

Non-Stoichiometry in Anion-excess ReO_3 Phases; the Structure of $\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3}(\text{MX}_{3.5})$ by Powder Neutron Diffraction

BRUCE C. TOFIELD*, MARCEL POULAIN† AND JACQUES LUCAS†

* *Materials Physics Division, AERE, Harwell, OX11 0RA, England*

† *Faculté des Sciences, Laboratoire de Chimie Minérale D, Université de Rennes, 35031 Rennes Cedex, France*

Received January 30, 1978; in revised form May 22, 1978

The structure of cubic $\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3}(\text{MX}_{3.5})$ (space group $\text{Pm}\bar{3}\text{m}$, $a_0 = 4.011 \text{ \AA}$), one of several known anion-excess phases based on ZrF_4 , with diffraction symmetry appropriate to the ReO_3 structure, has been determined by powder neutron diffraction. The anion-excess non-stoichiometry over that of the parent ReO_3 -type structure is found to be accommodated by interstitial anions as indicated previously by density measurements. Two anion sites are found, one, F1, slightly displaced (by $0.31 \text{ \AA}$) from an ideal lattice site, and the other, F2, more considerably so (by $1.11 \text{ \AA}$). The populations of the two sites (2.50 and 1.00 respectively) indicate that the principal structural feature explaining the nonstoichiometry is the existence of F2-F2 pairs across a vacant F1 site, with a maximum separation of $2.23 \text{ \AA}$, shorter than normally observed in ionic fluorides. Short fluorine-fluorine distances have previously been observed in CaF_2 heavily doped with YF_3 , and it seems that short fluorine-fluorine separations are allowed in anion-excess nonstoichiometric fluorides where no mechanism for their relaxation is available. Such non-stoichiometry may not be uncommon where the host structure does not have a close-packed anion lattice and contains an ion such as zirconium, yttrium or a rare earth ion which can accept a co-ordination by fluorine higher than that demanded by the basic structure type. The several possible near-neighbor anion-anion distances in $\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3}$ are tabulated, and the most likely arrangements of neighboring atoms assessed. The previously observed limit of non-stoichiometry in these phases (about $\text{MX}_{3.8}$) is rationalized on this basis. Implications of the results are mentioned both for chemical bonding, including possible features in common with crystallographic shear phases in oxides, and for the preparation of anion-excess perovskites or bronzes.

Introduction

Non-stoichiometric phases MX_{3+x} , with diffraction symmetry appropriate to the ReO_3 structure, are formed by solid solution of ZrF_4 with a range of other oxides and fluorides having lower anion-to-metal ratios. This behavior was demonstrated first of all in the $\text{ZrF}_4\text{-CaF}_2$ system (1), and has also been found for solid solution with transition metal oxides (2), rare earth oxides (3) and some rare earth fluorides (4).

A face-centered cubic supercell indicating ordering on metal sites is observed in some cases and often the range of non-stoichiometry does not extend down to the stoichiometric limit $\text{MX}_{3.0}$. For example, the solid solution range with Yb_2O_3 extends from 25% Yb ($\text{MX}_{3.37}$) to 8% Yb ($\text{MX}_{3.80}$); from $\text{MX}_{3.37}$ to $\text{MX}_{3.70}$ a simple cubic phase (space group $\text{Pm}\bar{3}\text{m}$) is obtained and from $\text{MX}_{3.70}$ to $\text{MX}_{3.80}$ a face-centred cubic phase (space group $\text{Fm}\bar{3}\text{m}$) (3). For YbZrF_7 ($\text{MX}_{3.5}$) either a metal-ordered or a metal-

disordered phase may be obtained depending on the conditions of quenching (on slow cooling an ordered monoclinic phase with perfect fluorine, as well as metal order is obtained) (4).

The range of the non-stoichiometric region is remarkably large in several of the systems described, but apart from these ZrF_4 -based phases¹ apparent anion-excess non-stoichiometry in compounds with the ReO_3 structure has not otherwise been observed. This is in contrast, for example, to fluorite based systems (5) where neutron diffraction results have revealed (6) a complicated situation based on a complete metal sublattice but with some normal fluorine sites vacant, and more interstitial fluorines than indicated by the empirical formula. Some unusually short fluorine-fluorine distances of about 2 Å were a novel feature revealed in this work (6). On the other hand, apparent anion-excess non-stoichiometry in the perovskite LaMnO_{3+x} , a structure type closely related to ReO_3 , has been shown by neutron diffraction to be compensated by metal vacancies on both types of metal site (7). It is thus of interest to understand the mechanism of the compensation of the non-stoichiometry in the ZrF_4 -based phases, and to compare this behavior with that of the other structure types.

Density measurements (1-4) indicated the non-stoichiometry in the ZrF_4 systems to be compensated by excess anions rather than by metal vacancies, but detailed knowledge of the disposition of the interstitial fluorines implied by the data has not been obtained hitherto. An X-ray diffraction study of a single crystal of metal-ordered YbZrF_7 definitely showed (8) the excess fluorine not to be at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site of the simple ReO_3 cube (Fig. 1) occupied by the large cations in the perovskite structure, in accord with the electrostatic potential at this position, but

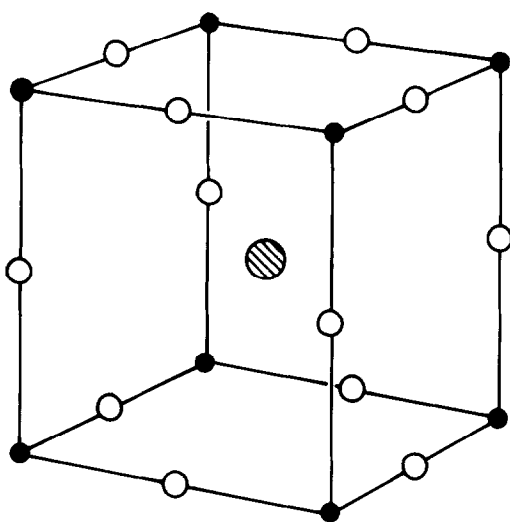


FIG. 1. One unit cell of the ReO_3 lattice. The cation (●) is at $(0, 0, 0)$ and the anions (○) at $(\frac{1}{2}, 0, 0)$ etc. In a perovskite, ABO_3 , the large A cation (⊗) is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the AO_3 layers are stacked in a cubic close-packed array along $[1, 1, 1]$.

rather that it was delocalised over several general positions in the cell. A full description of the fluorine positions was not, however, achieved. As the unit cell of the metal-ordered crystals is eight times the volume of the primitive ReO_3 cube, it is not surprising that the fluorine disposition is difficult to determine, especially as short range ordering and other effects causing local variations from unit cell to unit cell are likely to be significant. The large unit cell volume and the statistical nature of the fluorine disposition will also make it less straightforward to arrive at models compatible with the data to understand the likely atomic dispositions on the unit-cell level.

Single crystals of metal-disordered YbZrF_7 , or other $\text{Pm}3\text{m}$ -space group phases, suitable for X-ray diffraction, have not been readily obtained in the preparative work. In the present study, therefore, we have used neutron diffraction to investigate a polycrystalline primitive cubic phase and have chosen to examine initially the mixture $0.8 \text{ ZrF}_4 : 0.1 \text{ Yb}_2\text{O}_3$ ($\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3} \equiv$

¹ A few similar non-stoichiometric phases based on fluorides such as UF_4 or NbF_5 , which have many similarities to ZrF_4 , are also known.

