Optically detected ESR of clusters of rare earth ions and yttrium in fluorite crystals

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Optical detection methods are used to record the ESR spectra of clusters of the rare earth (R′) ions Er^{3+}, Tm^{3+}, and Yb^{3+} in CaF_2 crystals. It is found that the clusters are magnetically concentrated systems with a broad-band ESR spectrum. However, at significant dilutions of the paramagnetic R′ ions by the diamagnetic (R″) ions Lu^{3+} or Y^{3+}, the double activation of the fluorite crystals leads to simple ESR spectra of the Er, Tm, and Yb ions in Lu or Y clusters. The ESR spectra of these clusters are studied in $(CaF_2)_{1-y}(R''F_3)_y$ over the entire existence region of the solid solutions, for $0.001 < y < 0.4$, and in the solid solutions based on SrF_2 and BaF_2 at $y = 0.03$. It turns out that the symmetry of the R′ ions in all the systems studied is tetragonal and the crystalline fields are anomalous, giving rise to record-high values, approaching the theoretical limit, for the g factors of the Er^{3+} and Yb^{3+} ions and to an observable ESR of the Tm^{3+} ion, never before seen in fluorites. It is concluded that the clusters in the investigated systems are similar in structure to the Y_6F_{37} clusters which embed perfectly in the fluorite lattice and which have been observed previously by x-ray methods under the unique conditions of superstructural ordering of the crystal lattice of a $(CaF_2)_{1-y}(YF_3)_y$ solid solution of definite composition. It is shown that at activator concentrations higher than 0.2 mol% the clusters in the fluorites coagulate into "grains" which evidently have a composition $y = 0.2$–0.4 equal to the solubility limit for the compounds studied.

1. INTRODUCTION

Many important effects observed in rare-earth activated fluorite crystals—various cooperative processes,[1–5] the lowering of the temperature of the transition to the state with superionic conductivity,[6] and many other effects[7]—are due to the formation of clusters (i.e., aggregations) of activator ions. The existence of clusters can be regarded as established[1–11] for CaF_2, SrF_2, and BaF_2 crystals activated by ions (R^{3+}) of the second half of the rare earth series and by yttrium ions. However, up till now the structure of the clusters had remained unknown in spite of the fact that they had been studied by the methods of selective laser spectroscopy,[3–5] neutron scattering,[12] and NMR.[13] The ESR spectrum of the clusters had not been observed, and their magnetic properties were completely unknown. For example, the ESR spectra of the "classical" system CaF_2:Er^{3+} exhibits[11,14] only simple centers—cubic centers with nonlocal charge compensation and tetragonal and trigonal centers with local charge compensation (Er^{3+}–F^-)—distributed statistically inthe CaF_2 lattice. For activated CaF_2 crystals it is known that around 50% of the activator ions at total activator concentrations above 0.2 mol% are found in clusters, while the remaining ~50% form cubic centers. At concentrations ~0.1 mol% there is a noticeable presence of binary centers (R^{3+}–R^{3+}) as well as tetragonal and trigonal centers, which dominate at still lower concentrations where clusters do not form.[11]

From a crystal-chemical point of view, activated fluorite crystals are nonstoichiometric solid solutions of calcium, strontium, and barium fluorites with rare earth and yttrium trifluorides. X-ray diffraction studies of these systems have shown that they are single-phase systems and have the cubic fluorite lattice over a wide range of compositions of the type $(CaF_2)_{1-y}(YF_3)_y$ for $0 \leqslant y \leqslant 0.4$. Under special conditions of synthesis, compounds based on CaF_2 with compositions $y = 5/m$ (where the integer $m = 13$–19) exhibit superstructural ordering of the fluorite lattice.[15–16] The basic structural elements of the homologous series of the superstructures are clusters of the type Y_6F_{37}, which embed perfectly in the fluorite lattice. Here the Y^{3+} ions occupy the six nearest places in the cation sublattice, forming a Y_6 octahedron. The internal (to the Y_6 octahedron) cube of eight F^- ions in the fluorite lattice are rearranged into an F_{12} cubo-octahedron with one more, noncentral F^- ion in its cavity.

This paper reports the successful use of optical detection methods to record the ESR spectra of clusters of the paramagnetic ions Er^{3+}, Tm^{3+} and Yb^{3+} in nonstoichiometric solid solutions based on CaF_2, SrF_2, and BaF_2 even when a large fraction of these ions are replaced in the clusters by the diamagnetic ions Lu^{3+} or Y^{3+}. It is shown that these clusters are evidently similar in structure to the Y_6F_{37} clusters observed in superstructural fluorite phases.[16] Some of the results were described briefly in Ref. 17.

