

ASSOCIATION OF POINT DEFECTS IN NON-STOICHIOMETRIC $M_{1-x}R_xF_{2+x}$ FLUORITE-TYPE SOLID SOLUTIONS

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The review of cluster problem in solid solutions of rare-earth trifluorides (RF_3) in difluorides (MF_2) with fluorite-type structure has been made. The proposed cluster models, methods of their investigation, most likely cluster types for various combinations of RF_3 and MF_2 as well as percolation problem in $M_{1-x}R_xF_{2+x}$ solid solutions have been considered. Some perspective lines of investigations have been formulated.

FLUORITE STRUCTURE: POINT DEFECTS

The existence of anomalously wide areas of heterovalent solid solutions in $MF_2 - RF_3$ systems based on difluorides which have fluorite structure raises a problem of a defective structure of those solid solutions, precisely, a problem of the interaction of structure defects at a high concentration of the latter leading to formation of complicated complexes of defects, i.e., associates or clusters.

The association of structure defects in those solid solutions is to be expected according to the Pauling crystallochemical law of electrovalency local compensation.¹

In reality R^{3+} ion instead of M^{2+} ion gets into MF_2 lattice and carries an excess positive charge to be compensated. Such compensation can be effected either by formation of cation vacancies:



or by introduction of additional fluorine-ions into the fluorite lattice:



The experiments confirmed repeatedly the second scheme proposed by Goldschmidt² by study of density (for example, see³). Nevertheless, full quantitative coincidence with predictions of model 2 is not observed.^{4,104}

The realization of the electrovalency compensation mechanism through additional fluorine-ions rather than cation vacancies makes sense because of the type of intrinsic point thermostimulated defects typical for the type of fluorite. Formation of anti-Frenkel atomic defects is characteristic of all fluorite-type compounds. The defects involve displacement of fluorine ions from normally occupied positions 8c of space group Fm3m to positions 4b (the centres of hollow anion inbes in the lattice, Fig. 5, Table 1)*.

As the temperature increases and point defects accumulate, the defects start interacting which results in disorder of the anion sublattice and diffuse phase transition with abnormal physical properties^{5,6,7,8}.**

Goldschmidt (in 1926) supposed that it was precisely in position 4b that interstitial fluorine ions penetrated in the course of formation of solid solutions $M_{1-x} R_x F_{2+x}$. In this case two variants of location of an interstitial fluorine ion near a trivalent cation are possible. They are as follows: the position of a nearest neighbour (nn-dipole) having tetragonal symmetry C_{4v} and the position of the next ion following the nearest neighbour (nnn-dipole) having trigonal symmetry C_{3v} . Such dipoles have been found genuinely by an electron spin resonance method,⁹⁻¹¹ laser spectroscopy¹²⁻¹⁵, ionic thermocurrent^{16,17} in highly diluted solid solutions RF_3 in MF_2 .⁹⁻¹¹ It is found that, as a rule, in each specific system one type of dipole dominates. And at a small difference in ion radii of cations M^{2+} nn-dipoles are more stable, the stability of nnn-dipoles grows with increase of M^{2+} radius and decrease of R^{3+} radius. The same has been confirmed by energy calculations as well.¹¹ So, nn-dipoles dominate in CaF_2 systems and nnn-dipoles are dominant for BaF_2 ; the transition from nn- to nnn-dipoles takes place in series $SrF_2:RF_3$ and $PbF_2:RF_3$ with decrease of ion radius R^{3+} . The energy given out during formation of a dipole makes $E_A = 0.3 - 0.8$ eV.

* The schemes of various crystallochemical positions occupied by fluorine ions in the fluorite structure are represented in Fig. 5 and Table 1. In literature there is a wide disagreement in the system of notations of various types of interstitials. The given work (similarly to^{43,31}) follows the notations corresponding to the crystallographic notations for space group Fm3m.

** There exists relationship $T_2 = 0.009T_1^{1.61}$ between absolute melting point T_1 and difluoride phase transition T_2 .¹¹⁴

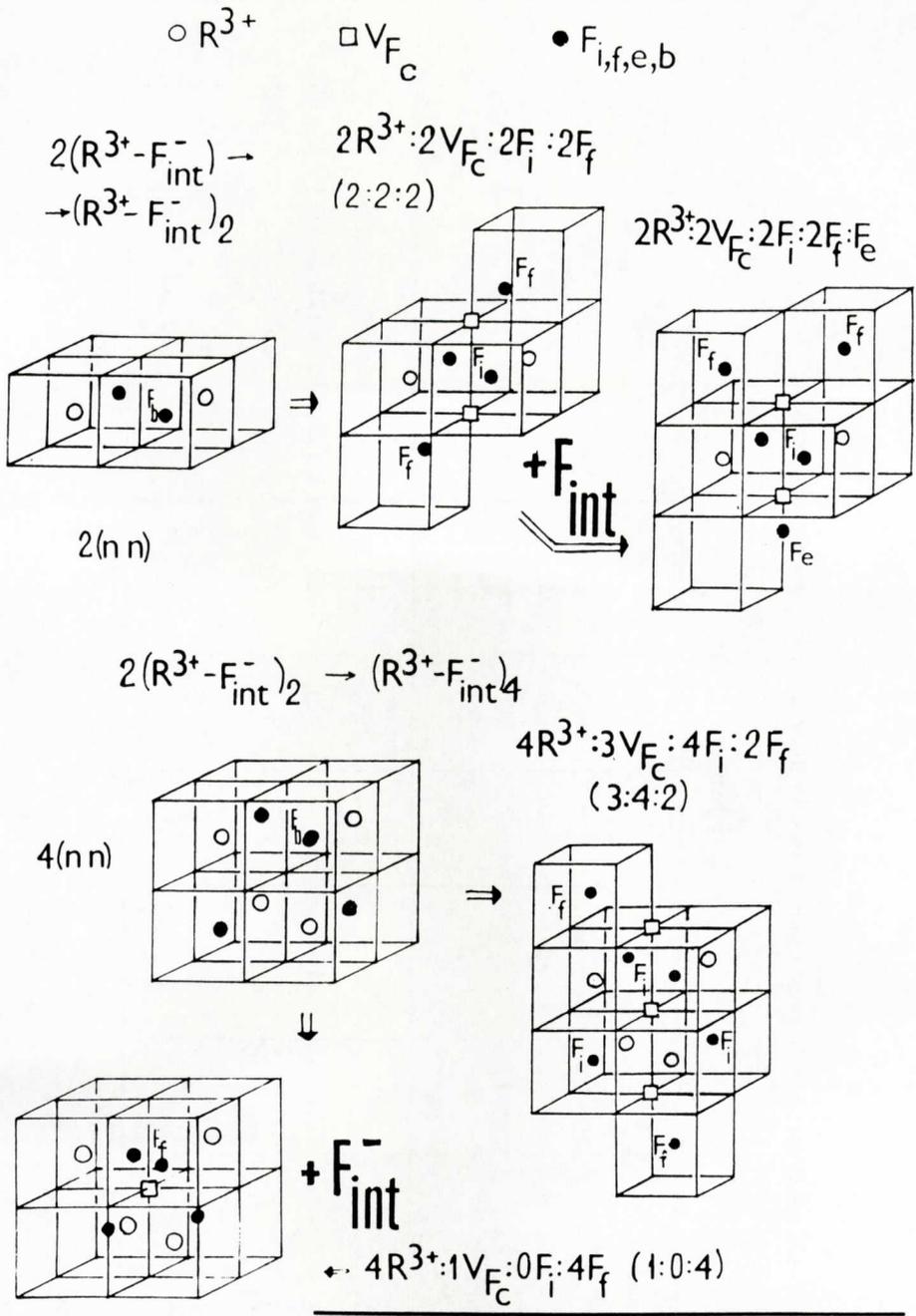


Fig. 1. Association of $R^{3+} - F_{int}^-$ nn-dipols with following relaxation of anionic sublattice.