$\text{MX}_{3.5}$) which is easily prepared in the desired form.

Neutron powder diffraction has been used with some success in solving structural problems in inorganic chemistry as in the fluorites and perovskites already mentioned (6, 7). In addition to general technical advantages such as the absence of surface texture problems and the Gaussian peak shapes obtained, neutron diffraction is advantageous in cases such as this in that the scattering powers of the light anions oxygen and fluorine are much closer to those of the metal atoms than is the case with X-rays.

We find the non-stoichiometry to be compensated by excess fluorine as indicated by the other measurements. The normal fluorine lattice is not undisturbed, however, and the results imply that anion pairs straddle empty ($\frac{1}{2}$ 0 0) sites. There are, therefore, some similarities to the anion-excess fluorites (6).

Experimental

Sample Preparation

The system $\text{Zr}_{1-x}\text{Yb}_x\text{X}_{4-2.5x}$ with $\text{X} = \text{O}$ or F is cubic over the range $0.08 < x < 0.25$ ($\text{MX}_{3.37}$ to $\text{MX}_{3.80}$) (3). Phases in this system may be prepared by direct reaction of ZrF_4 and Yb_2O_3 .

To obtain the $\text{MX}_{3.5}$ composition, ZrF_4 and Yb_2O_3 were carefully mixed in the molar ratio 0.8 to 0.1, sealed in a nickel tube under argon and heated at 850°C for 15 hr. ZrF_4 was prepared by fluorination of ZrO_2 in molten NH_4HF_2 and purified by successive sublimations under vacuum. Yb_2O_3 (Rhône-Poulenc) was of 99.9% purity.

After reaction, the nickel tube was quenched in water. No attack of the tube by the fluoride was observed. The white product was not hygroscopic. The value of the cubic lattice parameter ($4.011 \text{ \AA}$) provides a good check on the composition as the variation-with x is quite rapid (3).

Neutron Diffraction

Neutron diffraction data were collected first of all at Harwell at 4.2°K , on the CUR-RAN diffractometer using a wavelength of $1.368 \text{ \AA}$ from the (311) plane of a germanium monochromator with a take-off angle of 47.5° , and on the guide tube diffractometer (9) at room temperature to investigate the possibility of superlattice ordering with d -spacings up to about $100 \text{ \AA}$. The latter instrument has a pyrolytic graphite monochromator placed after the sample giving a wavelength of $4.7 \text{ \AA}$. A subsequent experiment was performed on the D1A diffractometer (10) at the Institut Laue-Langevin, Grenoble. A wavelength of $1.5118(1) \text{ \AA}$ was used² and the experiment was carried out at room temperature. The data were recorded on eight counters at $6^\circ 2\theta$ separation and the scan range was between 18° and $155^\circ 2\theta$ for the highest angle counter. The data from all eight counters were summed to produce the final diffraction pattern using the ILL 'POWDER' program written by A. Hewat. The input data to 'POWDER' for the counter separations and counter efficiencies were determined by Gaussian peak fitting to determine positions and areas for the 200, 220 and 410 reflections for all eight counters. The data were collected in 24 hr.

Both CURRAN and D1A data were refined using the Harwell 'TAILS' refinement program (11) with manually integrated intensities as the input data. 'TAILS' minimizes the agreement factor

$$AF = \frac{\sum_j \omega_j (I_{\text{obs}}^j - I_{\text{calc}}^j)}{(n - m)} \quad (1)$$

² The wavelength was determined assuming the X-ray determined lattice constant of $\text{Yb}_{0.2}\text{Zr}_{0.8}\text{F}_{3.2}\text{O}_{0.3}$, $4.011 \text{ \AA}$, to be correct. A least squares programme was used to estimate the wavelength and 2θ zero error using as input the positions of the eight strongest reflections above $40^\circ 2\theta$ determined by fitting to Gaussian peak shapes.

where ω_j is the weight ($1/\sigma_j^2$) of an observed peak intensity I_{obs}^j , determined from counting statistics, I_{calc}^j is the calculated peak intensity, n is the number of peaks used in the refinement and m the number of parameters varied. In both cases background counts were estimated manually, and the program also determined conventional and weighted reliability factors based on intensities. Scattering lengths of 0.714 (Zr), 1.28 (Yb), 0.580 (O) and 0.565 (F), all $\times 10^{-12}$ cm were used. In investigations of cubic systems of this type, where the number of data points is at a premium, and peak resolution is not the principal problem to be overcome, the use of profile refinement methods (12) is not necessary or desirable.

Results

The difference in neutron scattering lengths between Zr and Yb should have revealed whether any significant degree of metal ordering, leading to a real Fm3m unit cell, was in fact occurring, although not indicated in X-ray patterns. No superlattice reflections were seen in any of the neutron diffraction experiments and therefore the primitive Pm3m space group with a random Yb-Zr distribution was assumed to be the correct choice. In the low temperature run on CURRAN superlattice spacings of less than 20 Å arising from possible anion³ ordering effects below room temperature could also be discounted.

The inferior resolution at higher scattering angles of the CURRAN diffractometer, resulting from the rather low take-off angle, restricted the resolution of peaks to $2\theta < 90^\circ$. As a consequence, only fifteen reflections were available as input data and no more than five or six parameters could be varied at

any one time. A qualitatively satisfactory description of the unit cell could be obtained, but the higher quality D1A data were essential for the determination of accurate atom positions and occupation numbers.

The diffraction pattern obtained after summation is shown in Fig. 2. Peaks up to the (510, 431) were observed giving 23 intensities. All of these, including areas of background on either side to determine the background counts were completely resolved. Some diffuse scattering, presumably arising from short range order effects, is seen, particularly around the (110) to (200) reflections and was also apparent in the CURRAN data. Because of the manner of data reduction this did not cause any significant error in the peak intensities.

Initial refinement with the ideal fluorine lattice complete and the extra 0.5 fluorine atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 1) was unsatisfactory, in agreement with the result from YbZrF₇ (8), and allowing either the temperature factor or the occupation of the interstitial to vary removed it more or less entirely. The occupation numbers of two fluorine species were allowed to vary, with the sum being constrained to 3.5, and various displacements tested. The only satisfactory solution was one where the ideal fluorine lattice (F1) was slightly displaced to $(xx\frac{1}{2})$ and the interstitial fluorine (F2) was considerably further from an ideal position at $(xy\frac{1}{2})$. Displacements away from $x = 0.5$ were tested and rejected for both F1 and F2. The occupation numbers showed that the presence of an interstitial ion was associated with a vacancy on a normal site and that the majority of interstitial ions must occur as pairs. With the total fluorine occupation fixed at 3.50, and zirconium constrained at (000), the agreement factor was 1.61, R_I was 2.90% and wR_I was 1.91%.

