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Neutron Powder Investigation of Praseodymium and Cerium Nitride Fluoride Solid Solutions

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The investigation of CeN_xF_{3-3x} (a = 5.8027(2) Å) and PrN_xF_{3-3x} (a = 5.7723(1) Å) ($x \simeq 0.33$) solid solutions, using neutron powder diffraction, revealed that nitrogen atoms and fluorine atoms are occupying the tetrahedral holes within the fluorite type structure and that additional fluorine interstitials are observed on positions x, x, x ((32f) in $Fm\bar{3}m$) with x = 0.416. Some of the normal fluorite positions in 0.25, 0.25, 0.25 are relaxed on x, x, x (x = 0.321 for CeN_xF_{3-3x} and x = 0.331 for PrN_xF_{3-3x}) positions but can be considered rather as slightly relaxed normal sites than as true interstitials. The results have been interpreted with [1:0:3] and [1:0:4] defect clusters within these anion-excess-fluorite related structures.

Introduction

Synthesis and structure determination of nitride fluorides was initiated in 1967 by S. Andersson (*1*). The idea to substitute two oxide anions by one nitride and one fluoride anion to obtain pseudooxides (nitride fluorides) led only to a few investigations in this field. This was due to enormous problems in determining the anions analytically and in distinguishing them in the structure analysis. The improvement in both of these methods enables one now to recognize more details about these solid state compounds. Because of the significantly different atomic scattering factors for nitrogen and fluorine (b_N = 9.371fm, b_F = 5.65fm) the most efficient improvement in structure determination is the use of neutron sources for the diffraction work. In the past nitride fluorides have been investigated by X-ray methods and the anion positions have been refined with statistical disorder of N^{3-} and F^-. Nevertheless in one of the first investigated compounds Mg_3NF_3 it was shown by

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Andersson that nitrogen and fluorine are ordered on different crystallographic sites within space group $Pm\bar{3}m$ (*2, 3*). The structure determination of $In_{32}ON_{17}F_{43}$ by single crystal X-ray methods showed that it was not possible to distinguish between nitride and fluoride on the anion sites, but neutron powder diffraction revealed that nitrogen was ordered on 16*c* in space group $Ia\bar{3}$ (*4*). Under the aspect of full or partial ordering in nitride fluorides, we started to investigate nitride fluorides by neutron powder diffraction. First investigations have been carried out on the fluorite-related solid solutions CeN_xF_{3-3x} and PrN_xF_{3-3x} ($0.5 \geq x \geq 0.33$). Comparing the ionic radii of fluoride anions with coordination number 4 (1.17 Å) and nitride anions (1.43 Å) (*5, 6*), one would assume that within a fcc cation lattice, as in the fluorite structure, fluorine would be within the tetrahedral holes while nitrogen will favor the octahedral environment.

Experimental

CeN and PrN were prepared by nitridation of the metals at 900°C under 1 atm of ammonia (*7*). Guinier X-ray powder patterns confirmed the lattice constants for both of the cubic nitrides (CeN, $a = 5.021$ Å; PrN, $a = 5.157$ Å). The lattice constants correspond to those found by Holleck *et al.* (*8*) for an oxygen free nitride. Impurities of oxygen would cause an increase in the lattice constant in the case of CeN.

Neutron powder patterns also showed no further Bragg peaks other than those of the nitrides, indicating no impurities, different phases, or starting materials. Analysis of the nitrides showed both of the nitrides to be slightly substoichiometric $CeN_{0.97}$ and $PrN_{0.89}$.

CeF_3 and PrF_3 were obtained from ALFA Chemicals and fluorinated at 250°C with fluorine, in order to remove any oxygen and water.

CeN_xF_{3-3x} and PrN_xF_{3-3x} were prepared by the method of Tanguy *et al.* (*9*). In order to prepare the anion-excess $CeN_{0.33}F_2$ and $PrN_{0.33}F_2$ 1 mole metal nitride and 2 moles metal trifluoride were annealed for 1 week at 870°C in sealed Pt tubes and then cooled rapidly to room temperature. The cerium compound is a gray powder and is very sensitive to air, changing color from gray to dark brown. The praseodymium compound is yellow-green.