2. EXPERIMENTAL TECHNIQUES AND RESULTS

At $T = 1.8$ K, a study was made of the solid solutions $(CaF_2)_{1-x}(R'F_3)_x$ and $(CaF_2)_{1-x-y}(R'F_3)_x(R''F_3) \equiv CaF_2{:}R'_x,R''_y$ (in shortened notation), where $0 < x \leqslant 0.02$, $x \ll y$, $0.001 \leqslant y \leqslant 0.38$, $R' = $ Er, Tm, Yb and $R'' = $ Lu, Y, and the solid solutions $SrF_2{:}Lu_{0.03}R'_{0.001}$ and $BaF_2{:}Lu_{0.03}R'_{0.001}$, where $R' = $ Er and Tm.

The magnetic-circular-dichroism (MCD) spectra and their dependence on the magnitude of the external magnetic field H_0 and its orientation with respect to the crystallographic axes C_i were studied in the region of the optical absorp-

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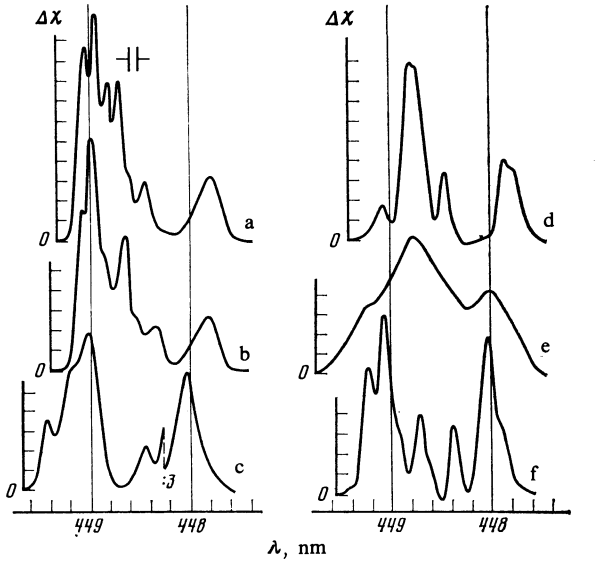

FIG. 1. The MCD spectra near the transition $^4I_{15/2}\to{}^4F_{5/2}$ in the Er^{3+} ions in clusters for the solid solutions: a) CaF$_2$:Er$_{0.005}$; b) CaF$_2$: Y$_{0.01}$Er$_{0.0005}$; c) BaF$_2$:Lu$_{0.03}$Er$_{0.001}$; d) CaF$_2$:Lu$_{0.01}$Er$_{0.005}$; e) CaF$_2$: Lu$_{0.38}$Er$_{0.001}$; f) SrF$_2$:Lu$_{0.03}$Er$_{0.001}$.

tion bands of the R′ ions with unfilled 4*f* shells in the clusters. Figures 1 and 2 show the spectral curves of the MCD for several transitions (the MCD is the difference $\Delta\chi$ in the absorption coefficients of a sample in a field H_0 for right- and left-circularly polarized light).[18]

It was found that the dependence of the MCD on the magnitude of the field H_0 in the absorption bands of the R′ ions in the clusters exhibits saturation:

$$\Delta\chi(H_0)=\Delta\chi^{max}\,\mathrm{th}\,(g\beta H_0/2kT).$$

It follows that the MCD is of a paramagnetic nature and is due to the circular polarization of the optical absorption spectrum of the R′ ions in the clusters as a consequence of the Boltzmann population of the Zeeman sublevels of their ground state, which is split in the magnetic field H_0. Here the *g* factor determined from the $\Delta\chi(H_0)$ curves recorded in the orientations $H_0\|C_2$, C_3 and C_4 obeys the relation $g=g_\|\cos\theta$, where θ is the minimum angle between the magnetic-field direction and the C_4 axes of the crystal. This result clearly indicates that the symmetry of the R′ ions in the clusters is tetragonal; in all the systems studied the principal axes of the *g* tensors are oriented along the C_4 axes, and $g_\| \gg g_\perp$. It is extremely important that the shape of the $\Delta\chi(H_0)$ curve and the corresponding value of $g_\|$ are independent of the relationship between *x* and *y*, i.e., of the dilution of the paramagnetic R′ ions by the diamagnetic ions Lu and Y, as has been established in a study of solid solutions based on CaF$_2$.

