

Dipolar Complexes in Calcium Fluoride Doped with Erbium*

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The rotation of $\text{Er}^{3+}-\text{F}_i^-$ dipoles in CaF_2 was studied by the ionic thermocurrent (ITC) technique. Relaxation peaks at 138 K ($E=0.380$ eV, $\tau_0=2\times 10^{-13}$ sec) and 54 K ($E=0.167$ eV, $\tau_0=3\times 10^{-15}$ sec) were observed, and it is proposed that these are produced by the reorientation of the tetragonal complex (nearest-neighbor interstitial fluorine) and the trigonal complex (next-nearest-neighbor interstitial fluorine), respectively. Twidell recently reported inducing movement of the interstitial fluorine with uv light and his results are compared with the effects on the ITC spectrum caused by uv and by electron irradiation at low temperature.

Trivalent rare-earth ions (RE^{3+}) dissolve readily in the alkaline earth fluorides and, in the absence of oxygen, hydroxyl, or monovalent cation impurities, are compensated by an equivalent concentration of interstitial fluoride ion (F_i^-). Some of the RE^{3+} is present as the isolated ion on sites which have been shown by means of electron-nuclear double resonance (ENDOR)¹⁻³ to have the cubic symmetry of the cation site; however, dipolar complexes composed of the RE^{3+} with the F_i^- in a nearby site are known to form. Heist and Fong⁴ have recently discussed these complexes. The predominant complex in CaF_2 is one with tetragonal symmetry in which the F_i^- occupies the nearest interstitial site (nn), and its presence and symmetry have been demonstrated by electron paramagnetic resonance (EPR)^{5,6} and ENDOR^{7,8} measurements. A complex with trigonal symmetry in which the F_i^- is assumed to occupy a site in the second shell of interstitial sites (nnn) has also been observed^{9,10} in the EPR spectra of SrF_2 and BaF_2 containing RE^{3+} . Twidell has recently shown¹¹ that in CaF_2 doped with Er, ultraviolet excitation causes the F_i^- in the nn sites to move to a more distant position, as indicated by a decrease in the tetragonal EPR signal and a corresponding increase in the cubic signal. We report here ionic thermocurrent¹² (ITC) measurements on this system in which we observe two relaxations, one which we ascribe to the nn complex and one arising from a related but less populated and more loosely bound complex, which we ascribe to the nnn complex.

The $\text{CaF}_2:\text{Er}$ samples come from the boule employed previously by Baker, Hayes, and Jones⁵ and by Twidell¹¹ and have a nominal Er^{3+} concentration of 10 ppm. The samples are known to be virtually free of oxygen or hydroxyl contamination. A specimen of cross-sectional area 0.162

cm^2 and thickness 0.047 cm was provided with sputtered platinum electrodes. The ITC spectrum was obtained by (a) polarizing with an applied voltage of 500 V for 5 min at 140 K, (b) cooling in the electric field to 12 K, and (c) warming at a rate of 0.1 K sec^{-1} from 12 to 80 K and at 0.2 K sec^{-1} above 80 K. The displacement current resulting from the reorientation of the dipoles was measured with a Cary model 401 vibrating-reed electrometer having an input resistor of 10^{11} Ω and a noise level of 5×10^{-16} A peak to peak. Two well defined peaks, shown in Fig. 1, located at 53.7 and 137.5 K were observed. It was possible to obtain an excellent computed fit to both of these curves using the first-order dipole-relaxation relation and the following values for the relaxation parameters E and τ_0 : 0.167 ± 0.005 eV and $(3\pm 2)\times 10^{-15}$ sec for the 54-K peak and 0.380 ± 0.005 eV and $(2\pm 1)\times 10^{-13}$ sec for the 138-K peak.