Zirconium displacements along (xxx) , $(xx0)$ and $(x00)$ were then tested but only the $(x00)$ displacement revealed an improvement in the refinement. The final parameters with both F1 and F2 occupations varied, are

³ Because of the very similar scattering lengths of oxygen and fluorine, they cannot be directly distinguished by neutron diffraction. An average scattering length was used in the refinement and the average anion is henceforth referred to as fluorine.

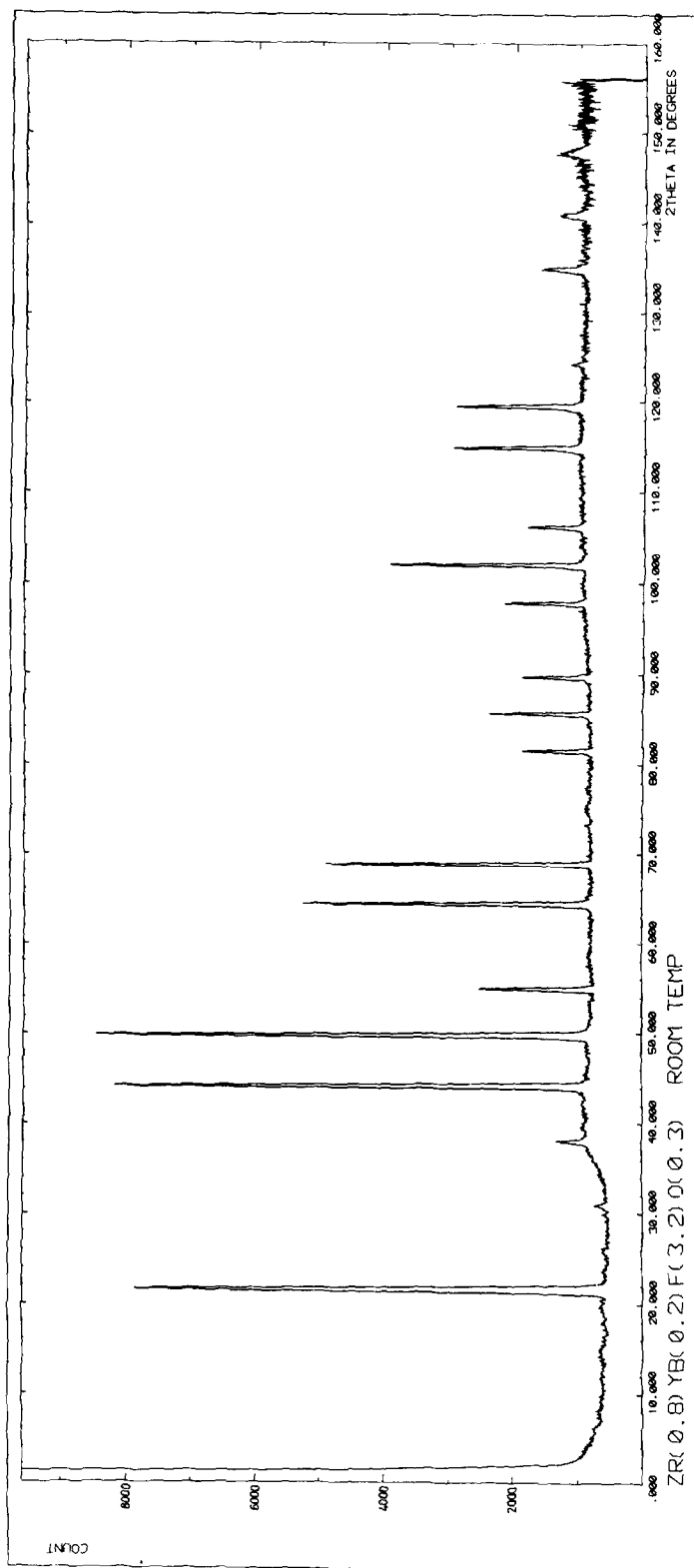


FIG. 2. The diffraction pattern of $Zr_{0.8}Yb_{0.2}F_{3.2}O_{0.3}$ obtained on the D1A diffractometer. The counts from all eight counters have been summed after interpolation and normalization to correct for the experimentally determined separations and counter efficiencies. 23 separate intensities are completely resolved.

given in Table I with observed and calculated intensities in Table II. The data were not sufficiently numerous to allow anisotropic temperature factors to be assigned. The agreement factor was 1.30, R_I was 1.64% and wR_I was 1.61%.

From Table I we see that the correlation between the displacement and the temperature factor of the zirconium atom is almost total, and the B -factor of $-0.02(0.45) \text{ \AA}^2$ is lower than expected at room temperature, even for a regular structure with no non-stoichiometry. Accordingly, a number of refinements were performed with fixed temperature factors. For $B = 0.3 \text{ \AA}^2$, $0.6 \text{ \AA}^2$ and $1.1 \text{ \AA}^2$ the agreement factor increased to 1.35, 1.40 and 1.50 respectively, while the R -factor increased to 1.96%, 2.18% and 2.58%. The displacement decreased only slightly to 0.064(1), 0.060(1) and 0.051(1) respectively. In spite of the correlation, therefore, it is clear that the displacement is real. Moreover, the metal atom seems to

have a well defined position with a normal (i.e. low) temperature factor. As a compromise between a reasonable value of B and the best agreement, the displacement of 0.060 found for $B = 0.3 \text{ \AA}^2$ was selected in the determination of interatomic distances, and an error of 0.010 assigned.

The occupation number of the fluorines totals 3.49(8). The ideal occupation numbers for the stoichiometry 3.50 would be 2.50 and 1.00 for F1 and F2 respectively so that each vacancy was occupied by one interstitial pair. The experimental values of 2.57(5) and 0.92(6) are equal to these within just over one standard deviation and good agreement was still obtained when the occupations were fixed at 2.50 and 1.00. The agreement factor was 1.38, R_I was 1.80% and wR_I was 1.87%, and the only parameter to change a little from the values of Table I was the temperature factor of F2 ($2.37(22) \text{ \AA}^2$) which reflected the slight population increase and the significant correlation (0.89) between

TABLE I
Zr_{0.8}Yb_{0.2}F_{3.2}O_{0.3}, D1A DATA: POSITIONAL AND THERMAL PARAMETERS AND OCCUPATIONS

Atom	Position	x	y	z	B	Occupation
Zr _{0.8} Yb _{0.2}	1a	0.068(6)	0.0	0.0	-0.02(45)	1.0
F1	12j	0.5	0.054(1)	0.054(1)	1.64(15)	2.57(5)
F2	24l	0.5	0.273(3)	0.053(3)	1.82(47)	0.92(6)

Total fluorine
occupation = 3.49(8)

$$AF = 1.30 \quad R_I = 0.0164 \quad wR_I = 0.0161$$

Atomic positions are in fractions of the unit cell edge ($a = 4.011 \text{ \AA}$) and the isotropic temperature factors are in units of $\text{\AA}^2$.

