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Defect Structure of Anion-Excess Fluorite-Related $Ca_{1-x}Y_xF_{2+x}$ Solid Solutions

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On the basis of the transformation of a cube within a fluorite-type matrix into an archimedean antiprism of the kind found in numerous ordered anion-excess fluorite-related superstructures, a new polyhedral cluster, labeled 4 : 4 : 3, [according to B. T. M. Willis, *Proc. Br. Ceram. Soc.* **1,** 9 (1964) and A. K. Cheetham, B. E. F. Fender, and M. J. Cooper, *J. Phys. C* **4,** 3107 (1971)], is proposed to explain the defect structure and short-range order in $Ca_{1-x}Y_xF_{2+x}$ solid solution. In agreement with the spectroscopic, dielectric, and electric experiments, this new structural model fits perfectly well the measured occupation numbers for normal F and interstitial F′ and F″ fluorine atoms for the whole range of compositions without requiring the too short F′–F′ distances generated by the previously proposed 2 : 2 : 2 or 3 : 4 : 2 clusters. Such 4 : 4 : 3 clusters and nearly identical 4 : 4 : 4 or 4 : 4 : 5 ones, are probably present in the other highly and moderately doped $Ca_{1-x}Ln_xF_{2+x}$ solid solutions; they could be precursors for the largest clusters, i.e., ordered microdomains, observed for samples annealed for a long time.

Introduction

Since 1961 the search for new and better solid state lasers has led to a great deal of work on rare earth doped alkaline earth fluoride materials with the fluorite structure (*1*). These fluorides are relatively easy to grow in the form of large single crystals and very high concentrations of trivalent rare earth fluorides can be incorporated into them, as much as 30–50 mole% near to the melting point (*2*). The defect properties of these fluorite compounds containing excess anions have been thoroughly investigated in recent years by theoretical calculations based on lattice simulation methods (*21, 22*) and by various experimental techniques: ionic conductivity (*3, 4*), dielectric relaxation (*5, 7*), ionic thermocurrents (*8, 9*), laser spectroscopy (*10, 12*), EPR and ESR (*13, 15*), NMR (*16, 17*), Bragg and diffuse neutron scattering (*18, 20*). Although no perfect model has been obtained yet, the fundamental features of the defect structure of these phases are well understood. It has been clearly established that the rare earth ions substitute for calcium ions and that interstitial fluoride F_i^- anions are formed as well as vacancies V_F on the normal fluorine sites.

For very low doping concentrations (<0.05 mole%) the charge-compensating F_i^- anion interstitials are mainly found, either in one of the nearest neighbor (*nn*) interstitial positions to the Ln^{3+} substitutional cations, thus forming tetragonal Ln_s^{3+}–F_i^- type I complexes, or in one of the next nearer neighbor (*nnn*) interstitial positions,

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forming trigonal Ln_s^{3+}–F_i^- type II complexes. Cubic sites for Ln^{3+} cations and free F_i^- anions have been found too.

For the moderately doped compounds (0.1 to 1 mole%), NMR (*16, 17*), laser (*10–12*), and electrical relaxation (*5*) studies have shown that most of the Ln^{3+} cations are located in dimers or higher order complexes, i.e., in more or less extended clusters. For instance, three-body energy transfers demonstrate that the clusters observed in CaF_2-doped defect crystals (≃0.2 mole%) contain at least three lanthanide ions (*10*).

For higher doping concentrations (> 5 mole%) by analyzing the Bragg neutron diffraction spectra of $CaF_2 \cdot Y^{3+}$ samples, Cheetham and co-workers (*18, 19*) found, in addition to vacancies on the normal fluorite anionic sub-cell, two kinds of F_i^- interstitials: one called F′, shifted along the ⟨110⟩ direction from the ideal $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ cubic sites ($\frac{1}{2}$,u,u with $u \simeq 0.37$) and the other called F″, shifted along the ⟨111⟩ direction from the ideal sites (w,w,w with $w \simeq 0.41$). Such a defect structure closely resembles that of UO_{2+x} (*23*), $Pb_{1-x}Bi_xF_{2+x}$ (*24*), and $Pb_{1-x}Th_xF_{2+2x}$ (*25*), and seems to be a general feature of fluorite compounds containing excess anions.

For UO_{2+x} and $Ca_{1-x}Y_xF_{2+x}$ solid solutions, closer study and diffuse scattering experiments of long wavelength (6.5 Å) neutrons reveal the presence of short-range order (*20*). Willis (*23*) and then Steele and co-workers (*20*) thought that this short-range order was a consequence of defect clustering, and proposed the so-called 2:2:2 and 3:4:2 clusters shown in Fig. 1.