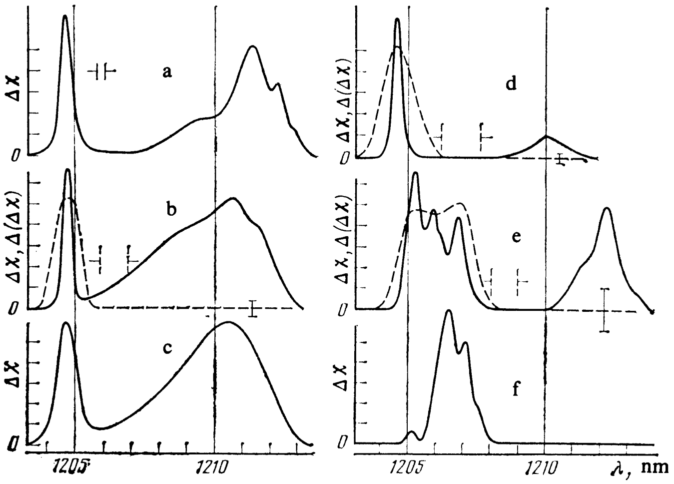

FIG. 2. The MCD spectra (solid lines) on the long-wavelength wing of the $^3H_6\to{}^3H_5$ band of the optical spectrum of Tm^{3+} ions in clusters for the solid solutions: a) CaF$_2$:Tm$_{0.002}$; b) CaF$_2$: Lu$_{0.02}$Tm$_{0.001}$; c) CaF$_2$:Lu$_{0.38}$Tm$_{0.001}$; d) CaF$_2$:Y$_{0.01}$Tm$_{0.0005}$; e) SrF$_2$:Lu$_{0.03}$Tm$_{0.001}$; f) BaF$_2$:Lu$_{0.03}$Tm$_{0.001}$. The dashed curves show the spectrum of the optically detected ESR signals for some of the compounds.

The optically detected ESR spectra at frequencies $\nu^{\rm mic}=9$ and 36 GHz were studied by the usual technique[18] with the samples placed in a TE_{011} microwave resonator having apertures for the passage of the probe light beam. As the external magnetic field H_0 was scanned, we detected the changes $\Delta(\Delta\chi)$ in the MCD in the absorption bands of the R′ ions in the clusters at a 100% modulation, at a frequency $\nu_{\rm mod}\ll(2\pi)^{-1}\tau_1^{-1}$, of the microwave power dissipated in the resonator. Near the extremum of the ESR lines for $\nu^{\rm mic}=36$ GHz the longitudinal relaxation time τ_1 was $\sim10^{-3}$ and 10^{-1} sec, respectively, for the investigated R′ ions in the clusters when undiluted and when appreciably diluted by diamagnetic R″ ions. Figures 3 and 4 show the optically detected ESR spectra for several of the compounds studied (see also Fig. 3 in Ref. 17).

For clusters containing only R′ ions at concentrations

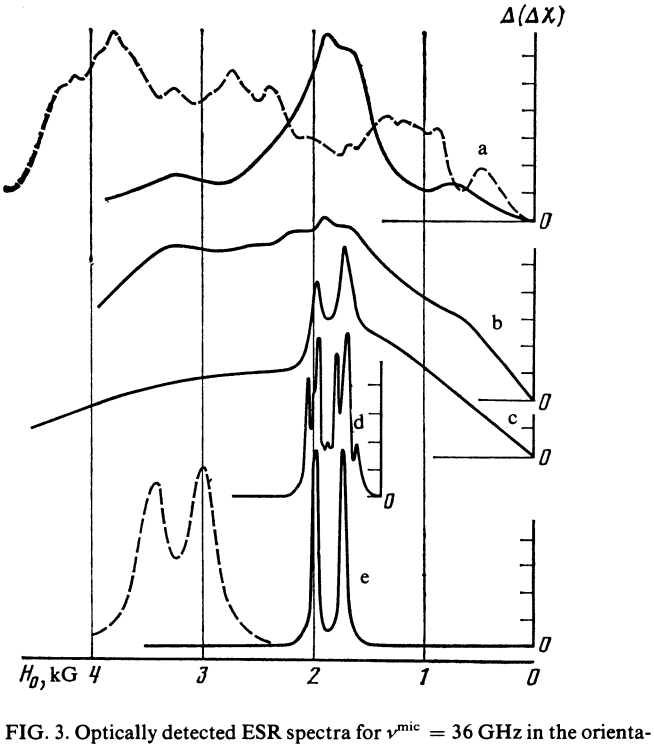

FIG. 3. Optically detected ESR spectra for $\nu^{\rm mic}=36$ GHz in the orientation H$_0\|$C$_4$ (solid curves) and H$_0\|$C$_3$ (dashed curves) for Tm^{3+} ions in clusters in the CaF$_2$ solid solutions: a) CaF$_2$:Tm$_{0.002}$; b) CaF$_2$:Tm$_{0.005}$; c) CaF$_2$:Y$_{0.01}$Tm$_{0.003}$; d) CaF$_2$:Y$_{0.0012}$Tm$_{0.0005}$; e) CaF$_2$:Y$_{0.01}$Tm$_{0.005}$.