Correlations greater than 0.5

Zr(x)–Zr(B)	0.99
F2(B)–F2(occ)	0.89
F1(z)–F2(B)	0.70
F1(B)–F1(occ)	0.65
F1(z)–F1(B)	0.65
F1(z)–F2(occ)	0.58
Zr(B)–F2(B)	0.54
F2(y)–F2(B)	0.52

TABLE II
D1A; OBSERVED AND CALCULATED INTENSITIES

<i>hkl</i>	2θ (degrees)	I_{obs}	σ_{Iobs}	I_{calc}	$(I_{\text{obs}} - I_{\text{calc}})/\sigma$
100	21.73	75432	330	75479	-0.1
110	30.91	1266	178	1457	-1.1
111	38.10	2976	350	3613	-1.8
200	44.28	55546	311	55741	-0.6
210	49.85	55260	307	54857	1.3
211	54.98	12720	216	12880	-0.7
220	64.62	29223	258	29014	0.8
300, 221	68.85	26115	245	26477	-1.5
310	73.16	371	185	551	-1.0
311	77.37	572	187	426	0.8
222	81.51	6532	201	6429	0.5
320	85.61	9318	210	9255	0.3
321	89.68	6432	206	6157	1.3
400	97.84	7636	215	7287	1.6
410, 322	101.98	18911	242	19192	-1.2
330, 411	106.17	5468	214	5406	0.3
331	110.46	0	201	13	-0.1
420	114.87	13068	315	13295	0.7
421	119.45	14354	519	13421	1.8
332	124.24	1022	319	1071	-0.2
422	134.81	6635	652	6730	-0.2
500, 430	140.87	4543	1057	5014	-0.5
510, 431	147.86	5084	1308	5525	-0.4

these two parameters (Table I). We have assumed in the discussion, therefore, that the ideal occupation numbers of 2.50 and 1.00 provide good agreement with the data.

It is pertinent to note that estimates of bond lengths derived from the CURRAN data, for example between F2 pairs, were fairly seriously in error. The F2-F2 separation was found to be 2.06 Å rather than 2.23 Å and such changes are significant in any discussion of the physical basis for the observed behavior. It does not seem likely that the differences between the two data sets resulted from structural differences between 4.2°K and room temperature and this comparison therefore provides a confirmation of the quantitative errors that can occur when the ratio of observations to parameters varied is low. Although a larger data set than obtained using D1A would clearly be preferable, we believe that the positional

parameters of Table I would be unlikely to show any significant changes.

Discussion

The Local Organisation of the Structure

The large multiplicities of the fluorine positions complicate the description of any individual unit cell and the large number of possible fluorine-fluorine distances entails that we can have no exact knowledge of the particular values within any one unit cell. After derivation of all the possible separations, however, we can assess their probability in the light of those found in more ordered fluorides. Distances of 2.4 Å, or greater, are well established (for example in ZrF₄ (13) or SmZrF₇ (14)), distances between 2.0 Å and 2.4 Å are unusual, apart from the situations found for the interstitial-

interstitial separation in this compound, and in non-stoichiometric fluorites (6). Distances shorter than 2.0 Å are altogether unlikely.

The distances F1–F1, F1–F2 and F2–F2 for fluorines located around an ideal ($\frac{1}{2}$ 0 0) position are all significantly less than 2 Å except for the two longest F2–F2 distances 2.190(17) Å and 2.231(17) Å (Fig. 3). Therefore the only reasonable manner in which the non-stoichiometry can be accommodated is if the F2 atoms occur almost entirely as pairs (as indicated by the occupation numbers) with a separation of around 2.2 Å. We notice that the diffuse scattering is peaked at about 40° 2θ (Fig. 2), corresponding to a *d*-spacing of 2.21 Å. This is in close agreement with the F2–F2 separations and the diffuse scattering may well reflect the fact that this interstitial separation is not absolutely defined by the structure and a range of values occurs with the average at about 2.2 Å. The movement of negative ions towards the face center is much less unfavorable than towards the cube center, a

metal site in perovskites. Both the present work and the X-ray study of YbZrF₇ (8) agree in that no significant concentration of anions is found in positions appreciably displaced from the unit cell edges and particularly not near the cell center.

The nearest F1–F1 separation for atoms located near neighboring ideal positions is 2.530(4) Å (Fig. 4, Table III) and thus there is no problem as regards the relative disposition of these atoms.

For an F2 atom at (0.5, 0.273, 0.053), the closest distances of neighboring F1 atoms (at ($0\frac{1}{2}$ 0) and ($1\frac{1}{2}$ 0)) are 2.007(6) Å and 2.053(6) Å (Fig. 4, Table III) which are short and closer than the F2–F2 interstitial pair separation. It seems most likely that F1 atoms closest to neighboring F2 pairs will be arranged to give the longer separations of 2.401(5) Å or 2.439(6) Å (Fig. 4, Table III), which are within the range found in normal fluorides. The closest F2–F1 separation for F1 near ($0\ 0\frac{1}{2}$) and ($1\ 0\frac{1}{2}$) is 2.681(9) Å and presents no problem.

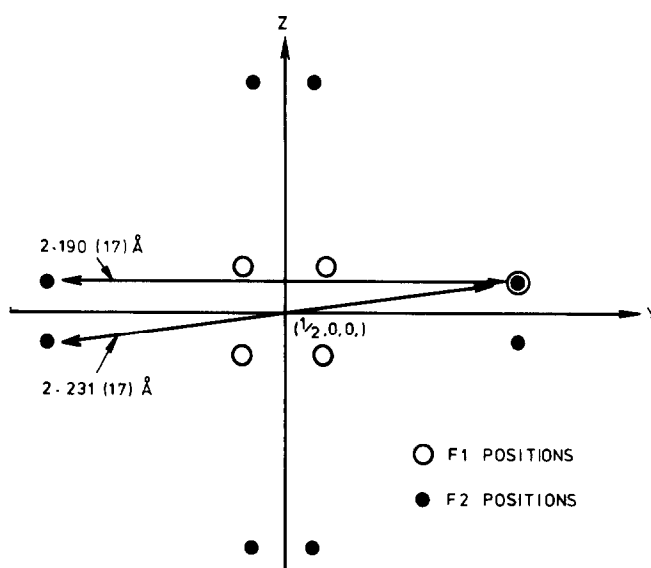


FIG. 3. Schematic diagram showing the four symmetry related F1 positions (○) and the eight symmetry related F2 positions (●) around the ideal fluorine site ($\frac{1}{2}$, 0, 0). The only likely fluorine–fluorine distances are the two longest possible F2–F2 separations of 2.190(17) Å and 2.231(17) Å shown relative to an F2 atom situated at (0.5, 0.273, 0.053).