Table I. Positions which may be occupied by F-ions in fluorite lattice, space group $Fm\bar{3}m$.

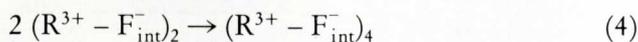
Our notations	Other systems of notations						Coordinates	Multiplicity
	Bendall, Catlow 1984 ¹⁸	Cheetham, Fender 1971 ¹⁹	Lucat, Portier 1980 ²⁰	Golubev, Simonov 1986 ²¹	Pontonnier, Parrat 1983 ²²	Ito, Koto 1986 ²³		
F_c	-	F^n	F_I	$F(1)$	$F1$	F_I	1/4 1/4 1/4	8
F_i	F_i	F'	F''_I	$F(2)$	$F3$	F''_I	u u 1/2	48
F_f	F_i	F''	F''_I	$F(3)$	$F2$	F'_I, F''_I	v v v	32
F_b	F_i						1/2 1/2 1/2	4
F_e	F_i						1/2 1/2 w	24

At high temperatures when the energy of thermal motion becomes comparable to the association energy, dissociation of dipoles, i.e., the displacement of an interstitial fluorine-ion from the positions nearest to cation to the crystal body, is possible and the first stage of dissociation is an "excited dipole" having a monoclinic symmetry.¹⁰

Nevertheless, the real structure of even diluted solid solutions $M_{1-x} R_x F_{2+x}$ is very complicated: as much as 5 types of relaxations³⁶ are observed in spectra of dielectric losses in solid solutions $M = Ca, Sr, Ba$ having $x = 0.001$, as much as 16, 9 and 7 types of various defect complexes have revealed in solid solutions of ErF_3 in CaF_2, SrF_2, BaF_2 , respectively, by laser spectroscopy.¹⁴ The relationships of the properties and RF_3 concentrations testify that the concentration of dipoles peaks and then decreases. The maximum concentration of dipoles takes place, for example, at $x = 0.001$ for $Ca_{1-x} R_x F_{2+x}$ ($R = Er,^{12,15,58} Ce^{59}$), $Ba_{1-x} Gd_x F_{2+x}$.⁶⁰

CLUSTERS: METHODS OF STUDY AND MODELS

The first explanations of the complicated nature of optical rare-earth centres in single crystals $M_{1-x} R_x F_{2+x}$ have been based on the idea of the association of dipoles $R^{3+} - F_{int}^-$ in a matrix through electrostatic forces. The first models of clusters containing 2 and 4 rear-earth elements have been proposed by Osiko and others,^{24,41,13} Table II:



In those models it has been assumed that interstitial ions occupy the centres of cubic voids in fluorite lattice (F_b) and the relaxation of the anion sublattice as a result of such association has not been considered yet. It has been done later by Catlow,^{26,61} see Fig. 1.

In 1969 to explain the abnormal growth of the number of simple cubic centres of ions R^{3+} with RF_3 concentration in solid solutions, there has been proposed also an idea of the existence of large clusters which unite rear-earth element ions and interstitial fluorine ions which incorporate into fluorite lattice in blocks.⁵⁷ As a result, areas depleted by impure ions appear in the matrix. To explain the existence of optical centres having a cubic symmetry, the cluster has been proposed by O'Hare as well,²⁵ Table II.

The progress in the study of the defect structure of fluorite solid solutions $M_{1-x} R_x F_{2+x}$ is related to diffraction methods. Just the first direct ex-

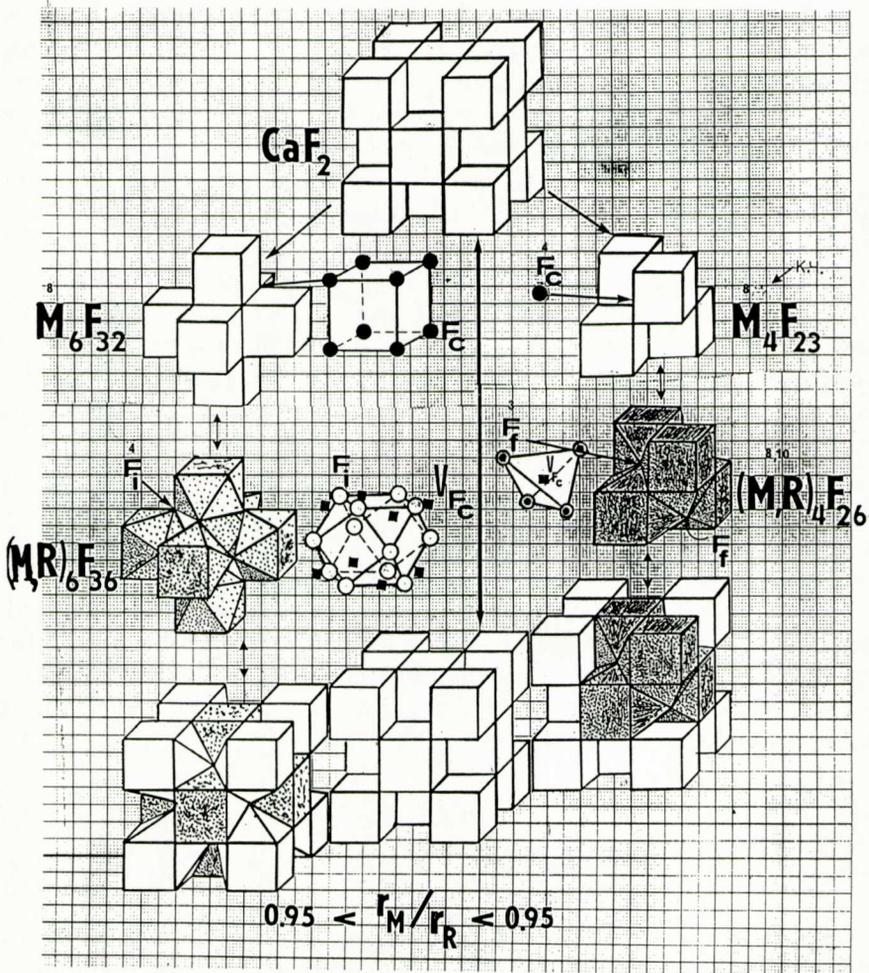


Fig. 2. Block-type isomorphic substitution in the fluorite lattice (Fig. made by B. P. Sobolev).

perimental investigation of the structure of concentrated solid solutions $\text{Ca}_{0.6}\text{Ce}_{0.4}\text{F}_{2.4}$ by an X-ray diffraction on a single crystal conducted by Soviet researchers³² have disclosed a sharp distinction from the Goldschmidt scheme. Interstitial fluorine ions do not occupy positions in the centres $(1/2, 1/2, 1/2)$ of hollow fluorine cubes but they are displaced along the axis $< 111 >$ by approximately 0.42 from these positions (positions F_i); vacancies have been revealed in the basic anion lattice. The works of the English researchers on the diffraction of neutrons on single crystals and powders $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ ^{19,33} reveal the displacements of interstitials in

two directions: $\langle 110 \rangle$ and $\langle 111 \rangle$ (positions F_i and F_f , respectively). Those results have been immediately rationalized by assuming the existence in solid solutions cluster defects (Table II) whose type varies with the composition of solid solutions.