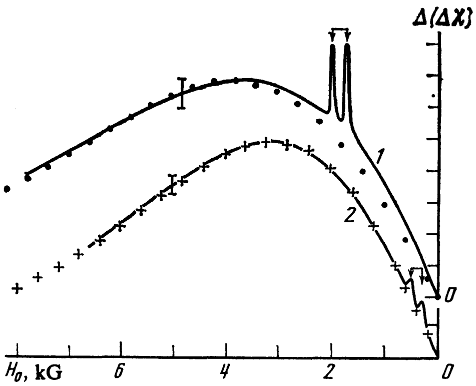

FIG. 4. Optically detected ESR spectra of Tm^{3+} ion in clusters for the compound CaF_2:$Y_{0.1}Tm_{0.002}$ at $\nu^{\rm mic} = 36$ GHz (1) and 9 GHz (2) in the orientation $H_0 \| C_4$. The dots and crosses are the theoretical curves for the broad-band ESR spectrum (see text) at $T_{\rm sam} = 2.35$ K (●) and 1.9 K (+). The arrows indicate the characteristic doublet in the ESR spectra of the Tm^{3+} ion.

exceeding 0.2 mol%, the ESR spectrum exhibits a broad background absorption and a barely discernable structure (see Figs. 3b and 3c in Ref. 17). However, when the R′ ions in the clusters are diluted by the diamagnetic ions Lu or Y, this background absorption "contracts" into a line (or into a doublet for clusters containing Tm^{3+} ions); the extremum of this line lies at a position which depends on the orientation of H_0 relative to the crystal axes and usually corresponds exactly to the position expected from an analysis of the H_0 dependence of the MCD (See Fig. 3 in Ref. 17). For clusters containing Er or Yb ions and diluted by diamagnetic ions, the observed ESR line nevertheless exhibits appreciable inhomogeneous broadening, and in solid solutions based on CaF_2 it even has a noticeable structure.[1)] In addition. in SrF_2:Lu, Er the extremum of the ESR line is shifted (within the linewidth) to higher fields relative to the position predicted from analysis of the $\Delta\chi(H_0)$ curve. This shift is apparently due to the circumstance that $g_\perp \to 0$ for the Er ions with $g_\| \to g_\|^{\max}$ in the clusters of Lu and Er which from this inhomogeneous ESR line. It should be noted that because $g_\perp$ is close to zero and so the intensities of the signals for the Er^{3+} and Yb^{3+} ions in the ESR spectra of the clusters diluted with diamagnetic ions are relatively weak, one can see several additional bands which are not related to the R′ ions in the clusters, e.g., in the region of the cubic Er^{3+} (see Fig. 3 in Ref. 17) and Yb^{3+} centers. The presence of the additional bands can be explained by a transfer of the energy of the absorbed microwave photons between different interacting centers on account of cross relaxation.[19]

The orientation dependence of the position of the ESR lines supports the conclusions reached from analysis of the $\Delta\chi(H_0)$ curves as to the orientation of the axes of the g tensor and the anisotropy $g_\| \gg g_\perp$. Noteworthy here is the anomalous broadening of the ESR lines in the orientations $H_0 \| C_2$ and C_3 (see Fig. 3e and 3c in Ref. 17). The observed broadening may be evidence of a random deviation of the axes of $g_\|$ from the preferred direction in a solid angle $\varphi \leqslant 3$–5° at a concentration $y = 0.01$. Estimates show that for $y = 0.38$ this angle is $\varphi \leqslant 20$–30°. The appreciable scatter in the orientations of the axes of $g_\|$ might be due to imperfections in the samples. For example, the single crystals with $y \geqslant 0.1$ exhibit clearly visible striations.

In solid solutions based on CaF_2 with $y \geqslant 0.02$ the optically detected ESR spectra begin to show a broad band which increases in intensity relative to the ESR lines of the clusters with increasing concentration y (see Fig. 4). Studies showed that the shape of this band does not depend on the frequency of the microwave photons but is determined solely by the sample temperature $T_{\rm sam}$ and the field dependence of the MCD at the probe-light wavelength; it is well approximated by

$$\Delta(\Delta\chi) \propto d\{\Delta\chi(H_0)\}/dT\,|_{T=T_{\rm sam}} = -(g\beta H_0/2kT_{\rm sam}^2)\,{\rm sech}^2(g\beta H_0/2kT_{\rm sam}).$$

These results indicate sample heating, by the microwave field, which is independent of H_0 and is not directly related to the paramagnetism of the R′ ions in the clusters. In the present experiments the heating reached some tens of degrees for $y = 0.1$.

