

# Superstructure regions in the lattice of the solid solution $(\text{CaF}_2)_{1-x}(\text{ErF}_3)_x$ with $x \geq 0.001$

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The question of the clustering of  $\text{Er}^{3+}$  rare-earth ions in  $\text{CaF}_2$  crystals has been resolved by means of an optically detectable electron spin resonance. At erbium concentrations above 0.1 mole %, a new crystalline phase is observed to be incorporated in the  $\text{CaF}_2$  lattice. This new phase has a high erbium concentration, tetragonal symmetry, and a factor  $g_{\parallel} \approx 15.5 \gg g_{\perp}$  for the  $\text{Er}^{3+}$  ion.

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It has been established elsewhere that  $\text{CaF}_2$  forms a continuous series of solid solutions with the trifluorides of rare earths and also with  $\text{YF}_3$ , which is isomorphic with these fluorides, over a broad range of compositions.<sup>1</sup> On the other hand, it has been found<sup>2</sup> that the optical spectra of  $\text{CaF}_2$  activated with rare-earth ions undergo substantial structural changes when the concentration of the rare-earth ions is increased above 0.1 mole %. The effect has been attributed to the formation of clusters or *D* centers containing rare-earth ions. The structure of these clusters is unknown, however, despite study of the question by selective laser spectroscopy,<sup>2</sup> neutron scattering,<sup>3</sup> and nuclear magnetic resonance.<sup>4</sup> The electron-spin-resonance (ESR) spectra of the clusters have not been observed, and nothing has been learned about the magnetic properties of the clusters. For example, the ESR spectra of the "classical" system  $\text{CaF}_2:\text{Er}^{3+}$  reveal<sup>2</sup> only simple cubic (Cub) centers with a nonlocal compensation and tetragonal *A* and trigonal *B* centers with a local charge compensation,  $\text{Er}^{3+} - \text{F}^-$ , which are distributed statistically through the  $\text{CaF}_2$  lattice.

In an effort to study the paramagnetism of the clusters, and we have now studied the magnetic circular dichroism—the difference  $\Delta\chi$  between the absorption coefficients for left—and right-hand circularly polarized light for a sample in a magnetic field  $H_0$  (Ref. 5)—in the absorption bands of  $(\text{CaF}_2)_{1-x}(\text{ErF}_3)_x$  crystals and also after an isomorphic replacement of most of the erbium by diamagnetic yttrium, i.e., the solid solutions  $(\text{CaF}_2)_{1-x-y}(\text{ErF}_3)_x(\text{YF}_3)_y$  with  $x \ll y$ , which we will refer to as  $\text{CaF}_2:\text{Er}_x\text{Y}_y$  for simplicity. Figure 1 shows the magnetic-circular-dichroism spectra of these solid solutions in the vicinity of the transition  $^4I_{15/2} \rightarrow ^4F_{5/2}$  in the  $\text{Er}^{3+}$  ion, along with an identification of these spectra according to Ref. 2. We note that the spectrum corresponds quite closely to the absorption spectrum (not shown). We can therefore trace the relative changes in the concentrations of the various centers<sup>1)</sup> upon changes in  $x$  and  $y$  working from Fig. 1. We thus have a new and nontrivial result: The sum of the concentrations  $x$  and  $y$ , i.e., the quantity  $x + y$ , is important for the predominance of cluster *D* centers. The effect of an yttrium admixture on the structural changes in the optical spectra of binary *C* centers,  $(\text{Er} - \text{Er}) \rightarrow (\text{Er} - \text{Y})$ , has been studied.<sup>6</sup>

