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A neutron diffraction study of the anion-excess cubic ReO_3-type derived phase $Fe_{0.80}Zr_{0.20}F_{3.20}$*

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Abstract

The environment of the cations has been determined in a powder of an anion-excess cubic ReO_3 phase of $Fe_{0.80}Zr_{0.20}F_{3.20}$ composition using the neutron diffraction technique. Two anion sites have actually been found: one (F1) is slightly shifted from the ideal lattice site; the second (F2) is situated further away. The experimental occupation rates of the two sites (2.83 and 0.37 respectively) are in very good agreement with the theoretical values. The non-stoichiometry can be explained by the formation of F2–F2 pairing across vacant F1 positions. The magnetic structure has been established. The parameter of the magnetic cell is double the nuclear one.

1. Introduction

The investigation of several $AZrF_6$–ZrF_4 systems (A = Ca, transition element) has shown the existence of non-stoichiometric composition ranges $(A,Zr)F_{3+x}$. Most of the concerned fluorides crystallize with a structure related to the ReO_3 type and exhibit the $Pm\bar{3}m$ space group when both cations are disordered or the $Fm\bar{3}m$ group when ordering occurs on the cation sites [1, 2]. Similar results have been obtained for the MF_3–ZrF_4 systems (M = Ti, In [3]; M = Fe [4]). Other types of homogeneity domains have also been found, for example in the $SmZrF_7$–ZrF_4 [5] or $UZrF_7$–ZrF_4 systems [6]. Such results can be correlated to the presence of zirconium(IV), which readily tolerates six-, seven- or eightfold coordination with fluoride anions. Various anionic arrangements have thus been detected in zirconium oxyfluorides [7–10].

In the phases based on the cubic ReO_3 type the anion excess has been found to result in the formation of F–F groups, giving rise to increasing zirconium coordination. Evidence of such a structural feature was given for two compounds of $MX_{3.5}$ formulation, namely the oxyfluoride $Zr_{0.8}Yb_{0.2}F_{3.2}O_{0.3}$

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*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

TABLE 1

Atomic coordinates and isotropic temperature factors of $Fe_{0.80}Zr_{0.20}F_{3.20}$ in the $Pm\bar{3}m$ space group (estimated standard deviations are given in parentheses); $a=3.8413(4)$ Å

Atom	Site	x	y	z	B_{iso} (Å^2)	Site occupation
Fe	6e	0	0	0.024(5)	0.5(1)	0.8
Zr	6e	0	0	0.024(5)	0.5(1)	0.2
F1	12j	0.50	0.045(1)	0.045(1)	0.8(1)	2.83(5)
F2	241	0.50	0.28(2)	0.15(2)	3.2(4)	0.37(5)

[11] and the ternary fluoride $YbZrF_7$ [12]. More recently a crystal study of $ZrF_{2.67}O_{0.67}$ has unambiguously established the simultaneous presence in the lattice of octahedra and pentagonal bipyramids [13].

On the basis of these various results it seemed worthwhile to investigate by neutron diffraction the environment of the cations for one of the compositions of the solid solution previously isolated by us in the FeF_3–ZrF_4 system [4], $Fe_{0.80}Zr_{0.20}F_{3.20}$, which exhibits at long range a cubic disordered ReO_3 symmetry. In addition the presence of iron(III) could lead to appropriate information on the magnetic structure.

2. Experimental details

Powder samples of $Fe_{0.80}Zr_{0.20}F_{3.20}$ were synthesized by solid state reaction at 850 °C for 1 day in a sealed platinum tube using appropriate mixtures of the binary fluorides FeF_3 and ZrF_4. The resulting product was reground in a dried glove-box and then annealed under similar conditions for 15 h. The reaction was followed by quenching to room temperature.

The room temperature lattice constant of the phase corresponds to that previously reported [4].

The neutron diffraction pattern was collected at 300 K on the D1B powder diffractometer at the high flux reactor of the Laüe–Langevin Institute (ILL Grenoble) using a wavelength of 1.285 Å. The sample was put into an air-tight cylindrical vanadium can (diameter 15 mm) held in a device allowing operation under vacuum.