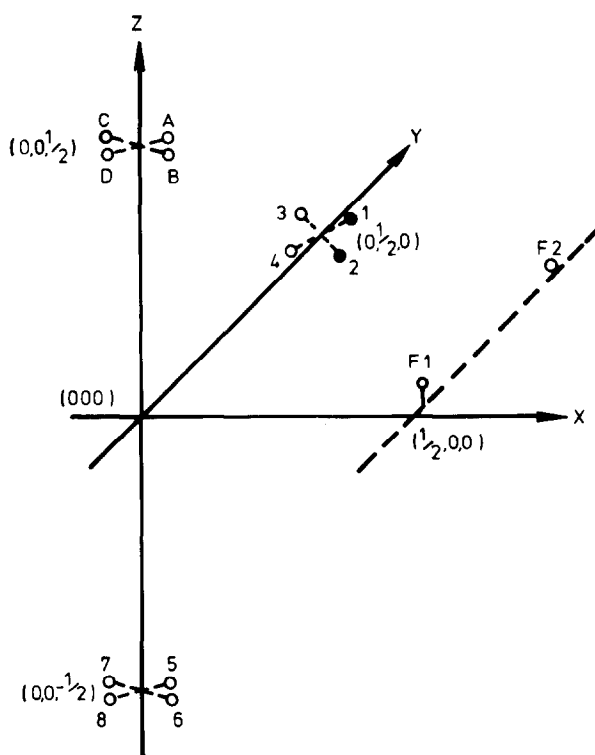


FIG. 4. Schematic diagram showing the disposition of F1 atoms near neighboring ideal sites relative to an F1 site at $(0.5, 0.054, 0.054)$ and an F2 site at $(0.5, 0.273, 0.053)$. F1 positions involving very short F2-F1 separations are emphasized by shading. The separations are listed in Table III.

It is interesting to investigate the interactions between neighboring F2 pairs. For an F2 atom at $(0.5, 0.273, 0.053)$ the closest separations to F2 atoms around $(0 \frac{1}{2} 0)$ and $(1 \frac{1}{2} 0)$ $1.288(12) \text{ \AA}$ and $1.356(12) \text{ \AA}$ are unacceptable (Fig. 5, Table IV) as are those to $(\frac{1}{2} 1 0)$ $1.821(17) \text{ \AA}$ and $1.870(17) \text{ \AA}$. The next nearest separations all provide at least one acceptable distance, however. To $(0 \frac{1}{2} 0)$ and $(1 \frac{1}{2} 0)$ we have $2.196(12) \text{ \AA}$, still probably too short, and $2.399(13) \text{ \AA}$, and to $(\frac{1}{2} 1 0)$ $2.844(17) \text{ \AA}$ and $3.003(17) \text{ \AA}$. This means that a neighboring F2-F2 pair can be accommodated even at the most hindered neighboring sites ($(0 \frac{1}{2} 0)$ and $(1 \frac{1}{2} 0)$), although there is probably no choice in the orientation. The distance to the further atom of the second pair in this case would be $2.555(12) \text{ \AA}$. The choice of orientation

becomes greater as we go to the $(\frac{1}{2} 1 0)$ position and then the $(0 0 \frac{1}{2})$ and $(1 0 \frac{1}{2})$ positions. For the latter cases, the nearest distances are by symmetry the same as the next-nearest distances to $(0 \frac{1}{2} 0)$ and $(1 \frac{1}{2} 0)$, $2.196(12) \text{ \AA}$ and $2.399(13) \text{ \AA}$, so that there is only one unlikely orientation.

The metal $(x 0 0)$ displacement is almost certainly in the direction of an interstitial pair, giving a Zr-F2 distance of $2.088(34) \text{ \AA}$. The first coordination shell of the metal is most likely completed by F1 atoms (Fig. 6). The distance to F1 at $(-\frac{1}{2} 0 0)$ is $2.267(39) \text{ \AA}$, and from the considerations outlined above the F1 atoms at $(0 0 \frac{1}{2})$ and $(0 0 -\frac{1}{2})$ are expected to be displaced in the negative x direction giving a metal-fluorine distance of $2.068(8) \text{ \AA}$. The only choice in M-F distance is to F1 atoms at $(0 \frac{1}{2} 0)$ and $(0 -\frac{1}{2} 0)$. For a $-x$

TABLE III

F1 —	①, ④	2.530(4)
	②, ⑧	2.567(4)
	③, ⑥, ⑤	2.853(4)
	④, ⑦, ⑥	2.885(4)
	⑦	3.143(4)
	⑧	3.172(4)
F2 —	①	2.007(6)
	②	2.053(6)
	③	2.401(5)
	④	2.439(6)
F2 —	④	2.681(9)
	⑧	2.852(9)
	⑥	2.987(8)
	⑦	3.142(9)
F2 —	⑤	2.982(9)

Separations in Å between F1 and F2 positions at (0.5, 0.054, 0.054) and (0.5, 0.273, 0.053), respectively, and F1 positions near neighboring ideal sites (see Fig. 4). The closest separations between F2 and F1 atoms (not shown) near $(\frac{1}{2}, 1, 0)$ are 2.699(12) Å and 2.733(12) Å. All other distances not included are greater than 3 Å.

displacement the M-F distance is again 2.069(8) Å; for a +x displacement, 2.017(7) Å. The average M-F distance, for a seven-coordinate metal atom is thus, in all likelihood, between 2.088 Å and 2.102 Å.

In monoclinic SmZrF₇ (4) the six Zr-F separations range from 1.996 Å to 2.018 Å with an average separation of 2.007 Å. In ZrF₄ (13) containing 8-coordinate Zr, the average Zr-F separation is 2.10 Å. In Rb₅Zr₄F₂₁ (14), the average Zr-F separations for six-, seven- and eight-fold coordinate Zr are, respectively, 1.99 Å, 2.06 Å and 2.08 Å or 2.11 Å. These variations with coordination number are in reasonable agreement with the increases in effective ionic radii (15) of 0.06 Å from six- to seven-fold and from seven- to eight-fold coordinate zirconium. The effective ionic radii of Yb³⁺ (15) are between 0.14 Å and 0.15 Å larger than for Zr⁴⁺ for six-, seven- and eight-fold coordination so that, by comparison, with the Zr-F distances mentioned, we might expect

TABLE IV

F2 —	$(0, \frac{1}{2}, 0)$ and $(1, \frac{1}{2}, 0)$	①	1.288(12)
		②	1.356(12)
		③	2.196(12)
		④	2.399(13)
		⑤	2.555(12)
		⑥	2.731(13)
		⑦	3.231(12)
		⑧	3.259(12)
F2 —	$(0, 0, \frac{1}{2})$ and $(1, 0, \frac{1}{2})$	①	2.196(12)
		②	2.399(13)
		③	2.536(12)
		④	2.852(12)
		⑤	3.350(14)
		⑥	3.596(14)
		⑦	3.689(12)
		⑧	3.813(12)
F2 —	$(0, -\frac{1}{2}, 0)$ and $(1, -\frac{1}{2}, 0)$	①	3.231(12)
		②	3.259(12)
		③	3.689(12)
		④	3.813(12)
		⑤	3.913(12)
		⑥	4.030(12)
F2 —	$(0, 0, -\frac{1}{2})$ and $(1, 0, -\frac{1}{2})$	①	2.555(12)
		②	2.731(13)
		③	2.852(12)
		④	3.137(12)
		⑤	3.596(14)
		⑥	3.826(13)
		⑦	3.913(12)
		⑧	4.030(12)
F2 —	$(\frac{1}{2}, 1, 0)$	①	1.821(17)
		②	1.870(17)
		③	2.844(17)
		④	3.003(17)
		⑤	3.251(17)
		⑥	3.391(17)

Separations in Å between an F2 position at (0.5, 0.273, 0.053) and neighboring F2 positions (see Fig. 5). Some of the separations are identical by symmetry. The separation between F2 and the position (0.5, 0.053, 0.727) (Fig. 5) is 2.844(17) Å. All distances not included are greater than 3 Å.