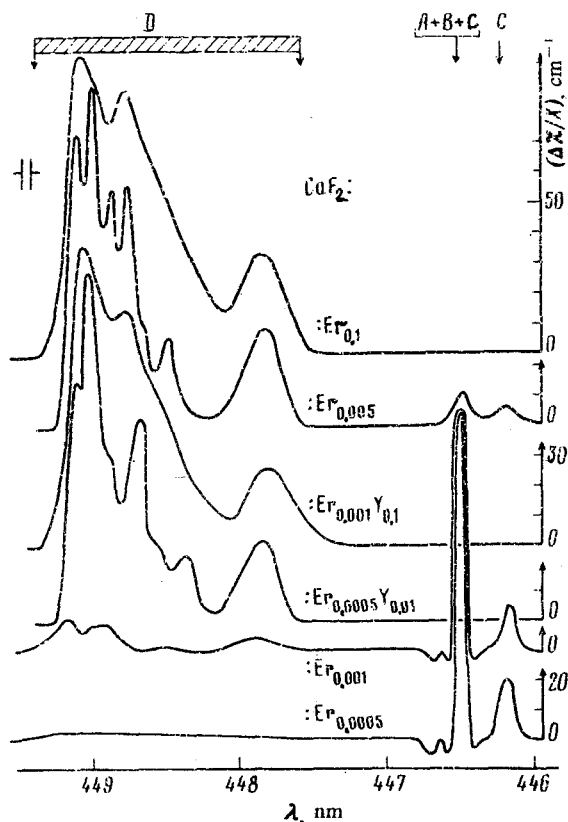


FIG. 1. Spectra of the magnetic circular dichroism of  $\text{CaF}_2:\text{Er}_x^{3+}\text{Y}_y^{3+}$  at  $H_0 \approx 3$  kG and  $T = 1.8$  K.

The field dependence of the magnetic circular dichroism in the  $D$ -center absorption bands (Fig. 2) exhibits saturation,  $\Delta\chi(H_0) = \Delta\chi_{\text{max}} \tanh(g\beta H_0/2kT)$ , with a definite orientational dependence. This behavior clearly implies that (1) the magnetic circular dichroism is of a paramagnetic nature<sup>5</sup> and (2) the  $\text{Er}^{3+}$  ions in the clusters have a tetragonal symmetry with a factor  $g_{\parallel} = 15.5 \pm 1 \gg g_{\perp}$ . A fact of extreme importance to the discussion below is that the  $\Delta\chi(H_0)$  dependence does not depend on the ratio of  $x$  and  $y$ , i.e., on the dilution  $\text{Er} \rightarrow \text{Y}$  for  $0.002 \leq x + y \leq 0.02$  cm (Fig. 2).

The ESR spectra of  $\text{CaF}_2:\text{Er}_x\text{Y}_y$  crystals have now been studied and identified (Fig. 3) in measurements of the changes in the magnetic circular dichroism,  $\Delta(\Delta\chi)$ , upon the application of an rf field ( $\nu = 37$  GHz), i.e., by the standard optical-detection method, which has several advantages<sup>5</sup> over the conventional methods. The primary result is that a broad absorption background (the hatched region in Fig. 3) in the ESR spectrum corresponds to  $D$  centers in  $\text{CaF}_2:\text{Er}_x$ . This background, however, is "compressed into a line" in  $\text{CaF}_x:\text{Er}_x\text{Y}_y$  ( $x \ll y$ ) samples, and the position of this line, which depends on the orientation of  $\mathbf{H}_0$  with respect to the crystal axes  $\mathbf{C}_i$ , corresponds precisely to that which would be expected from an analysis of the  $H_0$  depen-