During the years that followed a number of structure studies of solid solutions $M_{1-x} R_x F_{2+x}$ has been initiated and performed both on single crystals and powders of diffractions of neutrons and X-rays (see, for example, ^{20,23,30,31,43-46,56} and Alexandrov's revue for the given symposium).

In the main it has been informed as to the availability of occupied positions F_i and F_f and, as a rule, $u \approx 0.13$, $v \approx 0.4$. The position on fourth-order axis F_c has been revealed (along with F_f) at scattering of protons from single crystal $Ca_{0.99} Gd_{0.01} F_{2.01}$,⁵¹ while position F_b in the centre of a cubic fluorine void in CaF_2 has been found for saturated solid solution $Ba_{0.5} Ce_{0.5} F_{2.5}$.⁴⁴

It is a very important and rather delicate subject to reveal the nature of point defects and their quantity. The matter is that essentially different models of defects have sufficiently close and low values of R-factor. According to the experimental data it is very difficult to distinguish the displacement of fluorine ions from the principal positions through anharmonicity of thermal oscillations. At low site occupancies the respective peaks on the electronic (nuclear) density maps may be lost in the background.

In the work¹⁹ dealing with solid solution $Ca_{1-x} Y_x F_{2+x}$ two positions (F_i and F_f) have been given as the most probable ones because of the supposition that there exist clusters similar to those previously found in fluorite solid solution UO_{2+x} ,⁶² and obtained value $R = 2.3\%$ for single crystal having $x = 0.06$ is good. Nevertheless, the recalculation of the experimental data¹⁹ for composition $Ca_{0.94} Y_{0.06} F_{2.06}$ made in the works⁶³ and³⁰ has showed that the better convergence is attained when pure F_i -position having an anisotropy of thermal oscillations is assumed. New decoding of the structure of single crystal $Ca_{0.9} Y_{0.1} F_{2.1}$ ⁶⁴ has confirmed the presence of pure F_i -position. In the light of this the results of determination of the defect structure conducted with the use of powders should be considered unreliable, for example, the data²⁰ where R-factor is equal to 2,5-5%.

For crystal $Ba_{0.73} Pr_{0.27} F_{2.27}$ at 293 °K additionally fluorine ions are observed in F_i -position.⁴³ However, at 573 °K ellipsoids of thermal oscillations F_i grow and the peak is observed on the map showing the difference in the nuclear density in position F_f . The peak can interpreted as straddling of the wings of three peak from F_i bound by symmetry.⁶⁵

In the whole, the obtained data testify that in many cases practically pure positions F_i and F_f are present in concentrated solid solutions. Point defects of this type are called crystallochemical localized defects.⁶⁶

To our opinion, the works of Catlow^{26,61} are the clue for understanding the results of diffraction experiment. Catlow has shown by calculation in the model of incompressible ions that as a result of electrostatic interaction of two nn-dipoles relaxation of the fluorite lattice takes place, vacancies appear in anion sublattice and considerable displacement of both *basic* and interstitial fluorine ions along axes $\langle 110 \rangle$ and $\langle 111 \rangle$ is observed. The configuration obtained is much the same as 2:2:2 cluster (number of vacancies : number of F_i : number of F_f)^{*}, proposed in,¹⁹ stabilized by two cations R^{3+} (Fig. 1).

One more line of fruitful approaches to the study of the cluster structure of disordered solid solutions $M_{1-x} R_x F_{2+x}$ is to use the data on the structure of ordered phases. According to the third thermodynamics law at the temperature drop solid solutions should decompose either into components or with formation of ordered stoichiometric compounds. The first variant takes place, particularly, in systems $CdF_2 - RF_3$ and $MF_2 - RF_3$ ($M = Ca, Sr, Ba, Pb, R = La - Nd$).⁶⁷⁻⁷¹ In other systems $MF_2 - RF_3$ a set of ordered phases^{67-69,72,73} is observed, part of them is provided with structure decoding (see the revue and classification in^{72,21,55}). It is found that all those compounds $Ca_{14} Y_5 F_{43}$,⁵³ $Pb_4 R_3 F_{17}$,⁵⁴ $Ca_2 RF_7$,^{21,55} $Ca_{7+\delta} R_{7-\delta} F_{32-\delta}$,⁷² have the fragments of the structure consisting of 6 ions R^{3+} located over the octahedron and 12 fluorine ions occupying the vertices of the cubo-octahedron, in positions F_i as to space group $Fm\bar{3}m$ while 8 positions F_c are vacant. There is an void in the centre of the cluster. The void can accommodate one or two fluorine ions (or an ion of oxygen), inconsiderably displaced from the centre of the void and the energy barrier of passages of fluorine-ions inside the cluster over the equivalent positions (eight ones in case of displacement along $\langle 111 \rangle$) is very low. Fig. 2 shows the rearrangement of the fragment of fluoride structure $M_6 F_{32}$ in formation of such cluster, type $R_6 F_{36}$ (with unfilled void), $R_6 F_{37}$ and $R_6 F_{38}$ (with one or two fluorine-ions inside the cluster).

As the transition from ordered phases to disordered high-temperature solid solution is accompanied, according to the thermal analysis data, by small thermal effects, it may be assumed that disorder is not accompanied by destruction of clusters but only by disorder relative to one another.

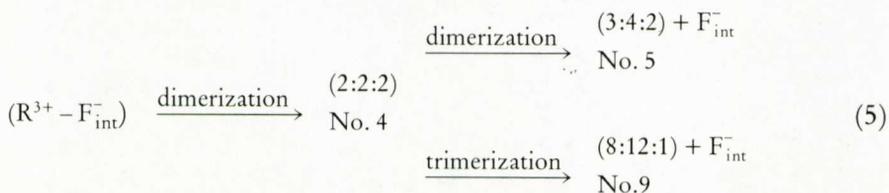
* In the main, it is this system of cluster notations and their numbers according to Table II that are used in the work. Notations¹⁸ $i/v/p/q_1s_2$ (where i is the number of trivalent substitute ions, v is the number of anion vacancies, p is the number of relaxed lattice anions, q is the number of interstitials in nn-positions, s is the number of interstitials in nnn-positions) are very convenient to be used in calculations of electrostatic relaxation as they are related to the initial configuration of defects but they are very inconvenient to be used for comparing with the experiment.



Fig. 3. A two-dimensional model of a defect crystal with the block-type isomorphism.

Ease of substitution of such fragments in fluorite solid solutions has been noted in.^{27,55} Such clusters are nominated as 8:12:0, 8:12:1 and 8:12:2, respectively, Nos 8-10, Table II. It is necessary to note that the charge of clusters $R_6 F_{36}$ and $R_6 F_{37}$ differs from fragment $M_6 F_{32}^{20-}$ they substitute in the structure and to compensate for the charge, one or more additional fluorine ions should be present in the lattice near such cluster.^{37,38,105}

Formation of $R_6 F_{36-38}$ clusters can be considered as trimerization of clusters 2:2:2 followed by relaxation which makes it possible to give a picture of associations of dipoles $R^{3+} - F_{int}^-$ in the fluorite lattice.⁷⁴



A limitation of this scheme, nevertheless, is the fact that clusters 2:2:2 appear through dimerization of nn-dipoles whose abundance in real systems at low concentration of RF_3 does not always correlate with F_i ions and octahedral clusters at high concentrations of RF_3 .

The assumption of the existence of clusters, type $R_6 F_{36-38}$, in solid solutions $M_{1-x} R_x F_{2+x}$ explains very well the availability of one type of additional positions F_i revealed by the diffractions experiment.