Both compounds crystallize with the fluorite structure and (refined powder neutron diffraction experiment) lattice constants: $a_F = 5.8027(2)$ Å, for the cerium compound (which corresponds, according to Pezat *et al.* (*10*), to $CeN_{0.38}F_{1.86}$) and $a = 5.7723(1)$ Å for the praseodymium compound.

The neutron powder diffraction experiments were carried out on the high resolution powder diffractometer D1A (*11*) at the high flux reactor of the Institut Laue-Langevin in Grenoble. The Pt tubes were opened in a Braun glovebox and the material was placed in a vanadium can which was sealed with indium wire and a copper spring joint. The wavelength used was 1.9119 Å. The detector, consisting of 10 ^3He detectors, was step scanned with a step size of 0.05°, over a range 2Θ, from 20 to 150°.

Results and Discussion

Figures 1a and b show the neutron powder patterns for the two anion-excess nitride fluorides, and Table I gives the corresponding intensities and 2Θ values. Both patterns are typical for the fluorite structure. The diffuse scattering before the (220) reflection is a typical feature seen in neutron powder diffraction patterns of anion-excess-fluorite related structures and is, in most cases, related to the interaction between defects, i.e., to short-range order effects.

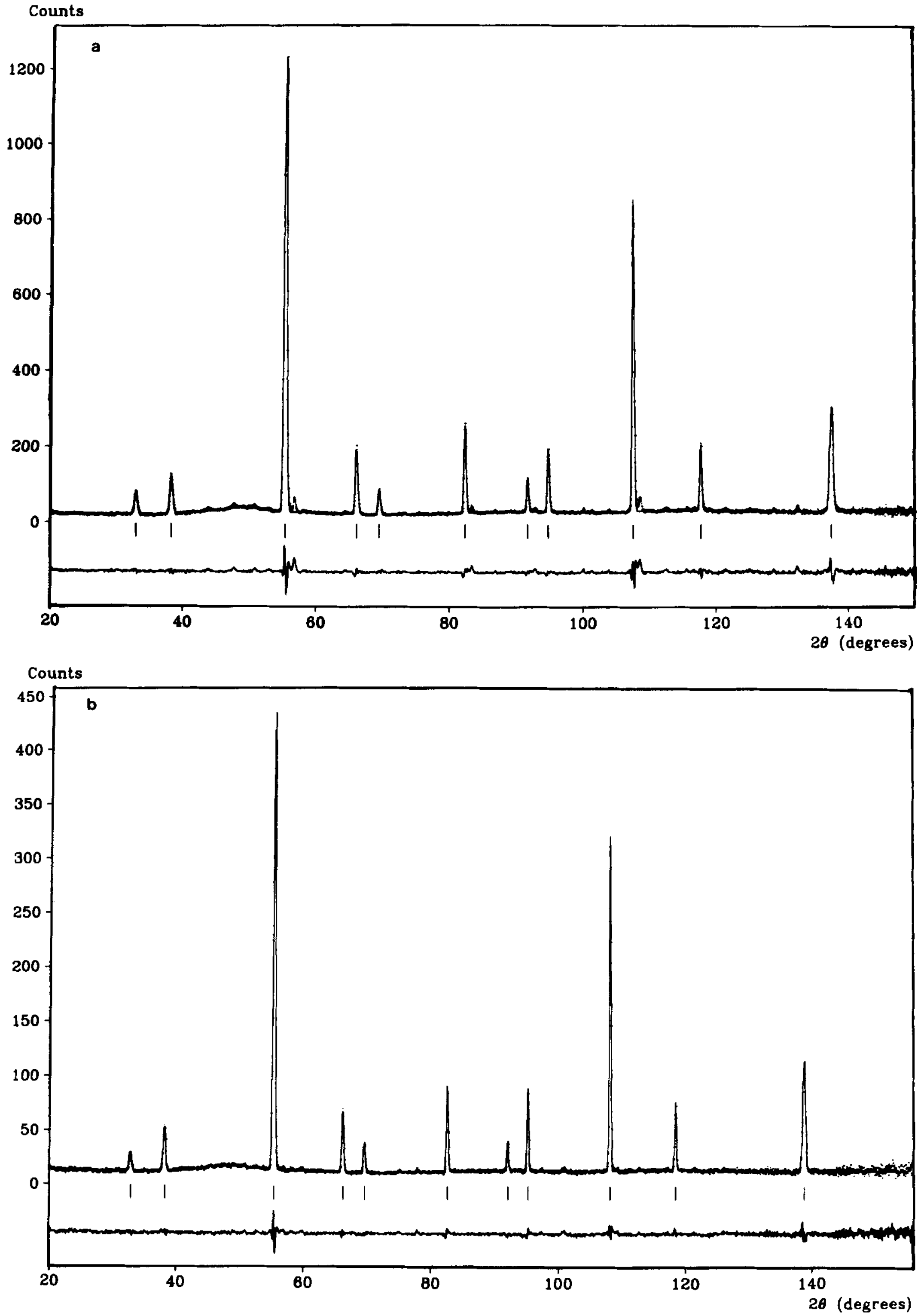