M-F separations of 2.03 Å, 2.10 Å and 2.14 Å for six-, seven- and eight-fold coordinations, respectively, for the composition Zr_{0.8}Yb_{0.2}. 2.10 Å for seven fold coordina-

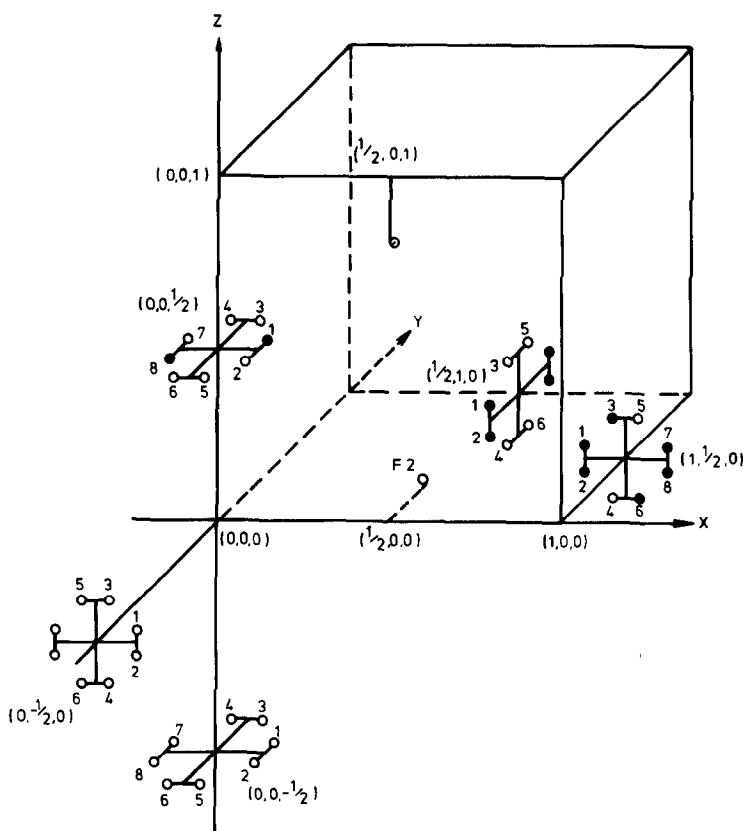


FIG. 5. Schematic diagram showing the disposition of an F2 atom at $(0.5, 0.273, 0.053)$ and F2 positions near neighboring ideal sites (F2 positions around $(\frac{1}{2}, 1, 0)$ are also shown). The separations are listed in Table IV. The closest distance to an F2 position based on a more distant ideal site is to the $(0.5, 0.053, 0.727)$ position which is also shown. Orientations of neighboring F2 pairs involving very short F2-F2 inter-pair separations are emphasized by shading.

tion is in good agreement with the range of experimental values just derived.

Figure 7 shows an ORTEP (16) view of a possible arrangement of eight MF_7 polyhedra which is consistent with the structure determination. One can describe these MF_7 polyhedra as pentagonal bipyramids derived from octahedra by replacing one corner (F1) by one edge (F2-F2 pair). The anionic positions shown in Fig. 7 have been chosen, as discussed above, to avoid short F-F separations, apart from those in the F2-F2 pairs. This local arrangement is, however, only one of numerous possibilities compatible with the average atom positions determined from

the diffraction data and it is also possible to have two F2 pairs adjacent to the same metal atom giving eight-fold coordination, or to preserve octahedral six-fold coordination. In the present compound of overall stoichiometry $\text{MX}_{3.5}$ the average metal is seven-coordinate and the large majority of cations are indeed probably thus disposed.

Stoichiometry and General Structural Implications

The existence of fluorine-excess non-stoichiometry may be a more common phenomenon than hitherto realized. Structural confirmation of the existence of inter-

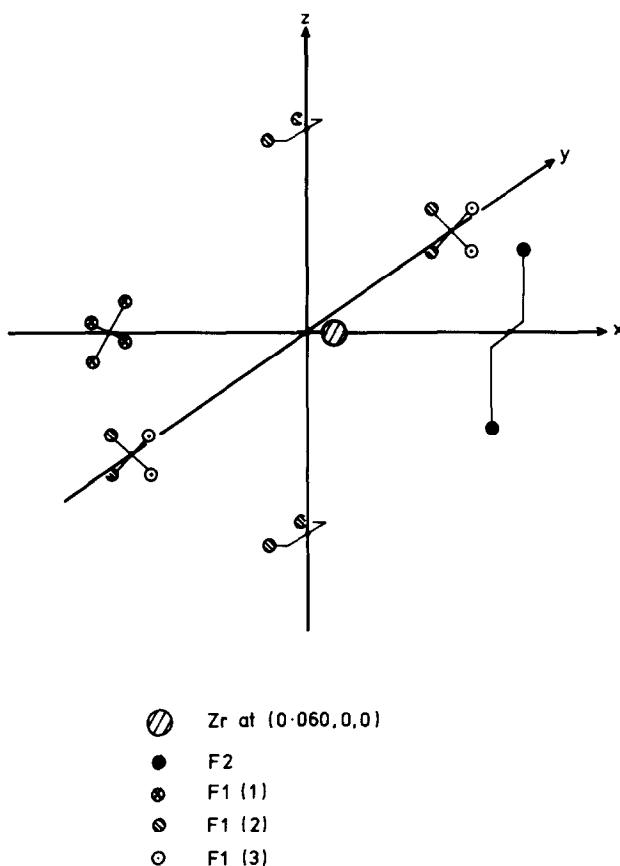


FIG. 6. Schematic diagram showing the coordination of the metal atom displaced along $(x00)$ and coordinated by two F2 atoms straddling $(\frac{1}{2}, 0, 0)$ and five F1 atoms. The alternative positions of these atoms and the associated metal-fluorine distances are indicated. The only uncertainty in M-F distance is for F1 atoms around $(0\frac{1}{2}, 0)$ and $(0 -\frac{1}{2}, 0)$. The differently shaded F1 atoms F1(1), F1(2) and F1(3) correspond to the three different separations from the metal atom of 2.267 Å, 2.068 Å and 2.017 Å respectively.

stitial fluorine with the probable presence of very short fluorine-fluorine separations between 2.0 Å and 2.1 Å has been given for fluorites (6) and now rather short F-F separations between interstitial atoms have been demonstrated for the ReO_3 structure type. Solution of considerable quantities of ZrF_4 in monoclinic SmZrF_7 has also been observed (17). The prime requirement for such non-stoichiometry would therefore seem to be the absence of a close-packed anion lattice in the host structure and the presence of an ion such as Zr, yttrium or one

of the rare earths which can easily accommodate an increase in coordination by fluorine over that found in the host structure.