The availability of homogeneity areas in ordered fluorite-type phases and certain structure data cause to assume the possibility of partial substitution of M^{2+} and R^{3+} in such clusters with formation of the following groups: $(MR_5 F_{36})^{19-}$, No. 14; $(MR_5 F_{37})^{20-}$, No. 13; & $(M_2 R_4 F_{36})^{20-}$, No. 11.^{72,55,38} Clusters No. 13 and No. 11 have the same charge as the substituted fragment of the fluorite lattice. Cluster No. 11 comprises 4 ions R^{3+} located in the vertices of the square. Notation CuAu is proposed for this cluster in²² and notation Cu_3Au is proposed for cluster $R_6 F_{36}$ based on the nature of ordering cations in the cubic face-centred lattice.

The energy calculations^{18,42} confirm the possibility of associations of defects in a fluorite matrix with formation of clusters, type $R_6 F_{36-37}$ as well as their defect forms $MR_5 F_{36-37}$. Clusters, type $R_6 X_{36}$ are revealed also in several intermetallic compounds having fluorite-related structures.⁷⁵

A certain information on the existence of clusters in solid solutions $M_{1-x} R_x F_{2+x}$ is given also by other physical methods, see Table III. Among other things, ESR³⁴ and NMR¹⁹ $F^{90,35}$ methods reveal microinhomogeneous, heterogeneous (from these methods) structure of concentrated solid solutions $M_{1-x} R_x F_{2+x}$ with large (from the atomic sizes) regions contain-

Table II. Cluster models for $M_{1-x}R_xF_{2+x}$ solid solutions.

Nos	Numbre						Excess (lacking) charge	Symbols ¹⁸	References	Ref. Nos
	R ³⁺	V _{Fc}	F _i	F _f	F _e	F _b				
1	2	0	0	0	0	2	-	Osiko, 1965	[24]	
2	4	0	0	0	0	4	-	Osiko, Shcherbakov, 1971	[41]	
3	4	0	0	0	1	0	-	O'Hare, 1972	[25]	
4	2	2	2	2	0	0	2/0/2/2 ₁	Cheetham, 1971 - Catlow, 1973	[19] - [26]	
5	4	3	4	2	0	0	4/1/2/4 ₁	- " -		
6	?	19	24	7	0	0	-	Cheetham, 1971	[19]	
7	?	16	18	10	0	0	-	- " -		
8	6	8	12	0	0	0	6/0/8/4 ₁	Bevan, Greis, 1980	[27]	
9	6	8	12	(1)	0	0	6/0/8/5 ₁	- " -		
10	6	8	12	(2)	0	0	6/0/8/6 ₁	Bendall, Catlow, 1984	[18]	
11	4	8	12	0	0	0	4/0/8/4 ₁	- " -		
12	4	8	12	(1)	0	0	4/0/8/5 ₁	Catlow, Chadwick, 1989	[42]	
13	5	8	12	(1)	0	0	5/0/8/5 ₁	Bevan, Strachle, 1982	[53]	
14	5	8	12	0	0	0	5/0/8/4 ₁	Catlow, Chadwick, 1989	[42]	
15	2	2	2	2	1	0	2/0/2/3 ₁	Catlow, Chadwick, 1983	[28]	
16	5	4	4	5	0	0	-	Laval, Frit, 1983	[29]	
17	4	4	4	4	0	0	-	- " -		
18	3	4	4	3	0	0	-	- " -		
19	2	4	4	2	0	0	-	- " -		
20	1	4	4	1	0	0	-	- " -		
21	3	1	0	4	0	0	3/0/1/3 ₁	Bendall, Catlow, 1984	[18]	
22	4	1	0	4	0	0	-	Maximov, Muradyan, 1986	[30]	
23	2	1	0	3	0	0	-	Laval, Abaouz, 1989	[46]	
24	10	20	0	24	6	0	-	Tsytsenko, Frank-Kamenetskaya, 1987	[31]	
25	?	2	0	4	0	0	-	Ito, Koto, 1986	[23]	
26	?	2	2	0	0	0	-	- " -		
27	24	8	0	32	0	0	-	Loshmanov, Maximov, 1989	[113]	

Table III. Methods of cluster investigation in solid solutions.

Nos	Methods	References	Information
1	Single crystal X-ray diffraction	32, 56	Positions of interstitial anions, numeral relation between numbers of anionic vacancies and various types of interstitial anions
2	Powder neutron diffraction	20, 45, 46	
3	Single crystal neutron diffraction	19, 43, 44, 113	
4	Neutron scattering	48	
5	Proton scattering	51	
6	EXAFS	42, 115	Coordinate numbers, inter-atomic distances, polihedra
7	Small-angle scattering	33	Size and shape of particles
8	Structure of ordered phases	53-55	Specific cluster models
9	Optical spectroscopy	13, 47	Types and symmetry of cationic centres
10	Laser spectroscopy	14, 15	
11	ESR	34	
12	NMR	35	
13	Dielectric relaxation	36, 49, 50	Types of defects dipolar centres, activation energy of relaxation
14	Ionic thermocurrent	39, 40, 52, 16	
15	Ionic conductivity	37, 38	Percolation threshold, size of defect areas
16	Computer simulation	18, 26	Comparison of energetic stability of various clusters Evaluation of activation energy of relaxation

ning only rare-earth trifluorites. For example, for crystals $\text{Sr}_{0.75}\text{Nd}_{0.25}\text{F}_{2.25}$ in case of random distribution of cations in the lattice each fluorine ion should have neodimium ion (the coordination number of fluorine-4) in the first coordination sphere. Nevertheless, in the NMR spectrum (Fig. 4)³⁵ there is a powerful component corresponding to SrF_2 in chemical shift, which does not obey the Curie-Weiss's law and has no orientation dependance, i.e., it is related to the space areas of a crystal containing only a fluorite-type lattice without paramagnetic ions. Besides, the spectrum contains several satellites obeying the Curie-Weiss's law with a distinct orientation dependence, related to ions of fluorine coupled with Nd^{3+} ions.

The list of methods used for investigations of clusters is given in Table III, while the list of proposed cluster models, in Table II. As to the data represented in those Tables, it is necessary to make some comments.

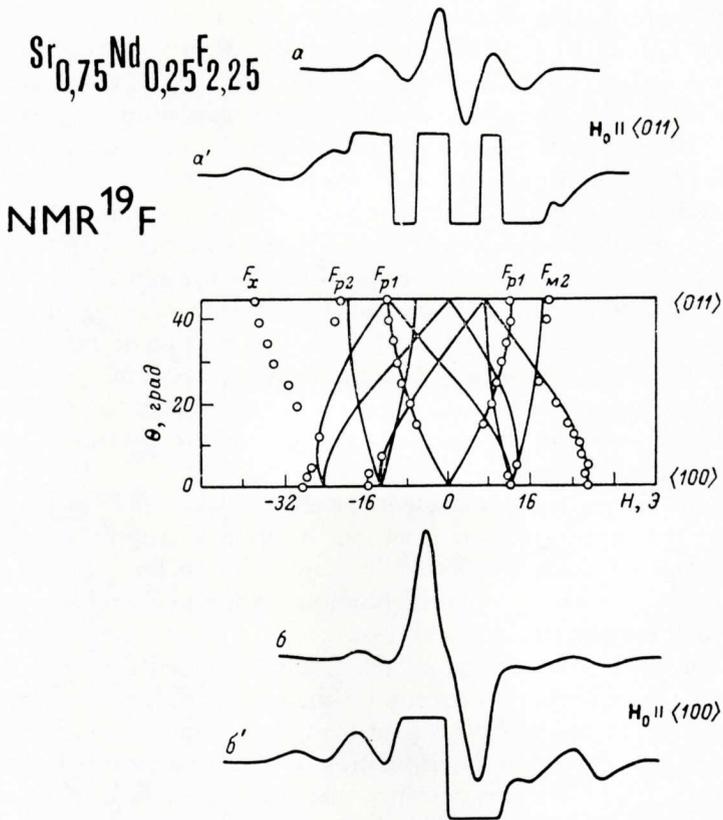


Fig. 4. Spectrum NMR¹⁹F of Single crystal Sr_{0.75} Nd_{0.25} F_{2.25}³⁵.