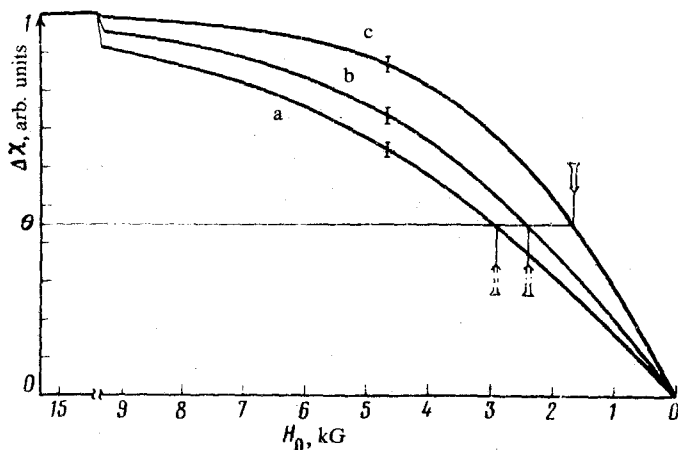


FIG. 2. Dependence of the magnetic circular dichroism ( $\lambda = 449 \pm 0.3$  nm) on  $H_0$  for  $\text{CaF}_2: \text{Er}_x^{3+} \text{Y}_y^{3+}$  at  $0.002 < x + y < 0.02$  in the following orientations: a— $\text{H}_0 \parallel \text{C}_3$ ; b— $\text{H}_0 \parallel \text{C}$ ; c— $\text{H}_0 \parallel \text{C}_4$ .  $\theta = \text{th}(\hbar v / 2kT) = 0.45$ ;  $T = 1.8$  K.

dence of the magnetic circular dichroism (as shown by the arrows in Fig. 2).<sup>2</sup> We can thus conclude that the  $D$  centers in  $\text{CaF}_2: \text{Er}_x$  samples correspond to the incorporation into the  $\text{CaF}_2$  lattice of a new crystalline phase with a high concentration (10–100 mole %) of rare-earth ions. The dilution  $\text{Er} \rightarrow \text{Y}$  in this magnetically concentrated phase causes a narrowing of the ESR spectrum without changing its extremum, as follows from Fig. 2. At  $x \ll y$ , the  $\text{Er}^{3+}$  ions are in a sense a probe in the  $Y$  phase having a tetragonal symmetry and apparently a record high factor  $g_{\parallel} \approx 15.5 \gg g_{\perp}$  for the  $\text{Er}^{3+}$  ion.

These experimental results show that only isomorphic tetragonal  $\text{Er}^{3+}$  centers are seen in the  $Y$  phase, the rare-earth phase, or the mixed phase at  $x + y \leq 0.02$ . It turns out that same centers are also predominant in  $\text{CaF}_2$  at  $x + y = 0.01$ . Lechtenböhmer and Greis<sup>1</sup> have shown by x-ray-diffraction analysis that super-structure fluorite phases are present in the corresponding concentrated solid solutions. These fluorite phases are<sup>2</sup> octahedra of six rare-earth ions, surrounded by 12 interstitial  $\text{F}^-$  ions, which appear in a periodic arrangement in the  $\text{CaF}_2$  lattice. The local symmetry of the rare-earth ions in the superstructure is apparently tetragonal, so that it can be identified with the rare-earth (and yttrium) phase observed in the present experiments. It is important to note that in our experiments the superstructure is seen at a concentration of only  $x + y \geq 0.001$ . At such low activator concentrations the superstructure should evidently occupy bounded regions, i.e., should form "gains" in the  $\text{CaF}_2$  crystal lattice.<sup>3)</sup>

The results of our study of  $\text{CaF}_2: \text{Tm}_x^{3+} \text{Y}_y^{3+}$  crystals are very similar. In the ESR spectrum of cluster  $D$  centers in  $\text{CaF}_2: \text{Tm}_x^{3+}$  crystals there is a broad absorption band, which contracts upon the dilution  $\text{Tm} \rightarrow \text{Y}$ . The field dependence of the magnetic circular dichroism measured in the absorption bands of the  $\text{Tm}^{3+}$  clusters is not affected by this dilution. It turns out that the  $\text{Tm}^{3+}$  ions form tetragonal centers in

