An idealized view of the FeF<sub>3</sub> structure in the ReO<sub>3</sub>-type [14,15] is compatible with these distances and moreover corresponds to the same type of magnetic interactions AF, F, AF, F, AF (AF = antiferromagnetic, F = ferromagnetic). Of course, all the Fe<sup>3+</sup> sites could not be occupied in the case of glasses but probably near half of them forming ramified chains of corner shared M<sub>1</sub>F<sub>6</sub> octahedra. Such chains exist in BaFeF<sub>5</sub> [16], closely related to Pb<sub>5</sub>Fe<sub>3</sub>F<sub>19</sub> [17] situated near the vitreous domain and the model of fig. 5 was built by interconnection of parts of chains encountered in these structures (with slight random displacement). A predominant linear arrangement of Mn<sup>2+</sup>–Mn<sup>2+</sup>–Mn<sup>2+</sup> ... with Fe<sup>3+</sup> in connection leads to the magnetic RDF results when all the Mn<sup>2+</sup> or Fe<sup>3+</sup> are replaced by diamagnetics ions: the first neighbours Fe–Fe number is less than for Mn–Mn; the  $a\sqrt{2}$  second neighbours distance exists principally for Fe–Mn pairs; the  $2a$  distance exists for both Mn–Mn or Fe–Fe pairs. This structural model appears to be valid in all the vitreous domains with more or less occupation of the Fe<sup>3+</sup> site of the FeF<sub>3</sub> type structure; for instance, the “PbMnFeF<sub>7</sub>” glass has shown previously [5] the same essential features of the magnetic RDF as “Pb<sub>2</sub>MnFeF<sub>9</sub>” but with a ferromagnetic peak at  $a\sqrt{2}$  twice the ferromagnetic peak at  $2a$ , and this increasing is expected if more vertex of FeF<sub>3</sub> cubic array are occupied.

#### 4. Conclusion

Our glasses are not “classical” spin glasses (produced by diluting magnetic ions in nonmagnetic metallic matrix at low concentration) but rather high concentrated magnetic glasses; the theory, although well debated on the point of view of a phase transition or not, relates the phenomenon to conflicting interactions between magnetic moments due to randomness of distances and/or frustration effects. The later case is probably more important in our glasses because distances variation for first neighbours M<sub>1</sub>–M<sub>1</sub> or even next-nearest neighbours cannot reach the large range of values expected in very diluted system. The magnetic RDF is not easy to correlate in magnitude with variables such that spin-freezing temperature (magnetic ordering occurs well above  $T_g$  in our case),  $|\theta_p|$  or frustration degree because very little is known about them and their relations with  $\langle S_0 \cdot S_R \rangle$  or between themselves in spin glasses. The fact that  $T_g$  decreases with  $|\theta_p|$  for the glasses studied here is perhaps a

coincidence and  $T_g$  decreasing could be more correlated with frustration decreasing, probably associated to less triplets configuration number produced by the dilution (in our model, the short range tridimensional magnetic ordering in “ $\text{Pb}_2\text{MnFeF}_9$ ” becomes unidimensional for “ $\text{Pb}_2\text{MnGaF}_9$ ” and “ $\text{Pb}_2\text{ZnFeF}_9$ ” with only linear octahedral chains). Knowledge of  $\langle S_0 \cdot S_R \rangle$  absolute values implies to estimate the pair number, which was not possible here; the interpretation of the purely nuclear part of our neutron spectra and an attempt to separate some partial pairs contribution ( $M_1 - M_1$  in particular) would give further evidence for our structural model and precise the  $\text{Pb}^{2+}$  insertion [18].

## References

- [1] J.P. Miranday, C. Jacoboni and R. De Pape, *Rev. Chim. Min.* 16 (1979) 277.
- [2] J.P. Miranday, C. Jacoboni and R. De Pape, *J. Non-Crystalline Solids* 43 (1981) 393.
- [3] J.P. Renard, J.P. Miranday and F. Varret, *Solid St. Commun.* 35 (1980) 41.
- [4] E. Velu, J.P. Renard and J.P. Miranday, *J. de Phys.* 42 (1981) L 237.
- [5] A. Le Bail, C. Jacoboni and R. De Pape, *J. Solid St. Chem.* 52 (1984) 32.
- [6] A. Le Bail, C. Jacoboni and R. De Pape, *J. Solid St. Chem.* 48 (1983) 168.
- [7] C. Dupas, L. Le Dang, J.P. Renard, P. Veillet, J.P. Miranday and C. Jacoboni, *J. de Phys.* 42 (1981) 1345.
- [8] J.P. Renard, C. Dupas, E. Velu, C. Jacoboni, G. Fonteneau and J. Lucas, *Physica* 108B (1981) 1291.
- [9] E.J. Lisher and J.B. Forsyth, *Acta Cryst.* A27 (1971) 545.
- [10] I.A. Blech and B.L. Averbach, *Phys. Rev.* 137A (1965) 1113.
- [11] J.L. Yarnell, M.J. Katz, R.G. Wenzel and S.J. Koenig, *Phys. Rev.* 7A (1973) 2130.
- [12] A.C. Wright, *Adv. Struct. Res. Diffr. Meth.* 5 (1974) 1.
- [13] E.A. Lorch, *J. Phys.* C2 (1969) 229.
- [14] M.A. Hepworth, K.H. Jack, R.D. Peacock and G.J. Westland, *Acta Cryst.* 10 (1957) 63.
- [15] E.O. Wollan, H.R. Child, W.C. Koehler and M.K. Wilkinson, *Phys. Rev.* 112 (1958) 1132.
- [16] R. Von der Muhl, J. Galy and S. Anderson, *C.R. Acad. Sci.* C267 (1968) 569.
- [17] C. Jacoboni, A. Le Bail, R. De Pape and J.P. Renard, *Solid State Chem., Proc. Second European Conf. Veldhoven, The Netherlands, Studies in Inorganic Chemistry* 3 (1983) 687.
- [18] A. Le Bail, C. Jacoboni and R. De Pape, *J. Non-Crystalline Solids*, this issue, following paper.