The shape of the $\Delta\chi(H_0)$ curves and the ESR spectra of the Er^{3+} ions in the clusters do not depend on the wavelength of the probe light [except for the system BaF_2:Lu, Er, where the $\Delta\chi(H_0)$ curve measured in the wavelength region $\lambda = 448$ nm (Fig. 1c) differs somewhat from the analogous curves recorded at other wavelengths; at the same time, the shape of the ESR spectrum did not depend on the wavelength of the probe light]. For Yb^{3+} ions this equation was not investigated. The MCD spectrum of the Tm^{3+} ions at the long-wavelength wing of the absorption band $^3H_6 \to {}^3H_5$ (Fig. 2) can be divided into two groups of lines: long-wavelength $\{\lambda_L\}$ and short-wavelength $\{\lambda_S\}$. The $\Delta\chi(H_0)$ curves for the two groups are similar in shape and correspond to tetragonal Tm^{3+} centers with approximately equal $g_\|$ factors. However, in the spectral region corresponding to $\{\lambda_S\}$ there is a detectable ESR spectrum of the Tm^{3+} ion, while the ESR spectrum is not seen for the group $\{\lambda_L\}$. In solid solutions based on CaF_2 the short-wavelength group degenerates into a single line in all the clusters studied, while the simplest, two-line MCD spectrum is observed for Tm^{3+} ions in Y^{3+} clusters (Fig. 2d). For Tm^{3+} ions in Y^{3+} clusters in BaF_2, only the short-wavelength group of lines is observed in the MCD spectrum (Fig. 2f), and the ESR spectrum is similar to the spectrum in Fig. 3e. For the analogous Tm^{3+} ions in SrF_2, both groups of lines are observed in the MCD spectrum, and the ESR spectrum recorded in the $\{\lambda_S\}$ region resembles the spectrum in Fig. 3d.

The values of $g_\|$ and $g_\perp$ estimated from the experiment are compiled in Table I, along with the experimentally determined linewidths ΔH_0 (for $\nu^{\rm mic} = 36$ GHz) of the optically detected ESR for the R′ ions in the clusters; also given, for the non-Kramers ion Tm^{3+} (configuration $4f^{12}$), are the initial splitting δ and the hyperfine interaction constants A_{IS} of the electron shell of Tm^{3+} ions with an isotope content of 100% Tm^{169}, which has nuclear spin $I = 1/2$ (Ref. 19). The estimates of δ were made only for solid solutions based on CaF_2 for the two groups of lines $\{\lambda_S\}$ and $\{\lambda_L\}$ in that part of the optical spectrum shown in Fig. 2; the estimates are

TABLE I. Parameters of the spin Hamiltonian and optical-detection ESR linewidths for Er^{3+}, Tm^{3+}, and Yb^{3+} ions in clusters in several compounds.

Solid solution	$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}^{\lim}$	$\delta^{(\lambda S}$, cm^{-1}	$\delta^{(\lambda L}$, cm^{-1}	A_{IS}, cm^{-1}	ΔH_0, kG
$CaF_2 : Tm_{0,005}$	14±0.5	0	14	0.3±0.1 [c)]	2±1 [b,c)]	–	3.5
$CaF_2 : Y_{0,01}Tm_{0,0005}$	14.2±0.2	0	14	0.15±0.05 [a)]	2±1 [b)]	0.165±0.003	0.05
$SrF_3 : Lu_{0,03}Tm_{0,001}$	~13.7	0	14	–	–	0.159±0.005	0.07
$BaF_2 : Lu_{0,03}Tm_{0,001}$	~13.8	0	14	–	–	0.161±0.005	0,03
$CaF_2 : Er_{0,005}$	15.5±0.5	<4	18	–	–	–	4
$CaF_2 : Y_{0,01}Er_{0,0005}$	15.2±0.3	<2	18	–	–	–	0.15
$SrF_2 : Lu_{0,03}Er_{0,001}$	16±0.5	<2	18	–	–	–	0.45
$BaF_2 : Lu_{0,03}Er_{0.001}$	17.2±0.3	<2	18	–	–	–	0.2
$CaF_2 : Yb_{0,01}$							
$CaF_2 : Y_{0,01}Yb_{0,0005}$	6.8±0.2	<2	8	–	–	–	10
			8	–	–	–	0.6

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a)–c) See text.

based on analysis of: a) the ESR spectra for $\nu^{\text{mic}} = 9$ and 36 GHz (see Fig. 4); b) the deviation of the $\Delta\chi(H_0)$ curve, which (with allowance for δ but in neglect of A_{IS} is of the form

$$\Delta\chi(H_0)\propto g\beta H_0[(g\beta H_0)^2+\delta^2]^{-1/2}\,\text{th}\,\{[(g\beta H_0)^2+\delta^2]^{1/2}/2kT\},$$

from the analogous curve for $\delta = 0$ (with $g_{\parallel} \approx g_{\parallel}^{\lim}$; see Sec. 3); c) the field dependence of the modulation signal $\partial[\Delta\chi(H_0)]/\partial H_0$ during a longitudinal modulation of the static magnetic field H_0 at a high frequency $\nu_{\text{mod}} \gg (2\pi)^{-1}\tau_1^{-1}$ (Ref. 20).