The 2:2:2 cluster contains two normal fluorine vacancies, two F′ interstitials and two F″ interstitials. The 3:4:2 cluster possesses three normal fluorine vacancies, four F′ interstitials and two terminal F″ interstitials. A projection of the 2:2:2 cluster is shown in Fig. 2 with all the possible anionic positions in the average fluorite cell as determined by Cheetham *et al.* for the $Ca_{1-x}Y_xF_{2+x}$ solid solution. We can see in Table I that the 2:2:2 and 3:4:2 cluster

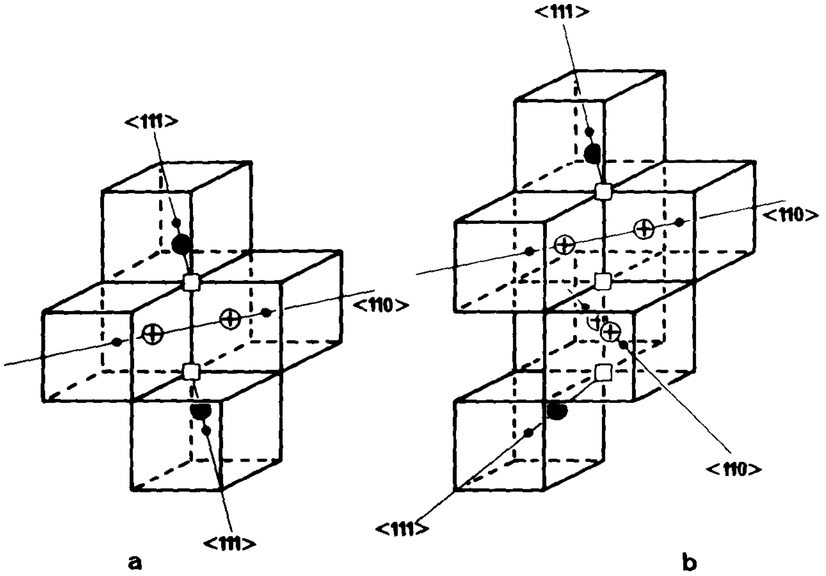

FIG. 1. Perspective drawing of the 2:2:2 (a) and 3:4:2 (b) clusters. The large cubes represent fluorite-type empty cubes of normal fluorine atoms. □, normal fluorine vacancies, ⊕, F′ interstitials; ●, F″ interstitials; ●, cubic (1/2, 1/2, 1/2) sites.