3. Data analysis

On the basis of previous research [11–13] the nuclear diffraction intensities were calculated by taking into account the most symmetrical space group $Pm\bar{3}m$ which characterizes the ReO_3 structure. The pattern obtained at 300 K was refined using programs available at ILL Grenoble based on the Rietveld method [14, 15] and assuming isotropic thermal factors for both cations and anions. The values of the scattering lengths were [16]

TABLE 2

Atomic coordinates and isotropic temperature factors for $Fe_{0.80}Zr_{0.20}F_{3.20}$ in the $Fm\bar{3}m$ space group; components and moduli of the magnetic moments are also indicated (estimated standard deviations are given in parentheses); $a = 7.6827(4)$ Å

Atom	Site	x	y	z	B_{iso} (Å^2)	Site occupation	M_y (μ_B)	M_z (μ_B)	M (μ_B)
Fe1	24e	0	0	0.0122(2)	0.5(1)	0.4	2.0(5)	−3.2(4)	3.8(2)
Zr1	24e	0	0	0.0122(2)	0.5(1)	0.1			
Fe2	24e	0.5	0.5	0.5122(2)	0.5(1)	0.4	−2.0(5)	3.2(4)	3.8(2)
Zr2	24e	0.5	0.5	0.5122(2)	0.5(1)	0.1			
F1	96k	0.25	0.0225(1)	0.0225(1)	0.8(1)	2.83(2)			
F2	192l	0.25	0.141(9)	0.073(7)	3.2(4)	0.37(2)			

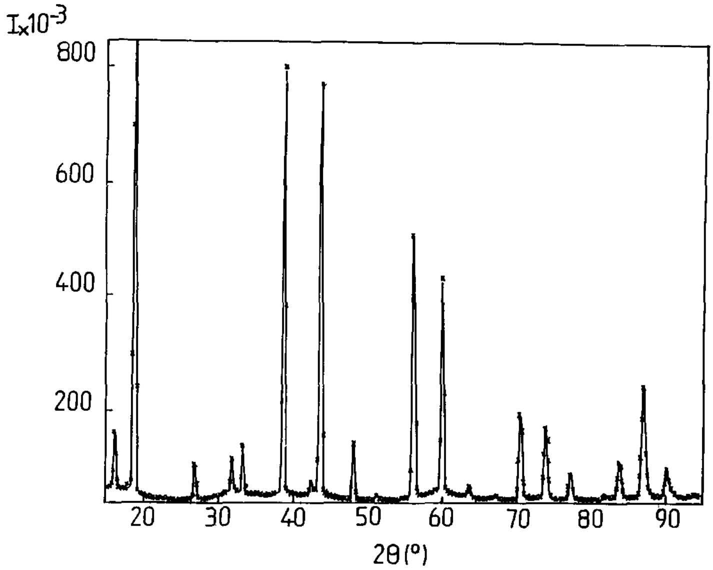

Fig. 1. Neutron diffraction patterns of $Fe_{0.80}Zr_{0.20}F_{3.20}$ at 300 K: ×, experimental spectrum; ——, calculated spectrum.

$b_{Fe} = 0.954 \times 10^{-12}$ cm

$b_{Zr} = 0.716 \times 10^{-12}$ cm

$b_F = 0.565 \times 10^{-12}$ cm

The reliability factor obtained after least-squares refinement is $R_I = 0.017$. The cell parameter and atomic coordinates are given in Table 1.

The composition $Fe_{0.80}Zr_{0.20}F_{3.20}$ has been found to exhibit antiferromagnetic behaviour with $T_N = 344 \pm 5$ K [4]. Such a magnetic ordering requires doubling of the parameter of the nuclear cell in order to refine the components of the Fe^{3+} magnetic moments. Refinement in the $Fm\bar{3}m$ space group leads to the reliability factors $R_{nucl} = 0.015$ and $R_{magn} = 0.115$. In Table 2 we report the cell parameter and atomic coordinates as well as the refined values of the components and moduli of the magnetic moments. The observed and calculated neutron patterns at 300 K are given in Fig. 1. A comparison between the calculated nuclear and magnetic intensities and the observed intensities is shown in Table 3.

These results allowed us to determine the orientation of the magnetic moments. The component along x is equal to zero. Thus the moments are located in the yOz plane and oriented in antiparallel directions, the angle with the z axis being $32 \pm 3°$.

4. Description of the structure and discussion

The structural determination was carried out assuming a random distribution of the Fe^{3+} and Zr^{4+} cations: these ions are slightly displaced from

TABLE 3

Intensities of calculated nuclear and magnetic lines and observed intensities ($Fm\bar{3}m$ space group) for $Fe_{0.80}Zr_{0.20}F_{3.20}$ (the indicated values must be multiplied by a factor 10^3)