FIG. 1. (a) Powder diffraction pattern of CeN_xF_{3-3x} at room temperature (D1A diffractometer) and profile fit. Dotted lines are measured intensities, full lines are calculated intensities, and tick marks indicate Bragg positions. The difference plot is between measured and calculated diffraction patterns. (b) Powder diffraction pattern of PrN_xF_{3-3x} at room temperature (D1A diffractometer) and profile fit.

TABLE I

INTEGRATED INTENSITIES AND 2Θ VALUES FOR CeN_xF_{3-3x} (a) AND PrN_xF_{3-3x} (b) ON D1A, AT ROOM TEMPERATURE AND λ = 1.9119 Å

h k l	2Θ	*I*(obs)	*I*(calc)	*I*(obs) − *I*(calc)
		(a)		
1 1 1	33.155	732.0	699.0	33.0
2 0 0	38.471	1130.5	1127.2	3.3
2 2 0	55.538	12340.6	12215.8	124.8
3 1 1	66.231	1583.0	1593.9	−10.9
2 2 2	69.587	627.9	583.9	44.0
4 0 0	82.432	1959.3	1949.4	9.8
3 3 1	91.782	682.6	672.8	9.8
4 2 0	94.897	1276.0	1280.6	−4.6
4 2 2	107.604	6371.3	6261.5	109.7
5 1 1	117.726	1170.9	1133.1	37.9
3 3 3	117.726	313.1	302.9	10.1
4 4 0	137.441	3632.5	3533.7	98.8
		(b)		
1 1 1	33.338	158.0	157.1	0.9
2 0 0	38.686	402.0	388.9	13.1
2 2 0	55.863	3603.9	3597.0	6.9
3 1 1	66.633	443.4	444.5	−1.1
2 2 2	70.016	204.0	207.3	−3.4
4 0 0	82.972	571.7	556.2	15.5
3 3 1	92.419	170.3	175.9	−5.7
4 2 0	95.570	472.3	471.6	0.6
4 2 2	108.450	1915.0	1885.3	29.7
5 1 1	118.753	343.7	320.1	23.6
3 3 3	118.753	74.3	69.2	5.1
4 4 0	139.052	1125.0	1118.4	6.6