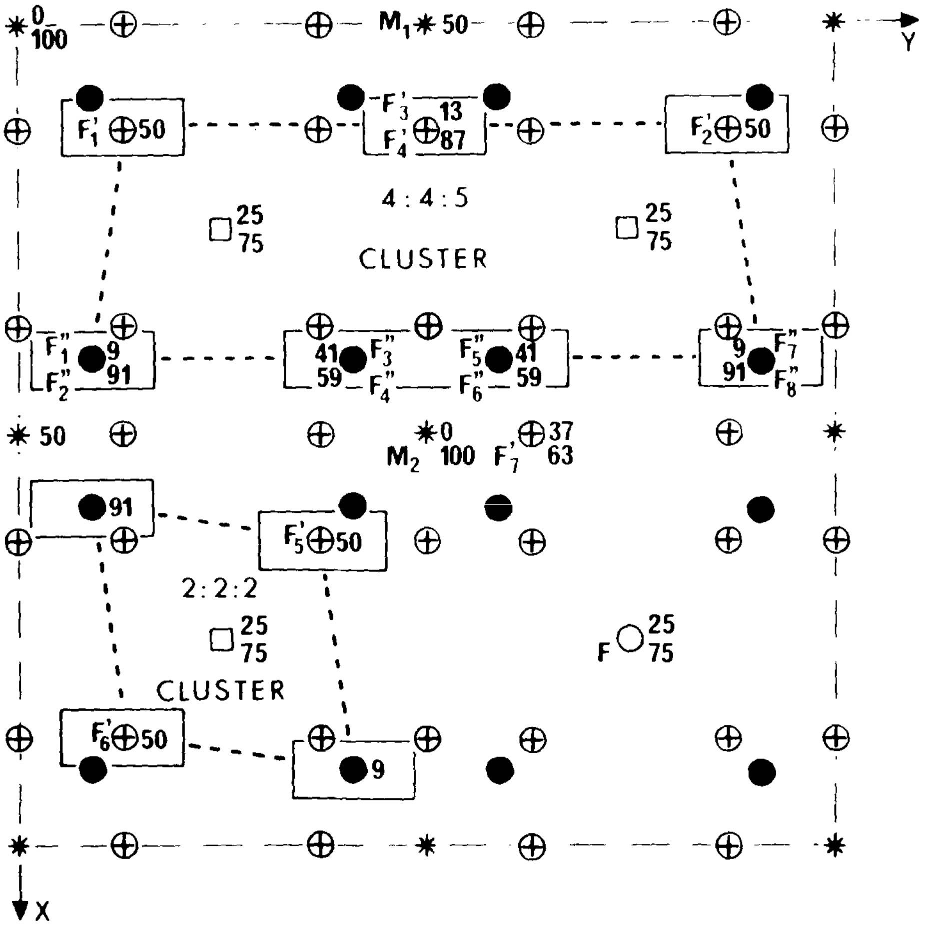

FIG. 2. Projection along the 0z axis of all the possible atomic positions (space group *Fm*3*m*) in the average cell of $Ca_{1-x}Y_xF_{2+x}$ solid solution (*18*). The positions occupied in 2:2:2 and 4:4:5 clusters (interrupted lines) are surrounded. Only one out of the four F_3'', F_4'', F_5'', and F_6'' positions is occupied at the same time. *, cations (Ca, Y); ○, normal F atoms; ⊕, F′ interstitials; ●, F″ interstitials; □, normal fluorine vacancies.

models fit (not perfectly, but well enough) the measured occupation numbers for normal F and interstitial F′ and F″ fluorine atoms, except for higher compositions $x = 0.25$ and $x = 0.32$, where very complex multiclusters are needed (*18*). The diffuse neutron-scattering experiments of heavily doped CaF_2–Y^{3+} samples (*19*) provided further evidence for F_i clusters. The measurements were not very sensitive to the position of cations, but nevertheless trivalent Y^{3+} substitutional seemed to be in loose association with the F_i clusters.

Two difficulties arise from this cluster model though. First, if the cation association with the F_i clusters is incomplete, these clusters possess net negative charges which would favor their dissociation. Theoretical calculations (*21, 22*) effectively showed that the trivalent cations should be in close association with the F_i clusters to stabilize them. Secondly, the two F′ interstitials (for

TABLE I

OBSERVED OCCUPATION NUMBERS IN $Ca_{1-x}Y_xF_{2+x}$ SOLID SOLUTION AND CALCULATED ONES FOR DIFFERENT POSSIBLE CLUSTERS

	x	0.06	0.10	0.15	0.25	0.32
	Observed (*18*)	0.05 (2)	0.12 (*4*)	0.19 (2)	0.38 (*3*) 0.35 (*3*)[a]	0.46 (2)
$M_\square$	2 2 2 4 4 4	0.06	0.10	0.15	0.25	0.32
	3 4 2	0.06	0.10	0.15	0.25	0.32
	Multicluster	—	—	—	0.37	0.44
	8 12 1	0.10	0.16	0.24	0.40	0.51
	4 4 3	*0.08*	*0.13*	*0.20*	*0.33*	*0.43*
	4 4 5	0.05	0.08	0.12	0.20	0.26
	4 4 2	0.12	0.20	0.30	0.50	0.64
	Observed (*18*)	0.064 (*13*)	0.14 (*3*)	0.21 (*3*)	0.47 (*3*) 0.34 (*4*)[a]	0.48 (*5*)
$M_{F'}$	2 2 2 4 4 4	0.06	0.10	0.15	0.25	0.32
	3 4 2	0.08	0.13	0.20	0.33	0.43
	Multicluster	—	—	—	0.47	0.50
	8 12 1	0.14	0.24	0.36	0.60	0.77
	4 4 3	*0.08*	*0.13*	*0.20*	*0.33*	*0.43*
	4 4 5	0.05	0.08	0.12	0.20	0.26
	4 4 2	0.12	0.20	0.30	0.50	0.64
	Observed (*18*)	0.046 (*10*)	0.08 (*3*)	0.13 (*4*)	0.16 (*4*) 0.26 (*4*)[a]	0.30 (*5*)
$M_{F''}$	2 2 2 4 4 4	0.06	0.10	0.15	0.25	0.32
	3 4 2	0.04	0.07	0.10	0.17	0.21
	Multicluster	—	—	—	0.15	0.27
	8 12 1	0.01	0.02	0.03	0.05	0.06
	4 4 3	*0.06*	*0.10*	*0.15*	*0.25*	*0.32*
	4 4 5	0.06	0.10	0.15	0.25	0.32
	4 4 2	0.06	0.10	0.15	0.25	0.32

