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CORRELATIONS BETWEEN MAGNETIC AND CRYSTALLOCHEMICAL BEHAVIOUR IN 3d-U^{4+} FLUORIDE GLASSES

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GLASSY SYSTEMS (1)

Large vitreous domains (figure 1) have been found in various ternary systems of general formula BaF_2-UF_4-MF_n (MF_n = MF_2 or MF_3 with M = 3d transition metal or Al, Ga). These systems allow the addition of numerous fluorides $M'F_n$ up to 20% mole (M' = Li, Na, K, Rb, Cs, Ag, Mg, Ca, Y, Ln). Thermal and main physical properties are identical to those of fluorozirconates or fluorohafnates glasses. These glasses are resistant to water environment in neutral or basic solution but their I. R. transparency is not so good. A study of the quaternary system BaF_2-UF_4-MnF_2-FeF_3 shows a large unique vitreous domain which do not fit with the classical concept of modifier assigned to large cations in the case of UF_4-MnF_2-FeF_3 system (figure 2).

MAGNETIC BEHAVIOUR (2, 3)

Magnetic measurements on those fluoride glasses which contain paramagnetic 3d elements and 5f elements allow to collect some informations about their crystallochemical behaviour.

From the $1/\chi = f(T)$ and $\sigma = f(H)$ curves performed in the 4 - 300 °K range, the following results have been pointed out:

* Spin glass behaviour at very low temperature (< 1.5 °K)
* $5f^2$ ($^3H_4$) electronic configuration for U^{4+} ($\mu \simeq 3.3\ \mu_b$)
* eightfold coordination for U^{4+}

Table 1 : Magnetic characteristics of some 3d-U^{4+} glasses

Glass formula				Magnetic moment	Curie Temperature
BaF_2	UF_4	MF_2	MF_3	$\mu(U^{4+})$ in μ_b	$-\theta_p$ ±3 °K
33	33	33(Mn)	-	3.30	32
33	33	33(Zn)	-	3.28	103
33	33	33(Cu)	-	3.56	65
33	33	-	33(Fe)	3.01	79
33	33	-	33(V)	3.40	76
33	33	-	33(Ti)	3.31	79
33	33	-	33(Ga)	3.22	81
-	33	33(Mn)	33(Fe)	3.48	94
33	-	33(Mn)	33(Fe)	-	146

* From the $|\Theta_p|$ temperature, we can obtain the nature of superexchange magnetic interactions:
  - Antiferromagnetic U^{4+}-U^{4+} ≃ Fe^{3+}-Fe^{3+} >> Mn^{2+}-Mn^{2+}
  - Ferromagnetic U^{4+}-M

Different magnetic behaviour observed for glasses containing MnF_2 and MF_3 fluorides indicates that Mn^{2+} could be more connected to the UF_8^{4-} polyhedra than the M^{3+} ions (figure 3a - 3b).

DISCUSSION

In these glasses, the magnetic behaviour of, respectively 3d and U^{4+} ions is in good agreement with the classical six and eightfold coordinations observed by optical absorption spectra (1), X-Ray diffraction and E.X.A.F.S. experiments.

Table 2 : Interatomic distances in Angstroems and coordination number in "$BaUMF_{6+n}$" glasses

	EXAFS	X-ray	C.N
U - F (Fe,Zn,Mn,Ga)	2.27	2.28	8
Ga - F	1.88		6
Fe - F	1.95		6
Zn - F	1.97		6
Mn - F	2.09		6
U - U / U - Ba / U - M Ba - Ba		4.32	

- EXAFS studies (figure 4 , Table 2) lead to the coordination numbers : 8 ± 1. for U^{4+} and 6 ± .6 for 3d transition metals. No evidence of different behaviour have been found between Mn^{2+} and M^{3+} ions environment as observed in crystallized fluoride compounds.
- Analysis of the X-Ray diffraction patterns (figure 5) gives the mean U-F and Metal-Metal distances (respectively 2.28 A and 4.32 A). This last value could be interpreted as the fact that UF_8^{4-} polyhedra are connected together to built up clusters of limited size linked by MF_6 octahedra; this view is consistent with the constancy of $|\Theta_p|$ temperature with the dilution in the BaF_2-UF_4-ZnF_2 glasses (2). Additionnal informations could be obtained by central peak diffusion in neutrons experiments.