Rietveld refinements (*12, 13*) in space group $Fm\bar{3}m$, with the rare earths on Wyckoff position (4*a*) 0, 0, 0 and fluorine on (8*c*) 0.25, 0.25, 0.25, converged to weighted profile reliability factors of 23.74 and 22.31% for CeN_xF_{3-3x} and PrN_xF_{3-3x}, respectively. Convergence in this context means that the shifts of the refined parameters are smaller than the estimated standard deviations. In both cases Fourier difference sections indicated structure factor density near 0.5, 0.5, 0.5. Refinements clearly indicated that, in addition to the normal anionic position (0.25, 0.25, 0.25 site, labeled *X*), significant occupancy occurred only on two different 32*f* (*x*, *x*, *x*) sites, at $x \simeq 0.41$ (X'' interstitial site) and $x \simeq 0.32$ (X''' site = normal *X* site). No occupancy is observed on (0.5, *x*, *x*) (X' interstitial site). Because of the difference in their neutron scattering lengths (b_N = 9.371*fm*, b_F = 5.65*fm*), N and F atoms can be distinguished. Therefore various N/F distributions among the different anionic sites have been tested. As the exact number of each anion is not accurately known, and therefore cannot be constrained to remain constant during the refinement, several N/F distributions can lead to almost the same *R*-values. Nevertheless, the most reasonable results (lowest R_{wp}-value = 7.93% for the cerium compound, 6.09% for the praseodymium compound; number of anions close to the expected value) correspond to a statistical distribution of N and F atoms on the normal *X* site and only F atoms on the X'' and X''' sites. Table II gives the final parameters for both compounds. They correspond to the structural formulas $Ce(N_{0.36}F_{1.27}F'''_{0.19}V_{x0.18})F''_{0.5}$ and $Pr(N_{0.37}F_{1.27}F'''_{0.13}V_{x0.23})F''_{0.54}$. It is well known from the literature that, in the case of the anion-excess-fluorite related structures, two different kinds of true interstitials may occur: X'

TABLE II

FINAL PARAMETERS FOR CeN_xF_{3-3x} (a)[a] AND PrN_xF_{3-3x} (b)[b] (STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å²)	Occupancy
			(a)		
Ce	0.0	0.0	0.0	1.92	1
F	0.25	0.25	0.25	1.926	0.635(0)
N	0.25	0.25	0.25	1.926	0.18(1)
F‴	0.322(8)	0.322(8)	0.322(8)	1.926	0.0234(3)
F″	0.416(1)	0.416(1)	0.416(1)	1.926	0.063(2)
			(b)		
Pr	0.0	0.0	0.0	1.92	1
F	0.25	0.25	0.25	1.926	0.635(0)
N	0.25	0.25	0.25	1.926	0.184(4)
F‴	0.327(8)	0.327(8)	0.327(8)	1.926	0.0164(3)
F″	0.414(2)	0.414(2)	0.414(2)	1.926	0.067(3)

[a] R_{wp} = 7.93%, R_I = 1.24%.

[b] R_{wp} = weighted profile *R*-factor = $\sqrt{\Sigma[w(y_{obs} - y_{calc})^2]/\Sigma w(y_{obs})} \times 100\%$ = 6.09%. R_I = Intensity Mod I R-factor = $\Sigma[\mathrm{mod}(I_{obs} - I_{calc})]/\Sigma(I_{obs}) \times 100\%$ = 0.75%.

(0.5, x, x; $x \simeq 0.37$) and X'' (x, x, x; $x \simeq 0.41$); they are generally associated with other defects (dopant cations, anion vacancies) in clusters. For the description the Willis notation will be used [No. of anion vacancies: No. of anion interstitials on 0.5, x, x: No. of anion interstitials on x, x, x] (*14–17*):

- X'-based clusters like

  —the cuboctahedral [8 : 12 : 1] clusters: In these discrete M_6X_{37} clusters, six MX_8 square antiprisms share corners to enclose a cuboctahedron of X' anions with an additional X'' anion at its center (*18*).

  —the columnar clusters [$2n + 2 : 4n : 2$] ($n = 1 \rightarrow \infty$) which consist of finite or infinite double columns of MX_8 square antiprisms (*19, 20*). In both cases ordered superstructures can appear.

- X'' based clusters like the [1 : 0 : n] clusters (n = 2, 3, 4) which are observed in solid solutions with dopant cations large enough to accept a tenfold coordination (*21–24*). In this case no ordered superstructures have been observed. However, ordered or semi-ordered vernier phases (*25*) have been recently described in terms of ordered [1 : 0 : 2] clusters (*26*).