3. DISCUSSION OF EXPERIMENTAL RESULTS

The experimental results of this study can be explained in a natural way if it is assumed that the clusters of the R ions in all the solid solutions are similar in structure to the Y_6F_{37} clusters observed in the superstructural fluorite phases[16] (see Sec. 1). It is easy to see that in this case all the positions of the R ions in the clusters are approximately equivalent, and the symmetry of the crystalline field around every R ion is nearly tetragonal. The proposed model, augmented with the obvious assumption that the occupation of the cation positions by R ions in the clusters is of a statistical nature, can explain many experimental facts, e.g., the narrowing of the ESR lines on dilution of the paramagnetic ions in the clusters by diamagnetic ions and also the tetragonal symmetry of the R′ ions in the clusters, with a constant value of $g_{\parallel}$ over the entire existence region of the solid solutions. The most puzzling result of the previous studies[3–9] was that the crystalline fields in the clusters (unlike the fields in simple centers), even at low concentrations of R ions in fluorites, are not completely definite, but vary over a certain range of values. As is shown below, these results are explained by the fact that the existence of isolated clusters of the Y_6F_{37} type in an "unperturbed" fluorite lattice is scarcely possible, and solid solutions usually exhibit larger or smaller groups of closely spaced clusters, which interact with one another and with lattice defects (the compensating ions F^-). Therefore, the optical and ESR spectra of the R′ ions contain information on both the structure of the clusters and their interactions.

Let us discuss first the experimental results for Er^{3+} ions in clusters. Their optical absorption spectra and their $\Delta\chi(\lambda)$ spectra (see Fig. 1), which, because of the paramagnetic nature of the MCD, preserve the structure of the absorption spectra, are considerably broadened in comparison with the spectra of the simple and binary centers. This broadening is inhomogeneous, and the methods of selective laser spectroscopy can distinguish in the optical spectra a large number (up to 20) of positions of the Er^{3+} ions with different crystalline field environments.[3–5] Among this diversity of positions, however, there are only a few main types, e.g., $D(2a)$ and $D(2c)$ for CaF_2.[11] One is led to the same conclusion by studying the absorption spectra[8] in CaF_2 and the MCD spectra of Er^{3+} ions in the vicinity of the transition ${}^4I_{15/2} \rightarrow {}^4F_{5/2}$ for various compounds (Fig. 1). The number of observable components in these spectra at $T = 1.8$ K is approximately twice as large as would be expected for a single Er^{3+} ion in a noncubic crystalline field for a single type of position (three components). Here the broadening of each component of the optical spectrum can be attributed to variations in the crystalline field in the clusters for a definite type of position. A study of solid solutions based on CaF_2 has revealed that the replacement of a large portion of the Er^{3+} ions in the clusters by the diamagnetic ions Lu^{3+} or Y^{3+} produces significant changes in the MCD spectra (see Figs. 1b and 1d). However, since the compounds of the second half of the rare earth series (and yttrium) with nearly equal ionic radii are isomorphous,[19] one can safely assume that the structures of clusters containing different ions of this series are approximately the same, and the observed changes in the optical spectra should be attributed to their "heightened" sensitivity to small changes in the crystalline field upon the replacement of the R ions in the clusters. It is well known that the ESR spectra are less sensitive to changes in the crystalline field than are the optical spectra, since the position and intensity of the lines of the optical spectrum are directly determined by the value of the crystal-field constants, whereas the ESR spectrum is due to the structure of the ground state of the paramagnetic ion and depends solely on the relationship of the crystal-field constants.[14] It is not surprising, therefore, that all the Er^{3+} ions in diluted and undiluted clusters in solid solutions based on CaF_2, in spite of a certain difference in the optical spectra, have the same $g_{\parallel}$ factor and tetragonal symmetry, while variations present in the crystalline field in the clusters lead to inhomogeneous broadening of the ESR lines. Analogous conclusions can be reached for Yb^{3+} ions in clusters in CaF_2 (their optical spectra were studied in Ref. 9). The optical spectra of the Tm^{3+} ion can also be divided roughly into two separate groups of lines, indicating the existence of two main types of positions of the Tm^{3+} ions in the clusters; the ESR spectrum is observed only for one of the types of positions. As in the case of the Er^{3+} ions, the optical spectra of the Tm^{3+} ions in the clusters differ noticeably in all the systems studied (Fig. 2), whereas their paramagnetic properties are extremely similar (see Table I).

By studying the optical and ESR spectra one can establish that the concentration of R ions in the samples has almost no effect on the existence of the main types of positions of R ions in the clusters. For example, it follows from an examination of the MCD spectra of Tm^{3+} ions in solid solutions based CaF_2 (see Figs. 2a–c) that the two main types of positions exist and apparently retain their structure both at low concentrations $x+y\approx 0.002$, at which the interaction between clusters is relatively small (see below), and also at the highest concentration of clusters in a fluorite, $x+y\approx 0.4$. Therefore, it is natural to explain the presence of several main types of positions by a deviation from cubic symmetry for an isolated cluster of the Y_6F_{37} type in the solid solution. Here the structure of the optical spectrum may indicate the direction of displacement of the noncentral ion F^- in the F_{12} cubo-octahedron. Then the simplest spectra of the type in Fig. 2d will correspond to symmetric displacements of the noncentral ion F^- (e.g., in the direction of the triangular face).[21]