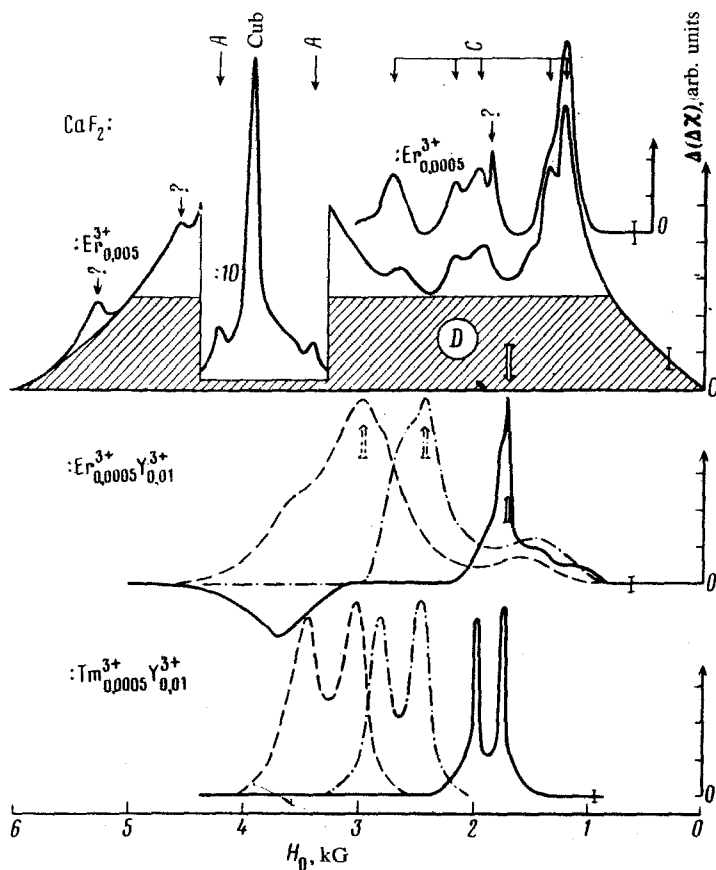


FIG. 3. Optical-detection ESR spectra of  $\text{CaF}_2: (\text{RE})_x^3+ \text{Y}_y^3+$  in several orientations: Solid curve— $\text{H}_0 \parallel \text{C}_4$ ; dashed curve— $\text{H}_0 \parallel \text{C}_3$ ; dot-dashed curve— $\text{H}_0 \parallel \text{C}_2$ .

both the rare-earth and yttrium phases with the highest possible value of  $g_{\parallel}$ ,  $g_{\parallel} \approx 14$  ( $g_{\perp} = 0$ ), for the  $\text{Tm}^{3+}$  ground state.<sup>7</sup> Figure 3 shows the optical-detection ESR spectrum of the  $\text{Tm}^{3+}$  ion in the Y phase. There is a characteristic doublet structure, formed by the hyperfine interaction of the  $\text{Tm}^{3+}$  electron spin with the nuclear spin  $I(\text{Tm}^{169}) = \frac{1}{2}$ . We might note that the ESR of  $\text{Tm}^{3+}$  ions with the  $4f^{12}$  configuration, with an even number of electrons, has not been observed previously, and its appearance in the present case is apparently a consequence of the anomalous sign of the crystal-potential constant,<sup>7</sup>  $A_2^0 < 0$ , for the rare-earth ion in the superstructure.

The conclusions which we have reached regarding the existence of superstructure grains in  $\text{CaF}_2$  crystals activated with rare-earth ions can explain certain anomalous results which have been observed previously: (1) the "high-temperature peak" at  $T = 0.8$  K in studies of the magnetic susceptibility of a dipole spin glass in the  $\text{CaF}_2:\text{Er}^{3+}$  system<sup>8</sup> and (2) the depolarization of  $\text{G}^{19}$  nuclei in  $\text{CaF}_2:\text{Tm}$  crystals during a low-frequency modulation of the static magnetic field in the absence of direct thermal contact between the nuclear subsystem and the electron spin-spin reservoir.<sup>9</sup>

I wish to thank V. A. Atsarkin for interest in this study.

- <sup>1)</sup>Except for the cubic centers, which are not seen in the optical spectra. These centers form  $\sim 50\%$  of the  $\text{Er}^{3+}$  ions which enter the  $\text{CaF}_2$  at  $x \geq 0.001$  (Ref. 2).
- <sup>2)</sup>The ESR lines of *C* centers (Er-Er) should evidently not be exhibited by the samples with *Y* at  $x \ll y$ . It can be seen from Fig. 1 that even the more probable *C* centers (Er-Y) are not observed at  $y = 0.01$ .
- <sup>3)</sup>According to preliminary data, attempts to detect grains of a rare-earth phase by direct methods have been successful. Specifically, local *x*-ray spectral analysis and analysis by means of an electron probe have revealed grains  $\sim 1 \mu\text{m}$  in size with an erbium concentration of 10–100 mole % in  $\text{CaF}_2:\text{Er}_{0.005}$ .

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