As seen from Table III, various methods of investigations give complementary information on clusters in solid solutions. Nevertheless, in some cases the interpretation of the data obtained exclude one another.

For example, the data on scattering of neutrons by single crystals Ba_{1-x} La_x F_{2+x} ($x \leq 0.4$)^{48,79} are interpreted as the existence of clusters, type 2:2:2 only, in this solid solution. Nevertheless, the data of the structure work are contradictory to such model (see below).

A number of works by den Hartog and his collaborators^{39,40,76-78,16} hold that formation of clusters counts very little in systems SrF₂ containing trifluorides of large-size rare-earth elements (R - La - Nd) in contrast, for example, to solid solutions SrF₂ and RF₃ (R = Yb, Er, Dy). For single crystals Sr_{0.75} Nd_{0.25} F_{2.25} this conclusion is unambiguously invalidated the NMR¹⁹F data,³⁵ see above. In general decline in the

tendency for formation of clusters has been observed with the increase of ion radius R^{3+} in diluted solid solutions $M_{1-x}R_xF_{2+x}$, for example, by methods of dielectric spectroscopy for series $MF_2 - RF_3$ ($M = Ca, Sr, Pb$), (relaxation R_{III}).^{36,50} The same tendency shows up also in the existence of ordered phases on the phase diagrams. Optical spectroscopy for series of systems $CaF_2 - RF_3$ points to the reverse.¹³

The conclusion of den Hartog is based on the fact that the method of thermostimulated depolarization (ionic thermocurrent) does not reveal specific peaks corresponding to clusters. Den Hartog explains the decrease in the number of dipoles with the concentration (according the data obtained by him) which is naturally interpreted as binding of dipoles into associates⁵⁹ by the fact that only the dipoles which have no other dipoles nearby contribute to dielectric relaxation. The width of the peaks observed coincides well with the calculated one taking into consideration dipole-dipole interaction only.

Nevertheless, the measurements have been taken only at temperatures higher than the liquid nitrogen one. At approximately 21 K an acute peak ascribed to clusters is found in solid solution $Ba_{1-x}La_xF_{2+x}$ ($x = 0.13$).⁷⁹ Besides, criticism of interpretations of the ITC high-temperature peak by den Hartog has been expressed.^{52,81}

In the work¹⁰⁷ of this group the results obtained for solid solution $Sr_{1-x}Ce_xF_{2+x}$ are interpreted already on the base of defect clusters.

The effect of previous heat-treatment of specimens can be one of the cause for disagreements in determination of defect structure of solid solutions $M_{1-x}R_xF_{2+x}$. There is evidence that clusters might be destroyed by annealing at a high temperature followed by quenching.⁸⁰ According to our data the parameters of the lattice of concentrated solid solutions $Ca_{1-x}R_xF_{2+x}$ depend upon the method of synthesis of the specimen, i.e., whether the specimen is obtained by melting or sintering. The effect of heat-treatment on the parameters of the lattice of PbF_2 and solid solutions based on it has been mentioned in.^{109,110} This is an indirect indication of the variation in defect structure.

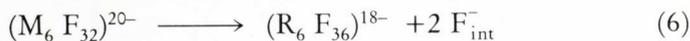
However, the most serious cause of disagreement is apparently an inadequate interpretation of the experiment.

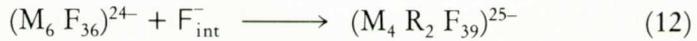
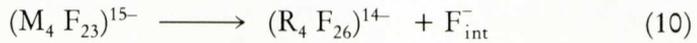
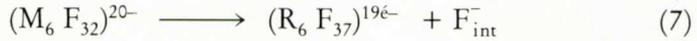
A number of cluster models represented in Table II have been devised specially to ensure the ratio of occupancies of positions F_i and F_f in solid solutions which are not always determined well correctly. In particular, it refers to clusters Nos 16 through 20; they are introduced²⁹ to explain the data¹⁹ pertaining to solid solutions $Ca_{1-x}Y_xF_{2+x}$ which are found later to be incorrect. The same is true about superclusters Nos 6, 7.¹⁹ The nature of clusters Nos 25, 26 is artificial, their stability as well as that of clusters Nos 6, 7, 16 through 20, 24 has not been calculated.

It is some complicated with cluster models comprising positions F_f for the most part as compared with clusters comprising fluorine ions in positions F_i . The point is that ordered fluorite like phases fail to be formed in all systems $MF_2 - RF_3$ where mainly F_f are found in structure $M_{1-x} R_x F_{2+x}$. Minor clusters type 2:2:2 give (except for system $Ca_{1-x} La_x F_{2+x}$) the same quantity of ions F_i and F_f (in the latter case the calculation¹¹ corresponds to the same quantity of F_i and F_e). Introduction and consideration of a charged gettered dimer captured one more fluorine ion (cluster No. 15)¹¹ fail to save the situation: the cluster gives a similar quantity of F_i and F_f at one-half quantity of F_e for systems with CaF_2 and SrF_2 (Fig. 1). The results of the experiment for $Ca_{0.95} La_{0.05} F_{2.05}$ coincide with the calculations for cluster No. 15 in quality only.²⁸ For systems with BaF_2 the configuration of gettered dimer obtained by the calculation is asymmetric and comprises general-position fluorine ion. Those cluster cannot explain the results of structure decoding in which practically pure positions F_f are present. In the work³⁰ a very likely model of cluster 1:0:4 (No. 22) with four ions R^{3+} spaced over a tetrahedron has been proposed. The cluster is charged as compared with the respective fragment of structure CaF_2 . The similar anionic configuration has been calculated in,¹⁸ but with three ions R^{3+} (see Table II No. 21). The data given in⁴⁶ for solid solution $Ca_{1-x} La_x F_{2+x}$ prevent the unambiguous selection of cluster 1:0:4 or similar cluster No. 23 containing only three ions R^{3+} (provided it is electrically neutral). Large-size cluster No. 24 proposed in³¹ explains a primary concentration of additional electron density in positions F_f observed in $Ca_{0.8} Nd_{0.2} F_{2.2}$. However, the experiments fail to prove the assumed existence of positions F_e on the fourth-order axes.

In⁷⁴ a good likeness of the geometry of trigonal cationic nets present both in cubic fluorite lattice and rare-earth trifluoride lattice has been noted (trigonal - tisonite and ortorhombic YF_3). The difference is that the fluorite structure is a three-layer packing of nets while RF_3 structures represents two-layer packings. This points to the fact that large-size "pancakes" of a tisonite-type structure may appear in the fluorite lattice perpendicular to axis $\langle 111 \rangle$. In this case displacement of fluorine ions observed takes place along the third-order axes. Serious disarrangement of the structure has to be observed over the "pancakes" edges. To preserve the general cubic symmetry, it is necessary to suppose statistical arrangement of such fragments perpendicular to all four three-order axes.

The substitution of the fluorite structure for the respective cluster (see Fig. 2, 3) is a block isomorphism in the spirit of Kopp's views back.⁸² Some most probable schemes of substitutions¹⁰⁵ are given below:





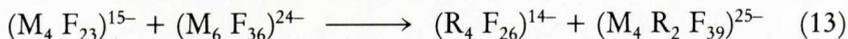
Those schemes correspond to introduction of the following clusters into the fluorite lattice: octahedral clusters Nos 8 and 9– (6) and (7); square cluster No. 11 (9); tetrahedral cluster No. 22 (10); dimer No 24 (11); gettered dimer No. 15 (12).