In both CeN_xF_{3-3x} and PrN_xF_{3-3x} this investigation assumes that only X'' interstitial anions are present and they are essentially fluorine anions. This accounts for the presence of [1 : 0 : n] clusters within the fluorite substructure and for the existence of a partial N/F order.

Simple electrostatic bond strength calculations using the Donnay method (*27*) indicate an electrostatic valence close to 1.5 for the normal tetracoordinated X anion and close to 1 for the tricoordinated X'' anion, which confirms the proposed N/F distribution. The same kind of O/F order has been evidenced in the tetragonal $LaF_{1.70}O_{0.65}$ fluorite-related phase (*22*).

These [1 : 0 : n] clusters can be described by choosing as the defect element a cube of eight anion cubes (see Figs. 2a and b). The central anion is removed to leave a vacancy. Four of these eight cubes have metal atoms (Ce, Pr) in the center and the other four are empty and can adopt X'' anion interstitials. Depending on how many of the four possible interstitial sites around the vacancy are occupied, a relaxation of normal fluorine sites occurs. For a [1 : 0 : 3] cluster, only three of these empty cubes are occupied by a fluorine interstitial, so from the octahedra of normal fluorite sites around the vacancy, three fluorine atoms will relax into the empty cube, along the body diagonals, toward the vacancy.

The [1 : 0 : 4] clusters do not have any F''' positions, so the ratio $F'' : F'''$ is 4 : 0. [1 : 0 : 3] clusters have a $F'' : F'''$ ratio of 3 : 3 and [1 : 0 : 2] clusters a ratio $F'' : F'''$ of 2 : 5. For CeN_xF_{3-3x} and PrN_xF_{3-3x} the ratio of F'' positions to anion vacancies is close to 3 : 1 for both systems, which could be interpreted with [1 : 0 : 3] clusters. The observed number of relaxed anions F''' ($\simeq$1/cluster) is lower than that in homologous $Ca_{1-x}Th_x F_{2+2n}$ solid solutions (*21*) and the ideal number (3/cluster). But this number, on the one hand, cannot be accurately determined because of the high correlations occurring between the parameters of the very close X and X''' sites (only the sum ($n_x + n_{x'''}$) and the number of true anion vacancies are accurately known). This number strongly depends on the cation size and on the anion charge (e.g., in $ThF_{4x}O_{2-2x}$ the O^{2-} anions are not relaxed (*23*)). Another possible explanation is that partial ordering of [1 : 0 : 3] clusters occurs which causes less relaxed F''' positions. In Fig. 3 possible partial ordering of [1 : 0 : 3] clusters is shown. In this case the [1 : 0 : 3] clusters and vacancies are ordered along the fluorite b-axis in a way that vacancies and clusters are paired along [010]. As stated earlier, isolated [1 : 0 : 3] clusters cause a relaxation of normal anion sites. However, if they are paired, each of