$h\,k\,l$	2θ (°)	I_{nucl}	I_{magn}	I_{tot}	I_{obs}
1 1 1	16.10	0	220	220	225
2 0 0	18.71	1760	0	1760	1770
2 2 0	26.85	110	0	110	120
3 1 1	31.71	0	108	108	110
2 2 2	33.19	125	0	125	130
4 0 0	38.62	1255	0	1255	1275
3 3 1	42.31	0	35	35	38
4 2 0	43.49	1500	0	1500	1500
4 2 2	47.95	185	0	185	190
3 3 3	51.11	0	5	5	5
5 1 1	51.11	0	15	15	15
4 4 0	56.09	1020	0	1020	1020
5 3 1	58.94	0	15	15	28
6 0 0	59.87	100	0	100	105
4 4 2	59.87	720	0	720	740
6 2 0	63.52	55	0	55	55
5 3 3	66.19	0	6	6	10
6 2 2	67.06	25	0	25	25
4 4 4	70.52	415	0	415	415
7 1 1	73.06	0	5	5	3
5 5 1	73.06	0	5	5	3
6 4 0	73.90	340	0	340	340
6 4 2	77.23	130	0	130	130
5 5 3	79.69	0	5	5	5
7 3 1	79.69	0	9	9	5
8 0 0	83.77	200	0	200	220
7 3 3	86.20	0	4	4	5
8 2 0	87.01	410	0	410	420
6 4 4	87.01	260	0	260	270
8 2 2	90.24	170	0	170	170
6 6 0	90.24	20	0	20	18
7 5 1	92.66	0	7	7	3
5 5 5	92.66	0	1	1	5
6 6 2	93.47	0.1	0	0.1	2

the ideal (000) position of the ReO_3-type structure. Two types of fluoride ions must be distinguished: most of them, called F1, are slightly shifted from the standard (1/2 00) position ((12j) site); a small number of ions, called F2 and located at (1/2 *yz*) sites, are further displaced ((24l) site) (Table 1).

Figure 2 gives an overview of the possible anionic positions around a cation. All cation–anion distances are given in Table 4. Only the characteristic F–F distances have been reported; for the other F–F separations a set of calculated values is given.

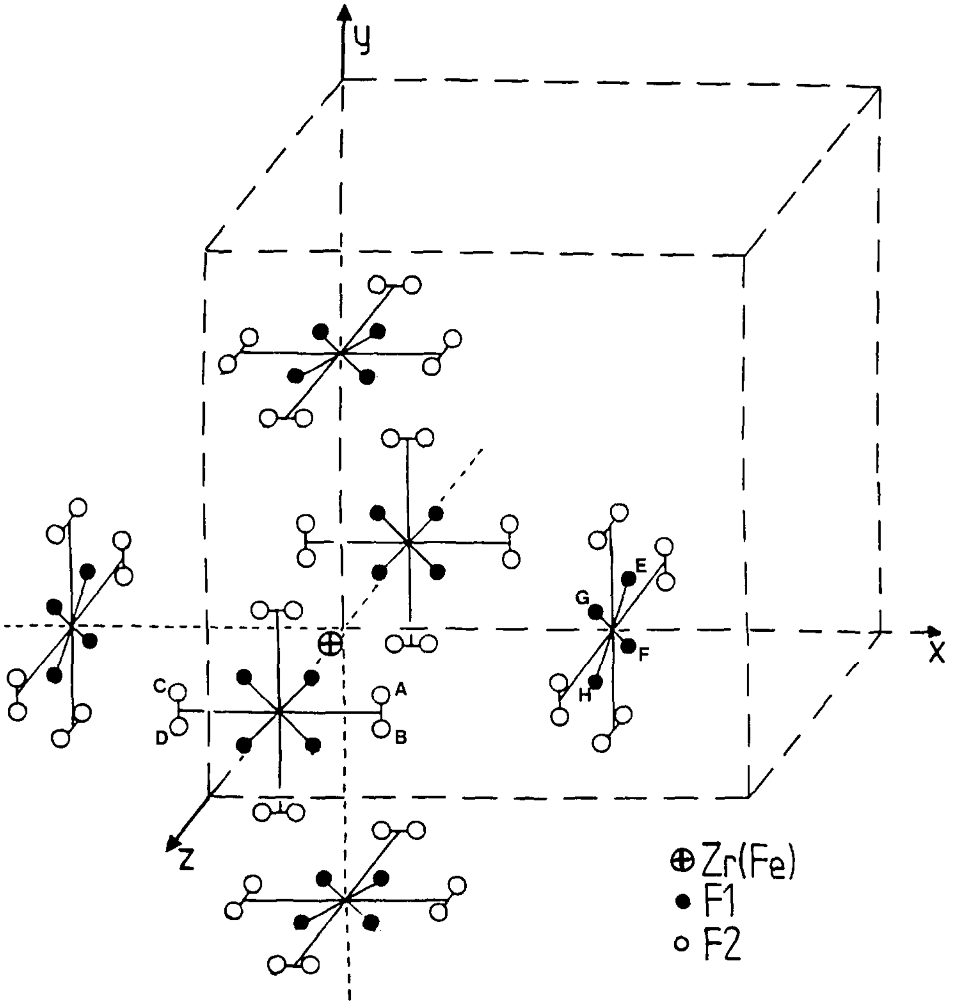

Fig. 2. General view of the possible anionic positions around the cations in $Fe_{0.80}Zr_{0.20}F_{3.20}$ (from ref. 13).