[a] These observed values correspond to our new refinements (see Table IV).

instance the F'_5 and F'_6 atoms in Fig. 2) are closer to each other (distances ranging from 1.71 up to 2.04 Å with various compositions) than is allowable theoretically. In order to explain these too short F′–F′ distances, Catlow (*21*) proposed a molecular orbital model in which an additional covalent attraction between the two F′ interstitials produced an F_2^{2-} complex anion whose negative charge was delocalized over the conduction band of the fluorite structure. However, such too short F–F distances, which are not observed in other anion-excess fluorite structures, are quite unlikely and the defect model proposed needs to be improved.

More important excess anions are locally accomodated in many fluorite-related ordered superstructures, without any steric problems of this kind. If we except the infinitely adaptive "Vernier-phases" (*26–28*), fluorite-related superstructures are systematically characterized by the presence of substitutional dopant cations in square antiprismatic coordination. In the yttrofluorite mineral tveitite, $Ca_{14}Y_5F_{43}$, for instance, structure analysis (*29, 30*) has shown the presence of discrete M_6X_{37} clusters which consist of an octahedral arrangement of six MX_8 square antiprisms sharing corners to enclose a cuboctahedron of anions with an additional anion at its center—a 13-member c.c.p. anion cluster (Fig. 3). These M_6X_{37} clusters are distributed in an ordered manner within a matrix of virtually unmodified fluorite-type structure. The same M_6X_{37} cluster is present in the $Na_7Zr_6F_{31}$ (*31*) and $Nd_{14}Cl_{32}O$ (*32*) compounds, and a very similar M_6X_{36} one, missing the extra anion at the center of the cuboctahedron, is present in phases like KY_3F_{10} (*33*) and its KTb_3F_{10} isotype (*34*), α- and γ-KYb_3F_{10} (*35*), $BaCaLn_2F_{10}$ (*36*), and α-KEr_2F_7 (*37*).

Greis postulated (*38, 41*) that all the superstructures obtained by longtime annealing of lanthanide highly doped $(Ca,Ln)F_{2+x}$ samples ($0.333 \leq x \leq 0.425$) could be accounted for on the basis of periodic arrangements of M_6X_{37} clusters within a fluorite matrix. Bevan *et al.* (*29, 30*) suggested that the integrity of these clusters was retained in normal disordered yttrofluorites, their concentration being simply too low for ordering to occur.

Unfortunately, such a structural model of progressive dilution within a fluorite matrix of Y_6F_{37} clusters, which according to Willis (*23*) and then Cheetham *et al.* (*18, 19*), can be labeled 8 : 12 : 1 clusters (see Figs. 3 and 4), fits neither the measured occupation numbers for normal F and interstitial F′ and F″ (see Table I) nor the spectroscopic and dielectric observations (*5, 12*). So, thinking like Aléonard *et al.* (*42*) that the conversion of a MX_8 cube into an MX_8 square antiprism, is surely a fundamental first step in the accomodation of excess anions in these kind of fluorite-related phases, we have tried to imagine for them, less extended polyhedral cluster models.

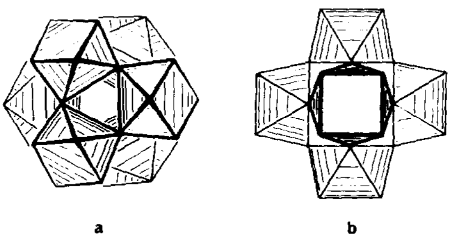

FIG. 3. Views of the M_6X_{37} (or M_6X_{36}) cluster. (a) Down a three-fold axis. (b) Down a four-fold axis.

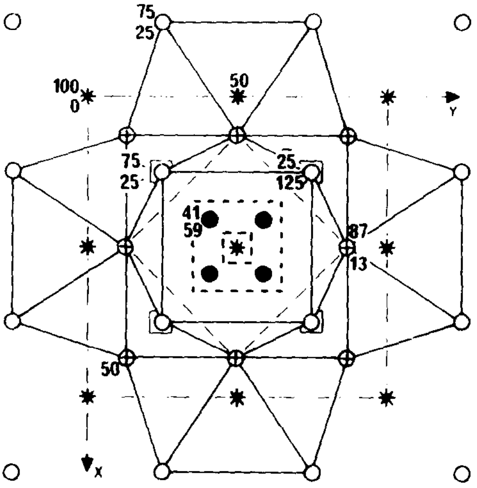

FIG. 4. The 8 : 12 : 1 cluster based on experimental atomic positions in $Ca_{1-x}Y_xF_{2+x}$ solid solution (*18*) and equivalent to the M_6X_{37} one observed in ordered superstructures. Only one out of the eight F″ positions (z = 41,59) surrounded is occupied at the same time. (Symbols for vacancies and atoms are the same as in Figs. 1 and 2.)