It was proposed in Ref. 22 that the noncentral ion F^- in the clusters is also responsible for the existence of two-level systems in the solid solutions under discussion. The presence of two-level systems leads to appreciable dielectirc losses at microwave frequencies; these losses also explain the microwave heating observed in the present study for solid solutions based on CaF_2 (see Sec. 2 and Fig. 4). The difference between the solid solution BaF_2:Lu, Tm, which has only one main type of position for the Tm^{3+} ions in the clusters, and the analogous solid solutions based on CaF_2 and SrF_2 is correlated with the two-level feature observed[22] in the series of basic constituents CaF_2–SrF_2–BaF_2 and possibly confirms the role of noncentral F^- ions in the formation of the main types of R-ion positions in the clusters.

The results of the present study show that the $g_\parallel$ factor of the ground states of Er^{3+}, Tm^{3+} and Yb^{3+} in the clusters (see Table I) have record-high values, close to the limit $g_\parallel^{\rm lim}=2Jg_J$, where J is the total angular momentum and g_J is the Landé factor of the lower multiplet for each of the R′ ions.[19] It follows that the ground state of these ions are approximately $|\pm J\rangle$ doublets. The crystal-field constants of the R ions in the clusters have not been calculated. Nevertheless, the present results can be explained under the assumption that the main contribution to the axial component of the crystalline field is described by the constant A_2^0, which here is negative. Let us consider the crystal-potential term $A_2^0\langle r^2\rangle\langle J\|\alpha\|J\rangle O_2^0$, where $\langle r^2\rangle$ is the mean square radius of the $4f$ orbital and $\langle J\|\alpha\|J\rangle$ is a numerical coefficient for each R′ ion.[19] The matrix elements of the spin operators O_2^0 are positive and have their maximum values for $J_z=\pm J$. Therefore, in an axial crystalline field the lower state is a doublet $|\pm J\rangle$ if the product $A_2^0\langle J\|\alpha\|J\rangle$ is negative. Usually for fluorites $A_2^0>0$, and a value of the factor $g_\parallel\sim g_\parallel^{\rm lim}$ can be attained for Tb^{3+}, Dy^{3+}, and Ho^{3+} ions,[14] for which $\langle J\|\alpha\|J\rangle<0$. For Er^{3+}, Tm^{3+}, and Yb^{3+} ions, however, $\langle J\|\alpha\|J\rangle>0$, and a value $g_z\sim g_\parallel^{\rm lim}$ can be attained only in anomalous crystalline fields for which $A_2^0<0$. To underscore this anomaly, we note that the ESR spectrum of Tm^{3+} ions has been recorded only for a few systems[23] and had never been observed in fluorites at all.

It is noteworthy that the ESR lines have an appreciable width in solid solutions containing only paramagnetic R′ ions at concentrations $x>0.002$ (see Table I). Hence, estimates made by the method of moments[19] show that the clusters coagulate in the CaF_2 lattice (for SrF_2 and BaF_2 this question has not been studied), forming "grains" of the R phase at concentrations as low as $x+y>0.002$, and that the concentration of R ions in the R phase is not less than 20–30 mol%, i.e., close to the solubility limit of RF_3 in fluorites. Here the constancy of the $g_\parallel$ factor on dilution of the paramagnetic ions in the grains by diamagnetic ions (as was established by studying the $\Delta\chi(H_0)$ curves, see Sec. 2) indicates that the average value of the local magnetic field acting on each of the paramagnetic R′ ions on the part of the other R′ ions[19] is equal to zero in the magnetically concentrated grains. The R-phase grains are small in size: ~ 100 Å (at $y=0.01$), according to indirect estimates.[22] Direct methods have so far failed to detect the grains.3) At low concentrations of the R ions ($x+y\leqslant 0.002$), isolated groups of several clusters apparently exist in CaF_2, but grains of the R phase do not form. For example, the ESR spectrum of CaF_2:Tm_x samples at $x=0.005$ is a broad band, typical of magnetically concentrated systems (Fig. 3b). However, when the concentrations of Tm^{3+} ions is decreased to $x=0.002$, the ESR spectrum (Fig. 3a) for $\mathbf{H}_0\|\mathbf{C}_4$ begins to show the characteristic doublet, while in the orientation $\mathbf{H}_0\|\mathbf{C}_3$ the ESR spectrum has a complex structure. The structure of the ESR spectrum is resolved and the background disappears on dilution of this low concentration of Tm^{3+} ions by Y^{3+} ions in a ratio of only 1:3 (Fig. 3d). In the last two cases isolated groups of several clusters containing Tm^{3+} ions with different values4) of $g_\parallel$ and δ are apparently observed. On a proportional increase in the concentration of Tm^{3+} and Y^{3+} ions from $x+y\approx 0.002$ to 0.013, the ESR spectrum of the Tm^{3+} ions (Figs. 3d and 3c) broadens noticeably and a background appears, because the clusters have coagulated into grains. The ESR spectrum of Tm^{3+} ions appreciably diluted by diamagnetic ions in the grains has a simple form (Fig. 3e) and and is characterized by single values of $g_\parallel$ and δ. A unified ESR spectrum is also observed for Tm^{3+} ions in Lu^{3+} clusters in BaF_2, whereas the analogous ESR spectrum in SrF_2 is characterized by a discrete set of $g_\parallel$ and δ.