Table IV. Most probable clusters types for concentrated $M_{1-x} R_x F_{2+x}$ solid solutions.

M	R	Dominant cluster types	Methods of investigations, references
Ca	La – Nd	N 21 or N 23, N 15	N 1 [32, 31]; N 2 [45, 46]; N 3 [64, 28] N 5 [51]; N 6 [42, 115]; N 8 [53, 55] N 10 [80]; N 13 [36, 49]; N 15 [105, 106] N 16 [42, 11, 18]
	Sm – Dy	N 21 or N 23, N 15, N 8, N 13	
	Ho – Lu, Y	N 13, N 8	
Sr	La, Ce	N 21	N 3 [93, 113]; N 12 [35]; N 13 [36] N 14 [17, 52, 40]; N 15 [105, 37] N 16 [18]
	Pr – Ho	N 21, N 13	
	Er – Lu, Y	N 13	
Ba	La – Ce	N 8, ?	N 1 [94]; N 3 [44, 66]; N 4 [48]; N 13 [36] N 8 [69, 72, 21, 55]; N 15 [105, 38]; N 16 [18]
	Pr – Lu, Y	N 8	
Pb	La – Ce	N 21	N 1 [23, 56]; N 8 [71, 73, 54] N 13 [50, 97]; N 14 [17] N 10 [98]
	Pr, Nd, Bi	N 21, N 8	
	Sm – Lu, Y	N 8	
Cd	La – Nd	?	N 9 [103]; N 12 [101]; N 15 [102]
	Sm – Dy		
	Ho – Lu, Y		

Schemes (8) and (9) as well as introduction of any other cluster with a charge equal to that of the lattice fragment into the lattice represent a classical version of a block isomorphism. Introduction of a charged cluster (as compared with isomorphic structure fragment) into the lattice is a new version, i.e., block isomorphism with interstition.

A scheme of combined block isomorphism can be conceived as well: for example, combined formation of clusters Nos 22 and 15:



PERCOLATION

The assumption of existence of isolated clusters in solid solution $M_{1-x} R_x F_{2+x}$ comes in conflict with the following fact: through a large concentration area of solid solution the quantities of clusters rapidly grow with concentration of RF_3 , so as to come into space contact forming a single space system ("network") in the crystal. Such physical phenomenon is called percolation.^{83,108} The idea of percolation in solid solutions $M_{1-x} R_x F_{2+x}$ has been put forward practically at the same time in the works^{39,84,85} in the context of the study of their electric conductivity. With introduction of RF_3 into MF_2 the ionic conductivity rises very sharply by several orders till a certain concentration (6-15 mol% RF_3) is reached, then it varies slightly (within one order).^{84-86,37,38} It is naturally to take a sharp deviation on the concentration dependences of the electric conductivity as the percolation threshold. The calculations performed for simple percolating systems have shown that in a three-dimensional system the volumetric fraction of particles at which the percolation threshold comes is about 0.25-0.30.⁸³ Hence, it is possible to evaluate an average size of percolating particles. The respective calculations for $M_{1-x} R_x F_{2+x}$ have given the following results: $v = 0.55 \pm 0.1a^3$ for $Sr_{1-x} La_x F_{2+x}$, $v = 3.5 \pm 0.3a^3$ for $Sr_{1-x} Lu_x F_{2+x}$, where a is the lattice parameter.³⁷ In solid solutions $M_{1-x} R_x F_{2+x}$, however, fluorine-ions forming a part of clusters are rigidly bound with rare-earth cations and should not contribute into the electrical conductivity. On the other hand, clusters penetrating into a fluorite matrix heavily deform the lattice around them. This leads to a more complicated model of "defect regions" which³⁷ consist of a rigid nucleus-cluster and deformed shell within which motion of fluorine-ions is lightened. The cluster periphery can be filled or not filled with additional fluorine-ions depending upon the cluster charge relative to the matrix. This model, in general, is close to the three-phase model calculated in^{87,88} and consisting of a matrix and particles-isolators with a well conducting shell.

The phenomenon of defect region percolation corresponds to creation of a set of continuous paths for motion of fluorine-ions with low potential barriers. The model of defect regions differs in a charged cluster rather than single ion R^{3+} can be located in the dipole centre.

Thus, the percolation threshold determined from concentration dependences of electrical conductivity correspond to contact of the cluster periphery rather than the clusters. Upon further increase of RF_3 concentration the joining of clusters should take place and the clusters associate (condensate) into superclusters. The first models of superclusters which might be of historical interest only (combination of clusters 2:2:2 and 3:4:2) have been proposed in the work.¹⁹ As far as condensation of the most probable tetrahedral (1:0:4) and octahedral (8:12:1, No. 9) clusters, the first of them well admits of association and each of rare-earth ion can belong to two clusters at the same time.¹¹³

In this way there opens a possibility of existence of infinite, including branched as well as closed, chains of clusters type No. 22. A typical closed chain is shown in the work.¹¹³ With condensation of tetrahedral clusters the ratio of the number of vacancies to the number of F_i ions (1:4) does not change, but the supercluster general charge varies.

Octahedral clusters comprising 6 ions R^{3+} cannot condensate so that ions R^{3+} belong to two clusters at the same time. They can associate only through common fluorine-ions of external square faces, precisely, through a common edge or three common vertices. These both cases are observed in the structures of ordered fluorite-like phases.^{21,55} Association through a common face is impossible, as in this case cation packing in fluorite body gets disturbed.

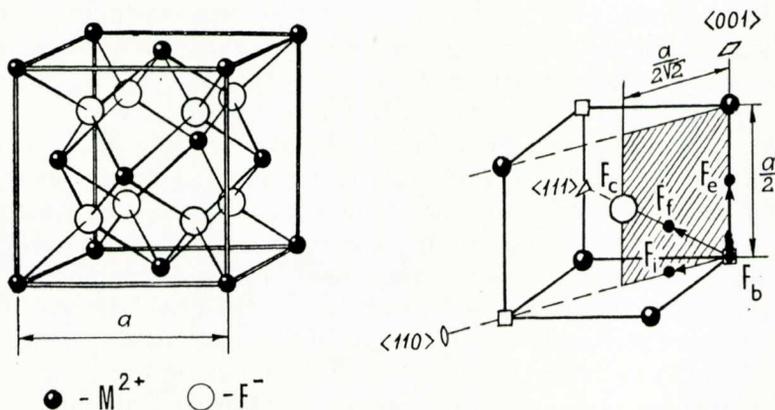


Fig. 5. Fluorite Lattice and Notation of Crystallographic Positions Occupied by Fluorine Ions.