The energetics which favor this type of non-stoichiometry are not, however, well understood. Shorter than normal fluorine-fluorine separations would appear to be an allowed feature, at least where the host structure does not allow relaxation to the normal range of 2.4 Å or more. Although some theoretical attention has recently been given to this aspect (18), one would have expected in the light of the supposed strongly

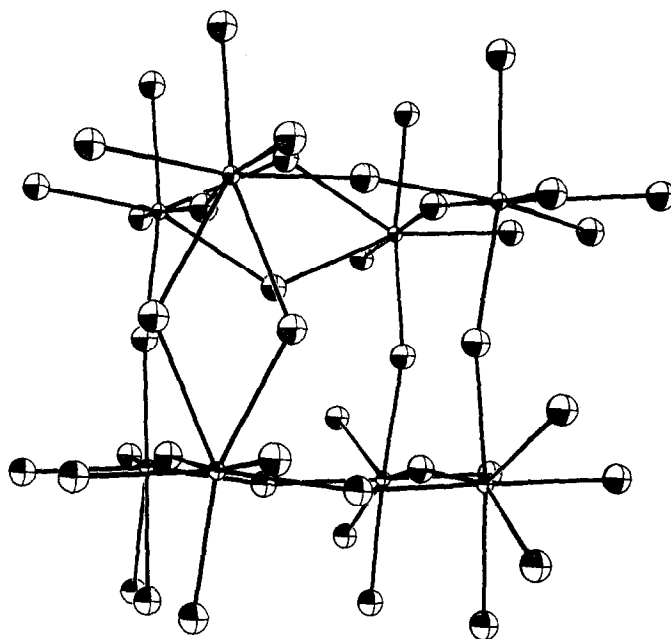


FIG. 7. ORTEP view of a possible arrangement of MX_7 polyhedra in agreement with the refinement results. In comparison with the ReO_3 structure drawn in Fig. 1, there is a small displacement of normal anions from the middle of the cell edges and a replacement of some normal F1 anions by F2-F2 pairs. Thus the fluorine at $(0, 0, \frac{1}{2})$ in Fig. 1 is replaced in this Figure by two fluorines at $(0.273, -0.053, \frac{1}{2})$ and $(-0.273, 0.053, \frac{1}{2})$.

ionic nature of the metal fluorides and the crystal radius (15), (19), of the fluoride ion, 1.19 Å, that the necessity of forming short fluorine-fluorine distances would be a strong disincentive to the formation of such non-stoichiometric phases. Measurements such as NMR or photoelectron spectroscopy which might permit the energy levels of the interstitial fluorine ions to be distinguished from those of the host lattice would be a valuable complement to structural characterization.

For the ReO_3 -based structures discussed in this work one can qualitatively invoke some degree of non-ionic bonding effects in making the formation of short F2-F2 distances less unfavorable. Although the magnitude of the covalent bonding energy in compounds such as ReO_3 and ZrF_4 is still a

matter for speculation,⁴ the ReO_3 lattice is not close-packed and may need to be stabilized by a certain degree of covalent interaction. The AO_3 layers of perovskite (Fig. 1) are cubic close-packed but in the ReO_3 structure the large A cations are not present, only one-quarter of the octahedral sites contain metal atoms, and the anions are thus only two-coordinate by the metal atoms. This is not a common circumstance for the fluoride ion in ionic crystals. The empty cation site may be eliminated by

⁴ We have suggested elsewhere (20, 21) that MoF_3 , which becomes antiferromagnetic below room temperature could usefully be studied by magnetic neutron diffraction to provide an estimate for the covalency in a second row transition metal ion. The magnitude of the covalency in ZrF_4 would of course be greater than the value found for MoF_3 .

transformation to hexagonal packing with one-third of the octahedral sites occupied, and most metal trifluorides with six-coordinate metal ions are intermediate between the two situations. There is no apparent correlation of the degree of transformation with cation radius but it is perhaps significant that RhF_3 and IrF_3 come closest to the hexagonal-packed structure (22). The metal-fluorine-metal bond angle is minimized in the hcp phase and we may relate this to a significant degree of σ -covalent bonding associated with these d^6 low-spin metal ions. Where there is strong ligand-to-metal σ -bonding a linear metal-anion-metal situation does not seem to be favorable relative to a bent situation where two different p_σ orbitals on the anion may become involved in the bonding.

For ions at the beginning of the transition series, on the other hand, a number of experiments such as NQR, ESR and neutron diffraction indicate (23) that ligand-to-metal π -bonding may be comparable to σ -bonding and different structural manifestations are expected; for example, the incidence of edge- and face-sharing of octahedra in the crystallographic shear phases of the early transition metal oxides. We anticipate that compounds such as ZrF_4 and the non-stoichiometric phases discussed in this work will be characterized by π as well as σ donation from fluorine to zirconium which will lower the ionic charge on the fluorines and thus their coulombic repulsion. In addition, in these compounds at least, the formation of fluorine pairs, which involves a change from corner to edge-sharing of polyhedra, may be assisted by the π -bonding and thus have, at least in part, a similar origin to the crystallographic shear observed in oxides, although there is no severe driving force for long range order because the defect is an interstitial atom rather than a vacancy. The actual fluorine-fluorine separation for the pairs shared by two metal atoms will then be a compromise between the repulsion between the fluorines,

the non-ionic bonding forces which permit the formation of pairs, and the repulsion between the fluorines of the pairs and neighboring fluorine atoms which will presumably maintain these separations in the "normal" range, i.e. $\geq 2.4 \text{ \AA}$. Only in suitable cases where there is also long range metal order can the non-stoichiometry be relieved by increasing the coordination of one metal atom preferentially. This is observed in the monoclinic MZrF_7 phases (4) where M is yttrium or a rare earth, where the zirconium atoms are six-coordinate and the rare earth atoms eight-coordinate.

Such aspects of chemical bonding as are significant in the crystalline non-stoichiometric phases and the probably related ability of Zr^{4+} to adopt six- or seven- or eight-fold coordination with variations in bond lengths and angles, are no doubt also important in permitting the formation of the fluoro-zirconate glasses recently reported (24). In these systems, however, the long-range periodicity of the metal lattice is broken by the presence of large modifier cations such as Ba^{2+} .

Although we have not pursued the topological aspects of the fluorine packing in quantitative detail, the rules developed above concerning the probable dispositions of neighboring fluorine atoms allow a rationalization of the observed limits to the non-stoichiometry. Systematic experiments (1-4) have shown that many $(\text{M}, \text{Zr})\text{X}_{3+x}$ phases exist but x is never found to be greater than about 0.8. The mechanism of replacement of normal fluorines by fluorine pairs explains why the lattice parameters do not increase with increasing non-stoichiometry and the necessity to avoid short $\text{F1} \dots \text{F2}$ or $\text{F2} \dots \text{F2}$ separations explains the limiting cell content of about 3.8 anions. As the number of F2-F2 pairs increases, the choice of position for neighboring atoms becomes rapidly restricted and we have not been able to construct a model with x greater than about 3.75 without having to include such

unfavorable fluorine-fluorine separations. In particular, a structure of composition MF_4 cannot be built in this way, in accord with the absence of a cubic disordered phase in ZrF_4 itself.

The results indicate that the preparation of anion excess perovskites or bronzes analogous to the ReO_3 -type phases may be possible. The distance from an F2 position to the center of the cell is about 2.01 Å. Taking the crystal radius of F^- as 1.19 Å (15, 19), this would indicate an appropriate crystal radius for a metal ion situated at the cube center to be 0.82 Å. This is reasonably close to the crystal radius for lithium (15), and indicates that genuine anion-excess, lithium fluoride or oxyfluoride bronzes or perovskites might be capable of existence. This possibility is being investigated and further structural work on both fluorides and oxyfluorides as a function of composition and temperature is in progress.