A Proposed Structural Model

In Fig. 5 part of the fluorite CaF_2 structure is presented, projected along a four-fold axis. One can see that the local transformation of a CaF_8 cube into a YF_8 ideal square antiprism by a 45° rotation of one of the square faces around a four-fold axis, does not change the positions of cations. This rotation creates 4 vacancies in the normal anionic sub-cell, 4 interstitials of F′ type equivalent to the four fluorine atoms of the rotated face: F'_1, F'_2, F'_3, and F'_4, and an empty volume suitable for extra fluorine interstitials.

If we assume that only cation–anion distances longer than 2.15 Å and anion–anion distances longer than 2.20 Å are acceptable in a fluorite unit-cell with a mean $a = 5.50$ Å parameter, possible positions for extra fluorine atoms are spacially localized inside volumes whose (001) sections at levels $z = 0$, 0.05, 0.45, 0.50, 0.55, 0.95 are shown on Fig.5. The 2.20 Å value, less than that usually observed (2.40–2.60 Å), is nevertheless, reasonable if we consider, first that the fluorine atoms surrounding the YF_8 square antiprism are probably relaxed from their ideal fluorite positions; second, that this distance is of the same order as the shortest F–F distances observed in ordered structures, i.e., 2.24 Å in $Na_7Zr_6F_{31}$ (*31*) and 2.22 Å in $PbZr_6O_2F_{22}$ (*43*).

A comparison with Fig. 2 clearly shows that the four corners of the rotated face of the YF_8 antiprism and the most probable positions for extra interstitials, i.e., positions shifted from the 1/2, 1/2, 1/2 ideal interstitial fluorite positions toward vacancies positions—are nearly the same as the respective experimental F′ and F″ interstitials positions. Moreover, as it can be seen on Table II, the experimental positions lead to Y–F distances inside the nonideal YF_8 antiprism in good agreement with observed values.

TABLE II

COMPARISON OF THE Y–F DISTANCES INSIDE YF_8 SQUARE ANTIPRISMS, FOR SOME ORDERED STRUCTURES AND FOR THE DISORDERED $Ca_{1-x}Y_xF_{2+x}$ SOLID SOLUTION

Compounds	KY_3F_{10} (*33*)	$Ca_{14}Y_5F_{43}$ (*30*)	$Ca_{1-x}Y_xF_{2+x}$ (*18*)
M–F distances (Å)	2.329	2.281 2.314 2.329 2.338 ⟨2.316⟩	2.38[a]
M–F′ distances (Å) (rotated square faces)	2.193	2.218 2.223 2.249 2.257 ⟨2.237⟩	2.16[a]

[a] Mean values calculated for $\langle a_F \rangle = 5.50$ Å and coordinates $u = 0.37$ and $w = 0.41$ for, respectively, F′ and F″ interstitials.

TABLE III

MAIN INTERATOMIC DISTANCES (Å) IN THE YTTROFLUORITE $Ca_{1-x}Y_xF_{2+x}$ SOLID SOLUTION CALCULATED FOR $\langle a_F \rangle = 5.50$ Å AND INTERSTITIALS COORDINATES $u_{F'} = 0.3700$, $w_{F''} = 0.4100$

M_1–F'_1 = 2.16
M_2–F = 2.38
M_2–F''_4 = 2.36
M_2–F'_5 = 2.93
F–F'_7 = 1.66
F–F''_6 = 2.25
F–F'_5 = 2.59
F'_5–F'_6 = 1.87
F'_1–F'_3 = 2.88
F'_1–F''_1 = 2.74
F'_1–F''_4 = 2.23
F''_1–F''_3 = 2.49
F''_1–F''_4 = 3.27

Note. Atoms are labeled as in Fig. 2.