Fig. 6 shows the process of electrical percolation in solid solution $\text{Ba}_{1-x}\text{Nd}_x\text{F}_{2+x}$ investigated by the ionic thermocurrent method.⁸⁹ The activation energy of electrical conductivity corresponds to the high-temperature nonhomogeneous-widened peak of electrical relaxation. The NMR¹⁹F method gives similar information. For example, for systems $\text{CaF}_2 - \text{LaF}_3$ the results⁹⁰ suggests a significant dynamic and structural inhomogeneity of solid solution at 2% of LaF_3 showing up in existence of wide and narrow components of the spectrum with various chemical shifts responding to stiff and migratory fluorine ions in a certain temperature interval. With increase of LaF_3 concentration the difference in the

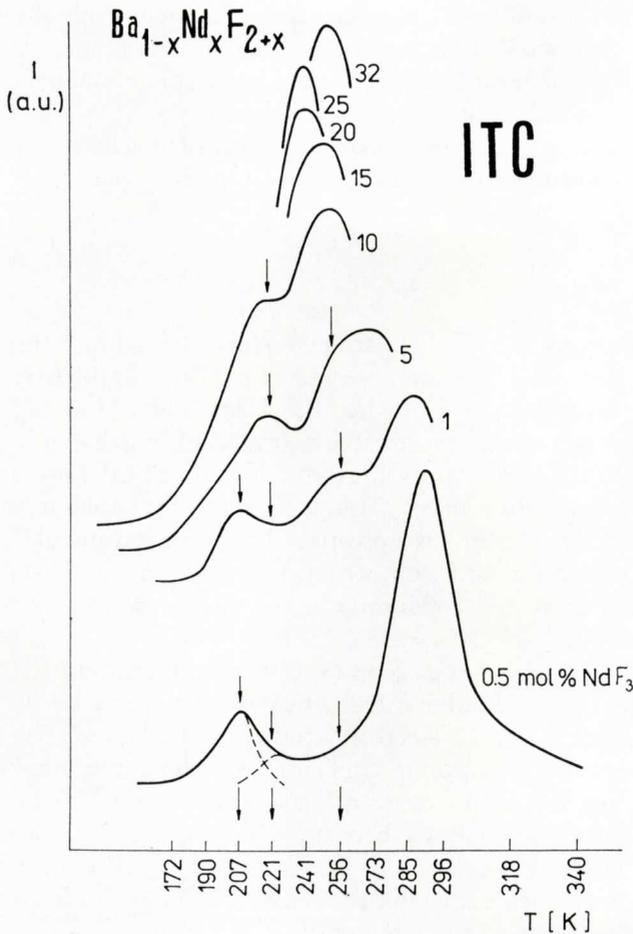


Fig. 6. Ionic thermocurrent of Single crystals of Solid Solution $\text{Ba}_{1-x}\text{Nd}_x\text{F}_{2+x}$,⁸⁹.

chemical shift of those lines decreases and for 35 mol% of LaF_3 it practically disappears which testifies that common dynamically sufficiently homogeneous anionic structure is formed. With increase of LaF_3 concentration, the difference in the energy of activation of fluorine motion in two components decreases as well.

Thus the structure of concentrated solid solutions $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ at $x > 0.15$ is very unusual: the crystals are disordered at the level of blocks approximating an elementary cell in size and the defect regions form a continuous framework. Such type of local disorder is similar to glass in many respects.^{85,112} Nevertheless, taking into account the long-range order (and cubic symmetry), term "antiglass" proposed for similar fluorite-like phases in oxide systems⁹¹ can be used for those materials. When single crystals of solid solutions are obtained from the melt, generally speaking, translational symmetry is distorted as the composition and, respectively, the parameter of the lattice varies over the length of crystal or, to be more precise, quasi-crystal, according to the terminology.⁹²

Now turn our attention to consideration of the defect structure of fluorite solid solutions in separate groups of binary systems.

Systems $\text{SrF}_2 - \text{RF}_3$,³⁸

Solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$ are positively divided into three groups: $\text{R} = \text{La-Ce}$; $\text{R} = \text{Er-Lu}$, Y and intermediate group. In the first group the ionic conductivity sharply rises when RF_3 is introduced into SrF_2 and passes practically over to saturation at $x = 0.12-0.15$ which can be naturally associated with the percolation threshold. The data of the investigations⁹³ point to pure F_f position in $\text{Sr}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ and probable presence of R_4F_{26} clusters. As this cluster has a positive charge, an additional fluorine ion is required for electrostatic compensation (equation 10). Precisely those fluorine ions are located apparently at the cluster periphery and ensure high ionic conductivity.

In solid solutions of the second group introduction of RF_3 into SrF_2 lattice changes the conductivity insignificantly. This, apparently, points to "hollow" cluster shell, i.e., electroneutrality in the lattice. The structural data attest to pure F_i position in concentrated solid solutions. Presence of strong relaxation R_{III} with a very small activation energy³⁶ makes it assume presence of fluorine in cuboctahedral cavities which along with electroneutrality is ensured in clusters $\text{Sr R}_5\text{F}_{37}$ and R_6F_{38} . Presence of clusters R_6F_{38} with two fluorine ions in the cavity is unlikely. So, in concentrated solid solutions of this group, apparently, block isomorphism according to equation (8) dominates.

For $R = \text{Gd} - \text{Ho}$ conductivity is intermediate between the first and second groups.

There is positive correlation between the properties of concentrated and diluted solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$. Over the area of low concentrations of RF_3 in solid solutions nn-dipoles (symmetry C_{4v}) form in the first group, nnn-dipoles in the second group and dipoles both of the first and second type are present for $R = \text{Gd} - \text{Ho}$.^{11,16,17,36}

Systems $\text{BaF}_2 - \text{RF}_3$,^{37,94}

As to the structural characteristics and dependences of ionic conductivity $\sigma(x, T)$ solid solutions $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$ differ inconsiderably from one another. Ionic conductivity sharply rises to $x_p \approx 0.05 \pm 0.02$, then it practically passes over to saturation. Values σ somewhat decrease from La to Nd and further they practically do not depend upon the type of rare-earth elements. The structural data point to filling of F_i position in concentrated solid solutions* both as in case of $\text{Sr}_{1-x}\text{Lu}_x\text{F}_{2+x}$ but values σ are considerably higher. This is testimony to existence of clusters, type R_6F_{37} or R_6F_{36} with additional fluorine-ions at the periphery in the lattice. As the data of dielectrical relaxation fail to show presence of relaxation R_{III} with a very small activation energy for barium solid solutions related to motion of fluorine-ion inside the cuboctahedral cavity,^{36,49} the most probable is type R_6F_{36} and, respectively, isomorphic substitutions according to scheme (6). The existence of cuboctahedral clusters in disordered solid solutions well agree with their presence in ordered fluorite-like phases (tetragonal and trigonal) in systems $\text{BaF}_2 - \text{RF}_3$.^{21,55} However, the presence of small areas of homogeneity of ordered phases requires the explanation.

nnn-dipoles are found in diluted solid solutions $\text{BaF}_2:\text{RF}_3$.

Systems $\text{CaF}_2 - \text{RF}_3$,¹⁰⁶

The structural data^{32,33,19,42,45,46,64,115} suggest that concentrated solid solutions are divided at least into two groups. For rare-earth elements of the series end octahedral type of clusters is dominant. According to^{80,49} at 10% ErF_3 practically all Er ions are bound into octahedrons. Nonequivalence of ions and comparatively low electrical conductivity^{86,96,106} make it

* The data given in the work⁴⁴ on the saturated composition of $\text{Ba}_{0.5}\text{Ce}_{0.5}\text{F}_{2.5}$ solid solution point to other defect structure of anionic sublattice which includes fluorine-ions in positions F_b , F_f and F_c .

assume that there exists a big portion of clusters, type $MR_5 F_{37}$ with a hollow periphery. Fluorine-ion available in the cluster cuboctahedral cavity associates with relaxation R_{III} with a very low energy of activation.³⁶ 2:2:2 clusters (No. 4) described in,^{19,26} whose stability is confirmed by the energy calculations,¹¹ exist at low concentrations (fractions %), they are further replaced by octahedral clusters.^{80,95} By this way association of defects is according to scheme (5) for this group of concentrated solid solutions.