Summary

The structure of $\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3}$ ($\text{MX}_{3.5}$) at room temperature has been solved by powder neutron diffraction and the non-stoichiometry shown to be accommodated by interstitial anions. 2.5 of the anions in a formula unit are on sites of the type $(\frac{1}{2} x x)$, only slightly (0.303 Å) displaced from the ideal $(\frac{1}{2} 0 0)$ sites of the ReO_3 structure. The remaining 1/6 of the "ideal" sites are vacant and the 0.5 anions from these sites, together with the 0.5 "interstitial" anions, are found as pairs of anions straddling the vacant sites with a maximum separation of 2.23 Å.

Genuine anion-excess non-stoichiometry has thus now been characterized in the ReO_3 structure as well as in the fluorite structure, and, as in the fluorites, unusually short fluorine-fluorine distances are found. The energetics of this phenomenon are not well understood but a qualitative discussion has been given of some aspects of the chemical bonding of early high-valent transition metal

ions such as zirconium, which show a tendency to form edge or face-shared polyhedra, for example in the crystallographic shear phases. In the present compound, the effective average coordination of the metal atoms is increased from six to seven by the incorporation of the anion excess, and this can also be represented as a change from corner-shared to edge-shared polyhedra.

Apart from any, possibly secondary, effects of chemical bonding, the prime requirement for finding genuine anion-excess non-stoichiometry is probably a non close-packed anion lattice and the presence of ions that can readily tolerate an increase in coordination number over that found in the basic structure. No systematic study of such compounds appears to have been made, but if anion-excess non-stoichiometry is a fairly general possibility the particular details of each structure will probably determine whether unusually short anion-anion separations need occur.

The metal ion is slightly displaced from (0 0 0) along $(x 0 0)$, almost certainly in the direction of an interstitial pair. The average M-F distance is probably between 2.09 Å and 2.10 Å, in good agreement with the distance of 2.10 Å estimated for seven coordinate $\text{Zr}_{0.8}\text{Yb}_{0.2}$ from the effective ionic radii.

All possible F1-F1, F1-F2 and F2-F2 distances were calculated for "normal" (F1) or "interstitial" (F2) fluorines near neighboring ideal sites, to allow an assessment of some likely features of the local order within the structure. There are rather strict limitations on the relative orientations of neighboring pairs if very short F-F separations are to be avoided, and displacements of F1 atoms away from neighboring fluorine pairs are also favored. It becomes impossible to build a structure model avoiding all the unlikely separations for a composition greater than about 3.75, and this result is in good agreement with the experimentally observed solubility limit in several systems and with

the absence of a cubic disordered phase in ZrF_4 itself.

The actually observed ranges of non-stoichiometry, which show quite wide variations from system to system, no doubt depend quite sensitively on the free energies and the kinetics of formation of the various alternative structures which could be formed. The displacement of the F2 atoms along the cube edge is probably quite general, however. The empty site at the center of the cube is unlikely to be occupied or approached by anions, as it is a metal site in the perovskite lattice. Even in the non-stoichiometric phases such as that studied in this work, there is still space at the cube center for a small cation such as lithium, so that the preparation of genuine anion-excess perovskites or bronzes remains a possibility.

A significant improvement in the quality of the refinement was obtained with the D1A data relative to the CURRAN data. Materials such as $\text{Zr}_{0.8}\text{Yb}_{0.2}\text{F}_{3.2}\text{O}_{0.3}$ with a cubic cell of small edge, but with several positional and other variables to be determined, present a considerable problem in a powder diffraction experiment in obtaining a sufficient number of intensities to allow a satisfactory refinement. This problem is made more severe by the relatively high effective temperature factors which entail a fairly rapid decline in the structure factor amplitudes as the scattering vector increases. An "ideal" diffractometer for studying such materials should have good resolution characteristics to high angle and a high effective flux down to a wavelength of around $1.0 \text{ \AA}$.

Acknowledgements

We thank A. W. Hewat for assistance with the use of the D1A diffractometer and M. W. Thomas for the peak fitting program and wavelength determination program.

References

1. H. L'HELGOUALCH, M. POULAIN, J. P. RANNOU, AND J. LUCAS, *C. R. Acad. Sci. Paris, Ser. C* **272**, 1321 (1971).
2. J. P. RANNOU, H. L'HELGOUALCH, AND J. LUCAS, *C. R. Acad. Sci. Paris, Ser. C* **274**, 612 (1972).
3. F. CHAMPLON AND J. LUCAS, *C. R. Acad. Sci. Paris, Ser. C* **276**, 1097 (1973).
4. M. POULAIN, M. POULAIN, AND J. LUCAS, *J. Solid State Chem.* **8**, 132 (1973).
5. E. G. IPPOLITOV, L. S. GARASHINA, AND A. G. MAKLESTLOV, *Inorg. Mater.* (English Translation) **3**, 59 (1967).
6. A. K. CHEETHAM, B. E. F. FENDER, AND M. J. COOPER, *J. Phys. C* **4**, 3107 (1971).
7. B. C. TOFIELD AND W. R. SCOTT, *J. Solid State Chem.* **10**, 183 (1974).
8. M. POULAIN, unpublished data.
9. B. C. G. HAYWOOD AND D. L. WORCESTER, *J. Phys. E* **6**, 568 (1973).
10. A. W. HEWAT AND I. BAILEY, *Nucl. Instrum. Methods* **137**, 463 (1976).
11. K. D. ROUSE AND M. J. COOPER, unpublished programme.
12. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969); A. K. CHEETHAM AND J. C. TAYLOR, *J. Solid State Chem.* **21**, 253 (1977).
13. R. D. BURBANK AND F. N. BENNEY, JR., U.S.A.E.C. Report, K-1280 (1956).
14. G. BRUNTON, *Acta Crystallogr. B* **27**, 1944 (1971).
15. R. D. SHANNON, *Acta Crystallogr. B* **32**, 751 (1976).
16. C. K. JOHNSON, ORTEP, Oak-Ridge National Laboratory Report ORNL-3794 (1965).
17. M. POULAIN, M. POULAIN, AND J. LUCAS, *Mater. Res. Bull.* **7**, 319 (1972).
18. C. R. A. CATLOW, *J. Phys. C* **9**, 1859 (1976).
19. F. G. FUMI AND M. P. TOSI, *J. Phys. Chem. Solids* **25**, 31 (1964).
20. B. C. TOFIELD, *Structure and Bonding* **21**, 1 (1975).
21. B. C. TOFIELD, *J. Physique, Coll. C-6*, 539 (1976).
22. A. F. WELLS, "Structural Inorganic Chemistry" 4th Ed., p. 355, Clarendon Press, Oxford, (1975).
23. B. C. TOFIELD, *Prog. Inorg. Chem.* **20**, 153 (1976).
24. M. POULAIN, M. CHANTHANASINH, AND J. LUCAS, *Mater. Res. Bull.* **12**, 151 (1977).