These results are quite similar to those previously obtained by other authors for the oxyfluoride $ZrF_{2.67}O_{0.67}$ [13]. An examination of the data leads to the following significant conclusions:

(1) While all Zr–F2 distances are consistent with the sum of the ionic radii, the same remark does not apply to the Zr—F1 distances: one of them, $d_{Zr-F1} = 1.84(1)$ Å, seems too short and must be excluded. Such a value can be expected to result from a cation shift in the z direction with respect to the ideal (000) position. As a consequence it seems reasonable to consider that every anionic polyhedron will involve at least one anion of F2 type.

(2) Whereas all F1–F1 or F1–F2 separations between the 12 anions surrounding the ideal (00 1/2) position are too short to be taken into account,

TABLE 4

Characteristic cation–fluorine and fluorine–fluorine distances in $Fe_{0.80}Zr_{0.20}F_{3.20}$ (standard deviations are given in parentheses)

Cation–fluorine distances (Å)			
Zr(Fe)–F1	1.84(1)	Zr(Fe)–F2	2.20(1)
	2.03(1)		2.23(1)
	1.93(1)		2.25(1)
	1.95(1)		2.30(1)
			2.32(1)
			2.35(1)
Fluorine–fluorine distances (Å) (letters in parentheses correspond to Fig. 2)			
2.47 < F1–F1 < 2.98			
2.38 < F2(A)–F1 < 3.73			
F2(A)–F1(E)	2.29(1)	F2(A)–F2(B)	1.12(1)
F2(A)–F1(F)	2.38(1)	F2(A)–F2(C)	2.16(1)
F2(A)–F1(G)	1.98(1)	F2(A)–F2(D)	2.44(1)
F2(A)–F1(H)	2.08(1)		

the longest F2–F2 distance, F2(A)–F2(D) = 2.44(1) Å, is on the other hand quite possible. Similar values had already been observed for cubic symmetry $YbZrF_7$ [12].

Therefore, in order to justify the existence of the anion-excess MF_{3+x} phase, it is reasonable to consider, as previously proposed for other zirconium compounds [7, 11–13], a substitution of some "normal" F1 anions by F2–F2 pairs, which increases the average coordination number of the cation from six to seven; the resulting ZrF_7 polyhedra thus become edge-sharing pentagonal bipyramids. Indeed, the cation (00*z*) displacement should occur in the direction of the common F2–F2 edge. Under this hypothesis, if we consider the total number of fluoride ions in $Fe_{0.80}Zr_{0.20}F_{3.20}$, the theoretical amounts of F1 and F2 anions would reach 2.80 and 0.40 respectively, since one F1 ion is now replaced by an interstitial pair. The calculated occupation rates (2.83 and 0.37 respectively) are in very good agreement with these values (Table 1).

Figure 2 allows us to explain clearly the arrangement of atoms in the cell. If we assume for instance that the F2(A) atom belongs to the common edge of the pentagonal bipyramid, the F2(B) position should obviously be vacant owing to the extremely short F2(A)–F2(B) bond length reported in Table 4. The F1 anions distributed around the ideal (1/2 00) site lead to two distances, F2(A)–F1(G) and F2(A)–F1(H), which are much too short. Consequently, only two positions, either E or F, could be possible for the F1 ion; nevertheless, they give rise to F2(A)–F1 distances (2.29 and 2.38 Å respectively) shorter than the F2(A)–F2(D) pair length which reaches 2.44(1) Å. Such a feature has previously been observed in $(NH_4)_3ZrF_7$ [17]. This result is probably related in $Fe_{0.80}Zr_{0.20}F_{3.20}$ to the significant displacement of the F2 fluorine from the (1/2 y0) position (Table 1). This description is consistent with the positions obtained from the neutron diffraction investigations.

The theoretical relative numbers of F1 and F2 anions can be estimated on the basis of the structural description for the $Fe_{0.80}Zr_{0.20}F_{3.20}$ formulation. They should correspond to the formation of two pentagonal bipyramids $[M(F1)_5(F2)_2]$ with respect to three octahedra $[M(F1)_5(F2)_1]$, which would yield an occupation rate of 2.50 for the F1 site and 0.70 for the F2 site. As pointed out, the experimental values obtained after refinement are 2.83 and 0.37 for F1 and F2 respectively (Table 1). The relatively high excess of F1 anions compared to the expected value probably arises from the presence of a larger number of octahedra owing to the large quantity of iron in the compound.

The structure can thus be described as a disordered three-dimensional framework of zirconium and iron polyhedra. The polyhedra surrounding Fe^{3+} would be octahedra comprising 5F1 + 1F2 atoms, the Zr^{4+} environments being either similar octahedra or pentagonal bipyramids (with 5F1 + 2F2 array).

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