As to concentrated solid solutions CaF_2 with large-size rare-earth elements of the series origin the fact that F_i ions dominate makes it suppose the existence of clusters No. 22 and No. 23.⁴⁶ The energy calculations are testimony to the high stability for those systems of gettered 2:2:2:1 (No. 15) which meet the requirements of the experiment for $Ca_{0.95} La_{0.05} F_{2.05}$.²⁸ In addition, fluorine-ions F_e displaced along the fourth-order axis whose existence are shown by the calculation for gettered 2:2:2 clusters are found in $Ca_{0.99} Gd_{0.01} F_{2.01}$ by experiments.⁵¹ We assume that for this group the dominant scheme is the isomorphism scheme (13) comprising charged clusters $R_4 F_{26}$ (No. 22). As the electrical conductivity⁸⁶ is low and, consequently, there are few free carriers of charge. In systems containing SrF_2 gettered 2:2:2 clusters fail to form as according to the calculations¹¹ the energy of formation of 2:2:2 clusters is very small and they simply absent in the lattice. Respectively, there are no traps for F_{int}^- and the electrical conductivity is high.

As to the middle of the series of the rare-earth elements solid solutions should comprise clusters typical both for the origin and the end of the series.⁴⁵ According to⁹⁶ structure $Ca_{0.9} Gd_{0.1} F_{2.1}$ is intermediate between $Ca_{0.9} La_{0.1} F_{2.1}$ and $Ca_{0.9} Y_{0.1} F_{2.1}$. As the experiment shows, the electrical conductivity of such mixed solid solutions of the systems abruptly rises.⁸⁶ Mathematical modeling has not be performed.

There is no correlation between the defect structure in areas of high and low (nn-dipoles) concentrations of RF_3 in series $Ca_{1-x} R_x F_{2+x}$.

Systems $PbF_2 - RF_3$

Presence of isostructural ordered phases with Ba-systems in the systems containing $R = Sm-Lu$, $Y^{71,73}$ makes it assume a similar structure in disordered solid solutions $M_{1-x} R_x F_{2+x}$. X-ray examinations of the structure of single crystals²³ $Pb_{1-x} Y_x F_{2+x}$ confirms existence only of F_i position both in systems BaF_2 and SrF_2 containing rare-earth elements of yttrium subgroup. The nature of 2:4:0 cluster proposed in²³ is artificial and there is nothing to confirm it. It makes sense to assume existence of octahedral

clusters with 6 ions R^{3+} in solid solutions revealed in compounds $Pb_4 R_3 F_{17}$.⁵⁴ Absence of low-temperature peaks of dielectrical relaxation which can be related to presence of fluorine-ions in cuboctahedral cavities^{50,97} is the testimony, apparently, that isomorphism systems dominate in this group according to the scheme (6).

The data on laser spectroscopy⁹⁸ and dielectrical relaxation^{50,97} in diluted (0.1-0.01 mol % RF_3) solid solutions suggest that their defect structure is very complicated.

As far as the systems comprising rare-earth elements of the series origin, absence of ordered phases and drastic simplicity of the dielectrical relaxation spectra attest to the decline of the tendency to complex formation. Closeness of geometrical characteristics of PbF_2 - and SrF_2 -based solid solutions showing itself in similar change of the type of dipoles $R^{3+}-F_{int}^-$ in diluted solid solutions (transition from nnn- to nn-dipoles with increase of ionic radius R^{3+} ,¹⁷) makes it to assume also change in defect structure of concentrated solid solutions $Pb_{1-x} R_x F_{2+x}$ for rare-earth elements of a cerium subgroup with appearance of positions F_f similar to Sr systems. Pure F_f position is found on a specimen of fluorite solid solution containing 70 mol % LaF_3 obtained at high pressure.⁵⁶ Therefore, isomorphism according to scheme (10) should be typical for this group of the systems.

For systems of the middle of the series mixed structure of solid solutions should be characteristic. Apparently, solid solution containing BiF_3 whose structure has revealed both F_i and F_f positions belongs precisely to this group.²³

Systems $CdF_2 - RF_3$

In spite of the fact that geometrical characteristics of solid solutions $Cd_{1-x} R_x F_{2+x}$ and $Ca_{1-x} R_x F_{2+x}$ are close, their atomic structure differs essentially. Absence of ordered phases in systems $CdF_2 - RF_3$ revealed in our study evidences to considerably less developed cluster formation in cadmium solid solutions as compared with calcium ones. The same is evidenced by the ESR method, ionic thermocurrent and spectroscopy:^{99,100} mainly, only phenomena pointing to unlocal compensation of the charge (cubic centres R^{3+} ; unique ionic thermocurrent peaks of free charge carriers) are found in diluted solutions RF_3 and CdF_2 .

In comparatively concentrated solid solutions (10% ErF_3 , 6% YbF_3), however, formation of clusters containing 2 ions R^{3+} each has been revealed by the NMR¹⁹F method.¹⁰¹ The proposed version of their structure (cluster No. 1) does not take into account electrostatic relaxation.

Rise of ionic conductivity in passing from rare-earth cerium subgroup to yttrium subgroup¹⁰² points to change in the conductivity mechanism and, respectively, in the structure of solid solutions as well.

High capture cross-section of neutrons by cadmium impedes the neutron diffraction study of the structure of crystals $Cd_{1-x} R_x F_{2+x}$. Spectroscopy of Nd^{3+} ions in crystals of concentrated solid solutions demonstrates similar nature of disordering of the structure of fluorite solid solutions $M_{1-x} R_x F_{2+x}$, where $M = Cd$ and alkaline-earth elements.¹⁰³

PERSPECTIVE OF INVESTIGATIONS

On the base of the revue on association of defects in solid solutions $M_{1-x} R_x F_{2+x}$ of fluorite type it is possible to formulate some problems and tasks for future investigations both general and specific.

1. The defect structure of solid solutions of rare-earth trifluorides in CdF_2 and PbF_2 as well as trifluorides of small cations (Sc, In, Al, Cr, etc.) in MF_2 , has been studied insufficiently until now.

2. The experimental data don't allow to decide if the dominant type of defects (F_i or F_i') changes with the concentration of solid solutions.

3. It is necessary to precisely investigate the influence of heat treatment of specimens on their defect structure. Some indirect data show that the complex investigations of the defect structure of the same, well-documented specimens are reasonable.

4. It is necessary to develop the notion of the structure of concentrated solid solutions beyond the percolation threshold. It is necessary to precisely determine the boundary between homogeneity and heterogeneity from the standpoint of various methods of solid-state physics and chemistry.

5. From the percolation theory the calculation of percolation processes in a mixture of several types of particles different in shape and size is of interest. Such cases may take place, for example, in solid solutions $Sr_{1-x} R_x F_{2+x}$ ($R = Nd-Ho$).

6. The theory of percolation predicts the anomaly of specific heat in the vicinity of the percolation threshold. The experimental verification of this phenomenon is desirable for series of concentrated solid solutions.

7. The study of thermodynamic properties (excess entropy and enthalpy) of $M_{1-x} R_x F_{2+x}$ solid solutions is at the initial stage. The development of thermodynamic models for this type of solid solutions is very tempting but very difficult.

The author is very grateful to V. B. Alexandrov, V. M. Buznik, A. M. Golubev, A. K. Ivanov-Shitz, A. A. Loshmanov, B. A. Maximov, B. P. Sobolev, N. I. Sorokin, V. Trnovcova, M. Švantner, S. V. Cheznov for valuable discussion of the problems touched upon in the present revue.

ABSTRACT

The revue of cluster problem in solid solutions of rare earth trifluorides (RF_3) in difluorides (MF_2) with fluorite type structure has been made. The proposed cluster models methods of its investigation, most likely cluster types for different combinations of RF_3 and MF_2 have been considered, as well as percolation problem for such solid solutions. Some perspective directions for future study have been formulated.

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