Nevertheless, the structural difference between Mn^{2+} and M^{3+} ions is seen with the conductivity measurements at 200°C :

- "$BaUMnF_8$" glass : $\sigma = 5\ 10^{-6}\ \Omega^{-1}.cm^{-1}$
- "$BaUFeF_9$" glass : $\sigma = 2\ 10^{-7}\ \Omega^{-1}.cm^{-1}$ and could be due to different linkage-type of $(\ UF_8^{4-}\ )_n$ clusters.

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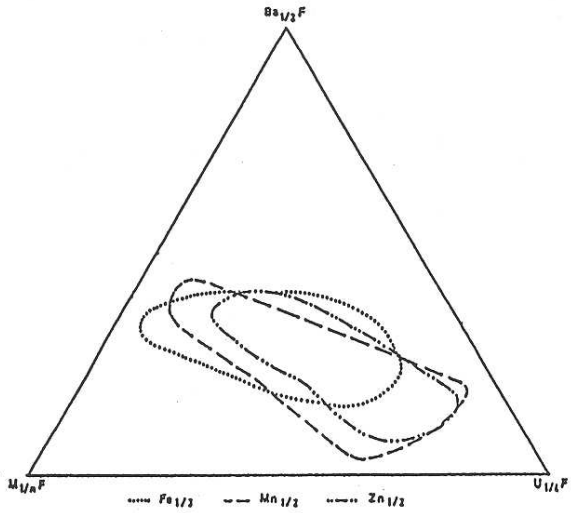

Figure 1: Glassy systems BaF_2-UF_4-MF_n

(MF_n = FeF_3, MnF_2, ZnF_2)

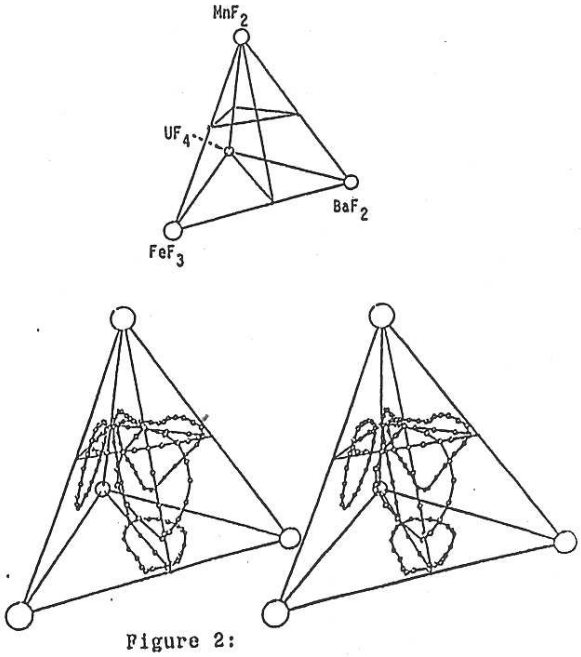

Figure 2:

Quaternary glassy system BaF_2-UF_4-MnF_2-FeF_3-MnF_2

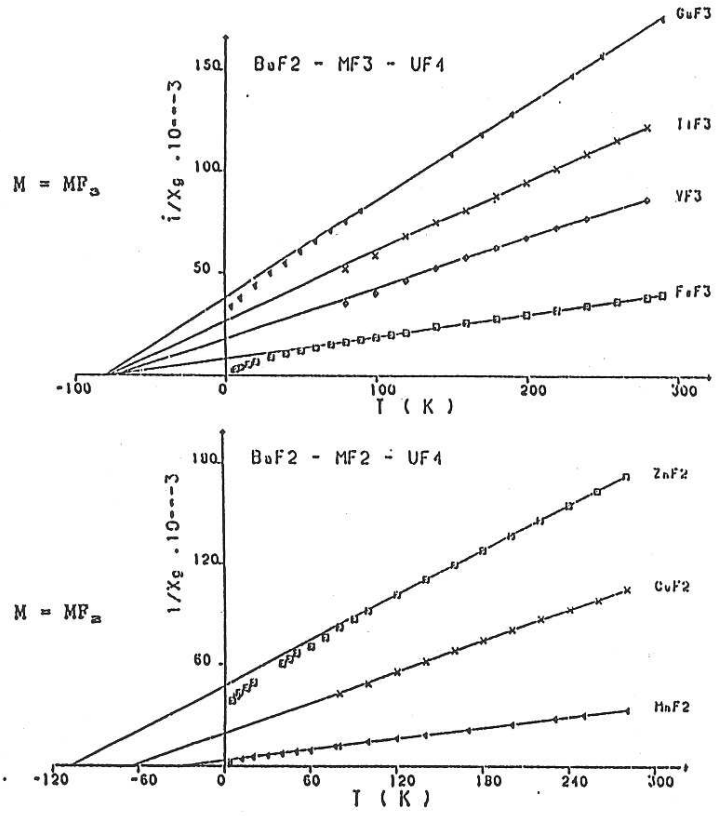

Figure 3: Magnetic behaviour of "$BaUMF_{6+n}$" glasses

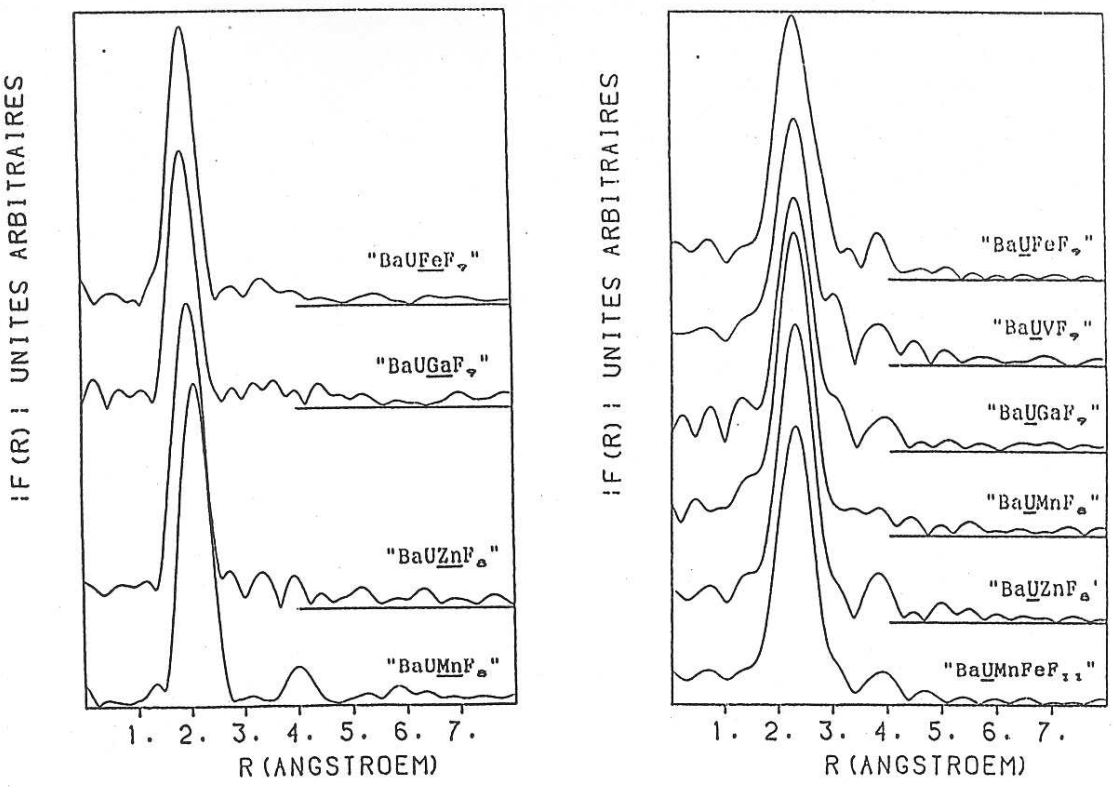

Figure 4: Fourier transform of $k^3\chi(k)$ EXAFS modulations corrected for phase shift

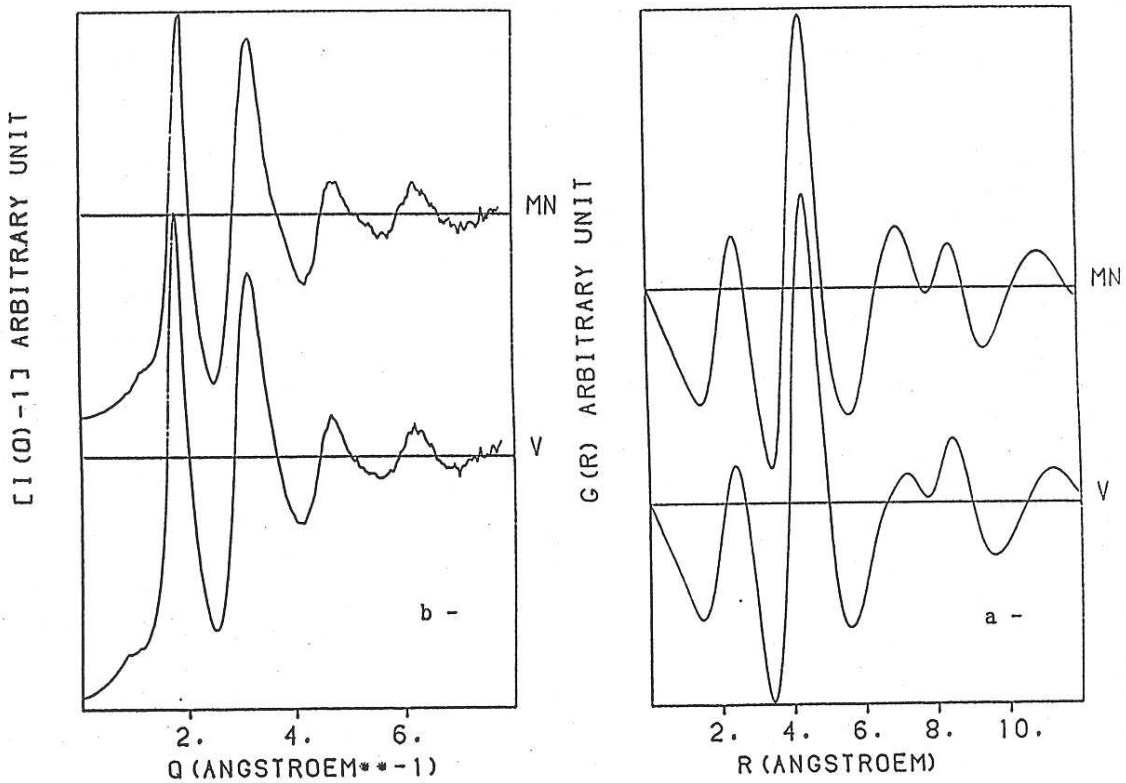

Figure 5 -a Reduced atomic distributions functions for "$BaUMF_{6+n}$" glasses

-b Interference functions for "$BaUMF_{6+n}$" glasses (λ = 1.541 A)