Calculations for all possible interanionic F–F′, F–F″, and F′–F″ distances in an yttrofluorite cell of mean parameter $a = 5.50$ Å, reveal that five of the eight possible F″ positions in front of the F'_1 F'_2 F'_3 F'_4 rotated face of the YF_8 antiprism, can simultaneously be occupied (F''_1, F''_2, F''_3, F''_7, and F''_8 interstitials for instance) without anion–anion distances shorter than 2.23 Å (see Table III). Moreover the shortest distance generated (F′–F″ = 2.23 Å) is a consequence of the occupation of one of the four F''_3, F''_4, F''_5, F''_6 positions. These latter positions correspond to the anionic sites occupied statistically by one extra anion in M_6X_{37} clusters for which we have seen that anion–anion distances of the same order are observed (2.22 Å in $PbZr_6O_2F_{22}$ (*43*), 2.24 Å in $Na_7Zr_6F_{31}$ (*31*)).

The association of the YF_8 square antiprism with the five F″ interstitials constitutes a new anion-excess defect cluster containing four vacancies, four interstitials F′, and five interstitials F″, and which can

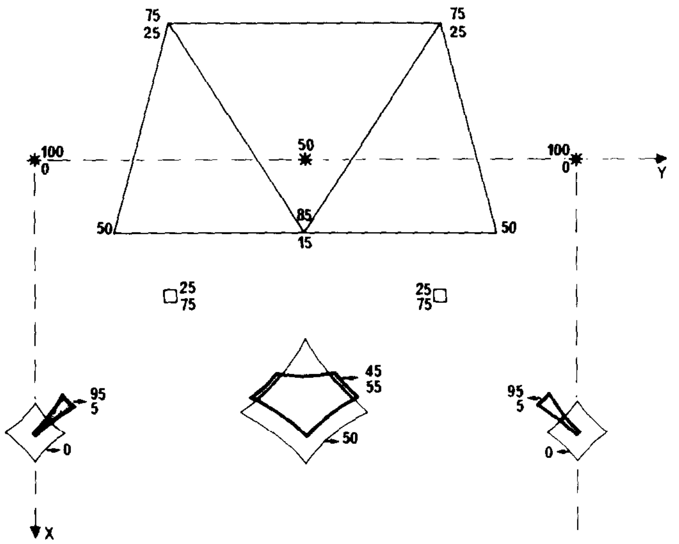

FIG. 5. Possible anionic positions generated inside a $Ca_{1-x}Y_xF_{2+x}$ cell ($\langle a_F \rangle$ = 5.50 Å) by the transformation of a CaF_8 cube into an YF_8 ideal square antiprism (all F–F edges equal to 2.75 Å). Symbols for vacancies and atoms are the same as in Figs. 1, 2, and 4, but for reasons of clarity the four cations at 1/2, 0, 1/2–1/2, 1, 1/2–1/2, 1/2, 0, and 1/2, 1/2, 1, have been omitted. Only the ideal square antiprism YF_8 and the possible F″-zones near ideal cubic (1/2, 1/2, 1/2, and 1/2, 0, 0) sites are outlined.

be labeled according to Willis, 4 : 4 : 5. This cluster is delimited within the fluorite cell in Fig. 2 and so can be compared to the 2 : 2 : 2 cluster. It must be pointed out that, in spite of a locally denser packing of anions, the too short F′–F′ distances characteristic of the 2 : 2 : 2 and 3 : 4 : 2 clusters are now avoided.

A possible polyhedral model, built up around such a 4 : 4 : 5 anionic cluster is schematically drawn on Fig. 6. The YF_8 square antiprism is surrounded on its sides by four voluminous MF_{10} polyhedra suitable for calcium atoms as quite similar to the CaF_{10} "centaur polyhedron" found for the Ca(2) atoms in tveitite (*30*) and which can be described as the combination of a half cube (on the side of the fluorite-type matrix) and a half icosahedron (on the side of the antiprism). This polyhedron derives from a primitive fluorite cube by substitution of a triangular face composed of one F″ and two F′ interstitials, for one F-corner. In front of its rotated square face, the YF_8 square antiprism connects to four complex polyhedra (three MF_{10}, one MF_9) preserving six F-corners of the primitive cube, the two others being replaced by one F′-corner and either two or three F″-corners. These latter polyhedra are suitable as well for Ca atoms as for Y ones.