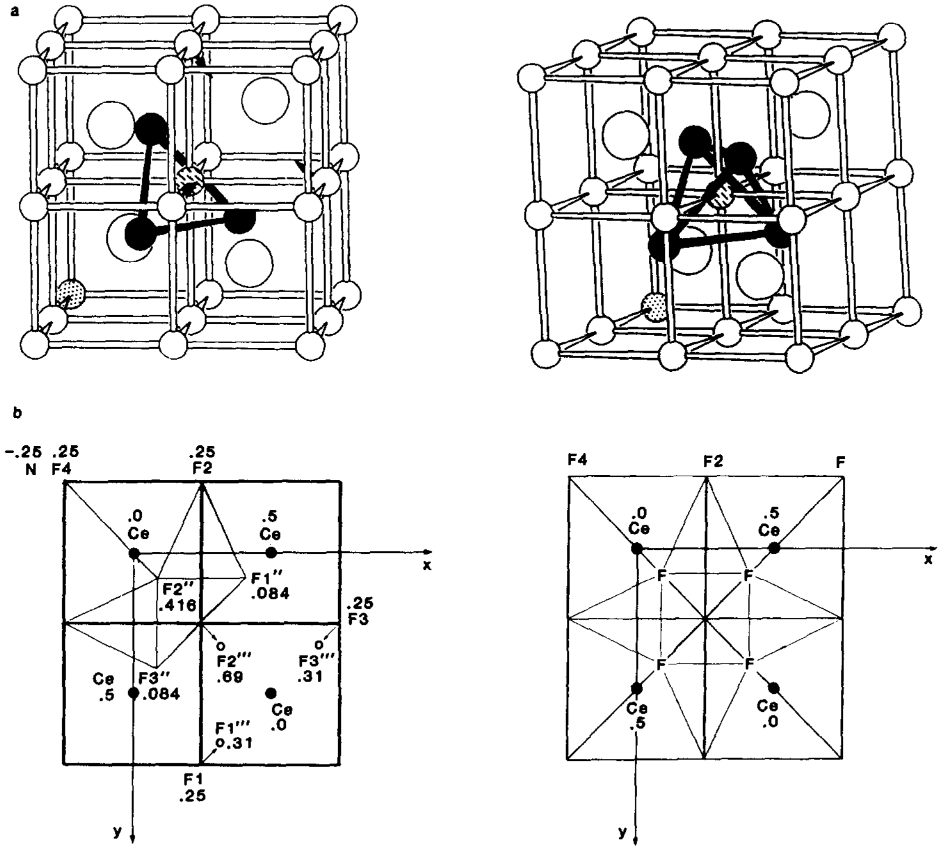

FIG. 2. (a) The [1 : 0 : 3] and [1 : 0 : 4] clusters in CeN$_x$F$_{3-3x}$ and PrN$_x$F$_{3-3x}$. Small circles represent fluorine atoms (nitrogen atom dotted) and large circle metal atoms. Full circles are fluorine interstitials in x, x, x ($x = 0.41$) and dashed circles represent an anion vacancy in 0.25, 0.25, 0.25. (b) The projection along [001] of Fig. 2a. Arrows indicate relaxed fluoride positions of the anions (F‴). Numbers are the heights in the z-coordinate.

TABLE III

BOND DISTANCES IN Å FOR CeN$_x$F$_{3-3x}$ (a) AND IN PrN$_x$F$_{3-3x}$ (b) (STANDARD DEVIATIONS ARE GIVEN IN PARENTHESES)

		(a)			
Ce–F	2.5127(0)	F1″–F2″	2.73(1)	F2‴–F3‴	2.92(4)
Ce–F‴	2.37(4)	F4–F2	2.90(0)	F1‴–F3″	2.47(3)
Ce–N	2.5127(0)	F2–F2″	2.36(7)	F4–F2″	2.90(7)
Ce–F″	2.513(8)	F4–N	2.90(0)		
		(b)			
Pr–F	2.4995(0)	F1″–F2″	2.86(1)	F2‴–F3‴	3.04(6)
Pr–F‴	2.36(4)	F4–F2	2.89(0)	F1‴–F3″	2.51(4)
Pr–N	2.4995(0)	F2–F2″	2.356(7)	F4–F2″	2.896(6)
Pr–F″	2.494(7)	F4–N	2.89(0)		

the four empty anion cubes of the defect element will be occupied by an interstitial fluoride anion and a relaxation cannot be observed.

Table III shows important distances for CeN$_x$Fe$_{3-3x}$ and PrN$_x$F$_{3-3x}$. Figure 4 shows the most probable coordination polyhedron of one metal atom surrounded by nine fluorine atoms and one nitrogen atom in the case of a [1 : 0 : 3] cluster. This polyhedron is a common cluster for ccp arrangements (*28*). It occurs also in ordered fluorite-related defect structures and might be de-