As was pointed out in Ref. 16, the condition of charge compensation is not satisfied in the Y_6F_{37} clusters, and even in the superstructural phases there is lattice disorder with respect to the distribution of the additional F^- ions. Therefore, the observation of a clearly defined structure (even in the presence of inhomogeneous broadening) in the optical spectra of the R′ ions in the grains (Figs. 1 and 2) is nontrivial and permits the assumption that a certain order is present in the distribution of the clusters in the R-phase grains. The breakdown of this order with increasing concentration of the solid solution can be detected by studying the bands in the optical spectra, which are most sensitive to the interaction between clusters. For example, in the solid solutions CaF$_2$:Tm$_x$ and CaF$_2$:Tm$_x$R″$_y$ at total concentrations $x + y \leqslant 0.02$ the MCD spectrum of the clusters in the vicinity of the transition ${}^3H_6 \rightarrow {}^3F_{2,3}$ in the Tm^{3+} ions ($\lambda = 665$–680 nm) contains narrow (of the order of several cm^{-1}) lines, which were studied in Ref. 24 for the system CaF$_2$:Tm. When the concentration of the solid solution is increased to $y = 0.1$ the fine structure of the spectrum vanishes, and at $y = 0.38$ a long-wavelength shift of approximately 40 cm^{-1} is also observed in the bands of the optical spectrum. The broadening of the optical spectra as the concentration is increased to $y \rightarrow 0.1$ is apparently evidence of the onset of an interaction between the R-phase grains in the sample. As the boundary of the existence region of the solid solution is approached ($y \sim 0.4$), the concentration of clusters in the samples reaches the maximum attainable value, and there is no order in their relative positions.

4. CONCLUSIONS

This study of solid solutions of calcium, strontium, and barium fluorites in trifluorides of yttrium and elements of the second half of the rare earth series has shown that nonstoichiometric fluorite phases, hitherto considered to be completely disordered, can in fact accomodate a change in stoichiometry in a comparatively ordered way: The crystal lattice of the fluorite undergoes a rearrangement involving the formation of the same structural elements (clusters) that are observed in the homologous series of fluorite-like superstructures.[16] This conclusion is consistent with the known tendency of nonstoichiometric compounds of various structural types to preserve a certain (sometimes nearly complete) order in the crystal lattice through the formation of extended defects, even at insignificant deviations from stoichiometry.[25] The uniting of the clusters into grains of the R phase (possibly ordered) in the present case is reminiscent of the formation of Suzuki phases in nonstoichiometric solid solutions of the type (NaCl)$_{1-x}$(CdCl$_2$)$_x$; the latter formation, however, is known to occur[26] at concentrations as low as $x \sim 10^{-7}$. A feature of the nonstoichiometric fluorite phases investigated in the present study is the coexistence of clusters and simple cubic centers (see Sec. 1).

The conclusions of the present study are confirmed by the results of other studies. Vernon and Stearns[27] showed by the EXAFS method that the nearest-neighbor environment of the Y^{3+} ion in (CaF$_2$)$_{1-y}$(YF$_3$)$_y$ solid solutions is similar in structure to that of the Y^{3+} ion in YF$_3$, viz., a tetragonal antiprism (as in the Y$_6$F$_{37}$ cluster). Neutron diffraction studies[28] apparently indicate the presence of R-ion octahedral sextuplets forming clusters in fluorites. An NMR study[29] has shown that the crystal lattice of nonstoichiometric fluorite phases contain regions having sharply different contents of rare earth ions. A study[30] of the magnetic susceptibility of the dipole spin glass in the system CaF$_2$:Er$_{0.01}$ indicates the existence of regions in the sample with a high (apparently at least 20 mol%)[31] content of Er^{3+} ions.

In summary, the currently available experimental data refute the earlier model[12] in which the clusters known as 2:2:2 and 4:3:2 (see Refs. 6, 7, 10) are possible structural elements of nonstoichiometric fluorite phases.

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[1] The hyperfine structure of the odd isotopes of Er (content 23%) or YB (30%), which have nuclear spins, is not resolved in the ESR spectra.[19]

[2] For the $\{\lambda_L\}$ group obviously $\delta > h\nu^{\mathrm{mic}}$.

[3] Preliminary data[17] suggesting the detection of grains by an electron microprobe technique have not been confirmed by further studies.

[4] It is easy to show that the spectrum in Fig. 3a cannot belong to an isolated Tm$_6$F$_{37}$ cluster.

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