Such a $(Ca,Y)_9F_{49}$ cluster—or more accu-

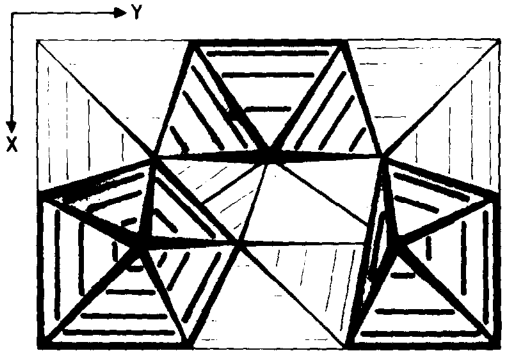

FIG. 6. Polyhedral model of the 4 : 4 : 5 cluster. Only the lower part is shown, i.e., the six anionic polyhedra around cations at levels z = 0 (light) and z = 1/2 (shaded).

rately $Ca_4Y_5F_{49}$ if we assume, which is quite reasonable, that the cluster is electrically neutral—which in terms of both external shape and volume, is virtually identical with the Ca_9F_{44} unit of fluorite, can be readily incorporated within a fluorite matrix without any important steric constraints. We think that it constitutes the simplest and densest way to accommodate excess anions in fluorite solid solutions. Obviously, all the possible F″ interstitial sites are not necessarily simultaneously occupied, particularly in phases like calcium yttrofluorites with relatively close-packed anionic subcell, and less dense 4:4:4 ($Ca_5Y_4F_{48}$), 4:4:3 ($Ca_6Y_3F_{47}$), 4:4:2 ($Ca_7Y_2F_{46}$), and 4:4:1 (Ca_8YF_{45}) neutral clusters can exist. As the ratio of F′ interstitials to F″ ones is changing drastically from one cluster to another, experimental occupation numbers for normal F and interstitial F′ and F″ fluorine atoms, should indicate without ambiguity which of them is actually present in the $Ca_{1-x}Y_xF_{2+x}$ solid solution.

We can clearly see in Table I that the occupation numbers predicted on the basis of a 4:4:3 cluster are in very good agreement with those observed by Cheetham *et al.* (*18*) for all compositions except the $x = 0.25$ one. Close examination of refined parameters reported by these authors, however, reveals that for this latter composition and without any apparent reasons the *u* and *w* positional parameters of, respectively, F′ (1/2, *u*, *u*) and F″ (*w*, *w*, *w*) interstitials, are far more different from the mean values ($u \simeq 0.37$ and $w \simeq 0.41$) than for the other compositions.

Supposing that these anomalies could be the consequence of constraints imposed by Cheetham *et al.* both to B_F temperature factors and to M_F occupation numbers of fluorine atoms during the refinement of structural parameters defining the contents of the average $Ca_{1-x}Y_xF_{2+x}$ unit cell, we decided on the basis of Cheetham *et al.* data to carry out new refinements of these parameters. The computer program used was an improved version of the special program elaborated for powder data by Perez and Saux (*44*). The refinements were performed for samples with composition $x = 0.15$, $x = 0.25$, and $x = 0.32$, in the same conditions as Cheetham *et al.*, with the same neutron scattering length, but by giving now a separate temperature factor *B* to each kind of fluorine atoms. In each case they converged quite well to satisfactory *R* values which are given with final parameters and previously reported ones on Table IV.

Although no significant changes can be observed for $x = 0.15$ and $x = 0.32$ compositions, the positional parameters and the occupation numbers of F′ and F″ atoms are greatly modified for the $x = 0.25$ sample. The anomaly observed for this composition has disappeared, the set of new values being now perfectly homogeneous, and we can see on Table I that the revised occupation numbers are now in perfect accordance with the calculated ones for a 4:4:3 cluster. Such a cluster ($Ca_6Y_3F_{47}$) is shown in Fig. 7, with the three Y atoms distributed around a three-fold axis of the fluorite cell.

Conclusions

The transformation within a fluorite-type matrix of a cube into a nearly perfect square antiprism, or a homologous polyhedron, and the correlative polyhedral 4:4:3 cluster generated, provide a short-range order model perfectly suitable for the whole range of compositions observed in the $Ca_{1-x}Y_xF_{2+x}$ solid solution and probably in the other $Ca_{1-x}Ln_xF_{2+x}$ solid solutions. Such a flexible model, which can also generate 4:4:4 and 4:4:5 clusters, can respectively account for $x = 0.33$, $x = 0.44$, and $x = 0.55$ anion excess without any covering of these clusters (maximum of anion excess observed corresponds to $x = 0.50$ for CaF_2–SmF_3 system (*2*)). It is in accordance with spectroscopic (*10–12*), dielec-