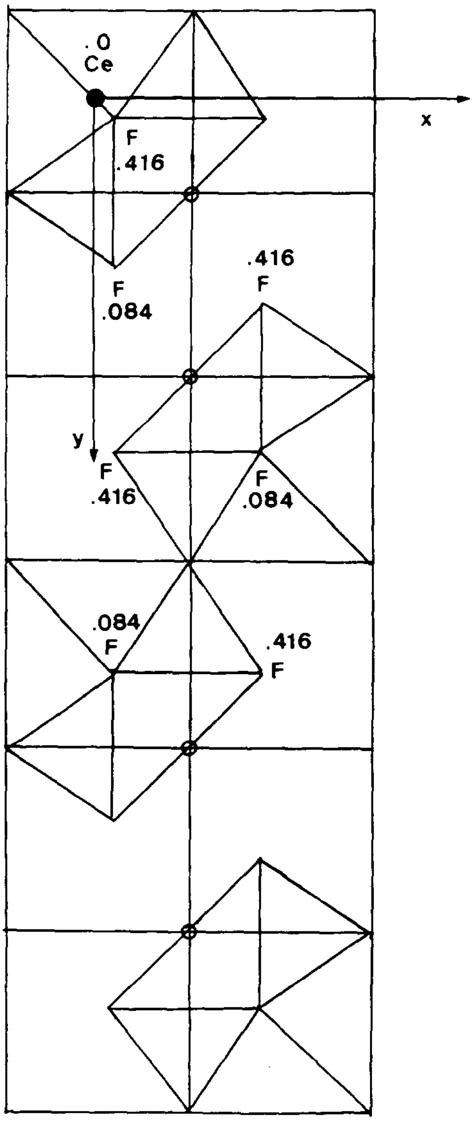

FIG. 3. Possible ordering of [1 : 0 : 3] clusters drawn in projection along [001]. Circles indicate vacancies in $z = 0.25$ and numbers are heights in the z-coordinate.

scribed best as being half cube and half icosahedron.

Conclusion

In the case of the fluorite-related solid solutions CeN_xF_{3-3x} and PrN_xF_{3-3x} ($x \simeq 0.33$) prepared by reaction of CeN and two CeF_3 at 870°C, the neutron powder diffraction revealed that nitrogen and fluorine are present in the tetrahedral holes of the fluorite structure and fluorine interstitials occupy the position $32f\ x, x, x$ ($x = 0.41$). In order to keep the stoichiometry in this model these clusters have to be packed very close. An explanation is that, in these solid solutions, clusters like them are assumed for the $CeN_{0.5}F_{1.5}$ and $PrN_{0.5}F_{1.5}$, with two nitrogen atoms paired along the body diagonal of the anion cube, and the 1 : 0 : 3 clusters with one nitrogen vacancy and three fluorine F″ interstitials are present. With such a hypothesis, the nonstoichiometric process would structurally correspond to the substitution within the basic $Ln\mathrm{N}_{0.5}\mathrm{F}_{1.5}$ fluorite matrix of three F″ interstitial anions for one N-normal anion, and the $Ln\mathrm{N}_x\mathrm{F}_{3-3x}$ formulation could favorably be replaced by the more appropriate one: $Ln\mathrm{N}_{0.5-x/2}\mathrm{F}_{1.5+3x/2}$ (structural formula: $Ln[\mathrm{N}_{0.5-x/2}\mathrm{F}_{1.5}\mathrm{V}_{Nx/2}]\mathrm{F}''_{3x/2}$).

The diffraction pattern of CeN_xF_{3-3x} however shows tiny peaks which might account for a superstructure. In the future it is planned to use longer reaction and annealing times to produce more ordered materials and to investigate possible superstructures.

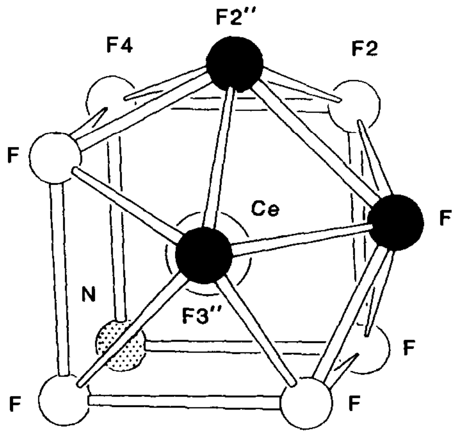

FIG. 4. The coordination polyhedra of the metal atoms (Ce and Pr).

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