TABLE IV

REFINED STRUCTURAL PARAMETERS FOR $x = 0.15, 0.25, 0.32$ SAMPLES OF $Ca_{1-x}Y_xF_{2+x}$ SOLID SOLUTION

	$x = 0.15$		$x = 0.25$		$x = 0.32$	
Composition	a	b	a	b	a	b
$B_{Ca,Y}$	0.76(8)	0.78(8)	1.18(7)	1.20(7)	1.43(7)	1.42(7)
M_F	1.81(2)	1.81(2)	1.62(2)	1.65(2)	1.54(2)	1.54(3)
B_F	1.17(5)	1.17(6)	1.40(6)	1.41(6)	1.78(6)	1.79(6)
$u_{F'}$	0.360(6)	0.359(7)	0.381(2)	0.362(3)	0.368(5)	0.372(6)
$M_{F'}$	0.21(3)	0.21(5)	0.47(2)	0.34(3)	0.48(4)	0.48(5)
$B_{F'}$	1.17(5)	1.17(8)	1.40(6)	2.01(7)	1.78(6)	2.39(7)
$w_{F''}$	0.411(5)	0.412(6)	0.359(6)	0.413(6)	0.410(4)	0.408(5)
$M_{F''}$	0.13(4)	0.13(5)	0.16(3)	0.26(5)	0.30(4)	0.30(5)
$B_{F''}$	1.17(5)	1.15(7)	1.40(6)	1.94(8)	1.78(6)	2.67(8)
$R = \Sigma \lvert I_0 - I \rvert / \Sigma I_0$	0.017	0.017	0.022	0.019	0.024	0.017

Note. (a) Cheetham *et al.* results (*18*); (b) our results. F = normal fluorine atoms; F′ = interstitials $(1/2,u,u)$; F″ = interstitials (w,w,w). Occupation numbers M are given as the contribution to $2 + x$ in the formula $Ca_{1-x}Y_xF_{2+x}$.

tric (*5–9*), and anionic conductivity (*45, 46*) experiments.

This model is proposed for $Ca_{1-x}Y_xF_{2+x}$ samples prepared at high temperature (*18*): each CaF_2–YF_3 mixture was fired twice under vacuum at 1100°C for 24 hr, then annealed under HF at 700°C for 36 hr and then quenched. However, this model is not contradictory with the existence of ordered microdomains as observed by Greis (*38*) for longtime annealed, highly doped $Ca_{1-x}Ln_xF_{2+x}$ samples $(0.33 < x < 0.45)$. These microdomains, too small to be revealed by X-ray diffraction, are probably of the same nature as the corresponding *t*, *rhδ*, *rhα* superstructure phases, i.e., they are based on M_6X_{37} (or 8 : 12 : 1) clusters. For an anion excess of more than $x = 0.33$, strong interaction can occur between 4 : 4 : 3 clusters, making easier the cation diffusion, which is obviously the limiting process for ordering at low temperatures. In proportion to the aggregation of YF_8 antiprisms, the number of F′ interstitials increases while the number of F″ interstitials readily decreases, and it can easily be imag-

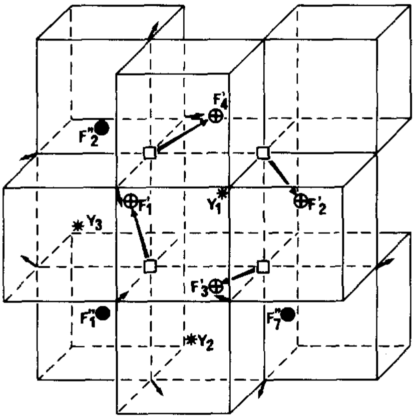

FIG. 7. One of the most probable short-range order model for the 4 : 4 : 3 cluster (6 Ca, 3 Y, 4□, 4 F′, 3 F″). The large cubes represent fluorite-type filled cubes of normal fluorine atoms. Only the three Y_1, Y_2, and Y_3 cations, distributed around a three-fold axis of the fluorite cell are shown. The three F″ interstitials are in a nearest-neighbor (*nn*) position with respect to Y_2 and Y_3 atoms. The long arrows illustrate the mechanism of cooperative diffusion of four normal F atoms toward F′ interstitial sites, corresponding to the transformation of a cube into a square antiprism. The short ones indicate the direction of the slight relaxation movements of some normal F atoms necessary to avoid too short F–F″ distances (Symbols for atoms and vacancies are the same as in Figs. 1, 2, and 4.)

ined that a convenient association of two 4 : 4 : 3 clusters leads to a 8 : 12 : 1 cluster. It is probable that neutron diffraction experiments carried out on highly doped $Ca_{1-x}Y_xF_{2+x}$ samples, annealed for long and different times at low temperature, would provide interesting information about short-range to long-range order transition.

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