The results for the 138-K peak are consistent with the EPR and dielectric-loss measurements of Franklin and Marzullo¹³ on the tetragonal complex in $\text{CaF}_2:\text{Gd}$ and are in reasonable agreement

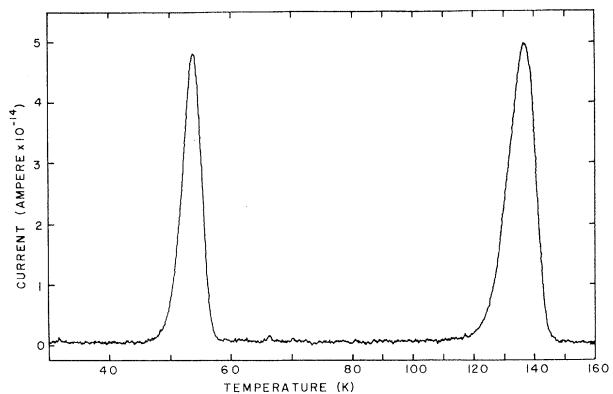


FIG. 1. ITC spectrum of $\text{CaF}_2:\text{Er}$. Heating rate: 0.1 K sec^{-1} below 80 K, 0.2 K sec^{-1} above 80 K.

Table I. Some dipolar relaxation results in CaF_2 .

Complex	E (eV)	τ_0 (sec)	Technique	Reference
$\text{Er}^{3+}-\text{F}_i^-$ (54)	0.17	3×10^{-15}	ITC	This work
$\text{Er}^{3+}-\text{F}_i^-$ (138)	0.38	2×10^{-13}	ITC	This work
$\text{Gd}^{3+}-\text{F}_i^-$ (nn)	0.40	5×10^{-14}	EPR	12
$\text{Gd}^{3+}-\text{F}_i^-$	0.38	6×10^{-14}	Dielectric loss	12
$\text{Ce}^{3+}-\text{F}_i^-$	0.46	6×10^{-15}	ITC	13

with ITC measurements on $\text{CaF}_2:\text{Ce}$ reported by Royce and Mascarenhas.¹⁴ These results are summarized in Table I. The ENDOR measurements⁸ show that both the distortion of the complex and the extent of the covalent bonding are relatively small and we assume that, to a reasonable approximation, the electric dipole moments associated with the complexes are those of the undistorted point-ion dipoles. Using this nn point-ion dipole moment to account for the area under the 138-K peak yields a concentration of 22 ppm of the Er^{3+} in this configuration, which is comparable to the nominal total Er^{3+} concentration. The EPR results^{5,11} show that approximately 95% of the Er^{3+} detected was on these sites. It is reasonable to conclude from this discussion that the 138-K peak corresponds to relaxation of the nn $\text{Er}^{3+}-\text{F}_i^-$ complex.

Assigning the 54-K peak is more difficult. EPR spectra having trigonal symmetry have been observed¹⁵⁻¹⁷ in $\text{CaF}_2:\text{Er}$ and one has been ascribed¹⁵ to an $\text{Er}^{3+}-\text{F}_i^-$ complex. However, these spectra have generally been too weak for their origin to be conclusively established. The EPR results mentioned above^{9,10} on related materials show that such complexes are definitely possible. Using the nnn point-ion dipole moment to account for the area under the 54-K peak, our data yield a concentration of 1.3 ppm (5% of all the Er^{3+}) in the trigonal form prior to any treatment. This low concentration and the trigonal symmetry of the nnn site would result in a weak set of anisotropic EPR lines and neglect of the trigonal complex in EPR work is not surprising since this has been confined to the strong components of the EPR spectrum. In contrast, the low polarization temperature and larger dipole moment would greatly enhance the 54-K peak relative to the 138-K peak.

Twidell¹¹ found that irradiation with light from a low pressure mercury lamp at 273 K enhanced the cubic EPR spectrum at the expense of the tetragonal. From similar experiments we found

that a decrease in the 138-K peak was accompanied by an increase in the 54-K peak and an overall loss of bound Er^{3+} . The change was stable at low temperature and could be reversed by annealing above room temperature, in qualitative agreement with Twidell's results.

In order to obtain more information about the nature of the complexes, the sample was irradiated in the temperature range 80 to 200 K with 1.5-MeV electrons through a 0.25-mm aluminum window in the cryostat. The ITC was then measured without warming the sample above 200 K. The effects after irradiation at 80 K were small and increased markedly with temperature of irradiation, the 54-K peak being most affected. A dose of 3×10^{13} electrons cm^{-2} at 200 K reduced the 54-K peak by 95% and the 138-K peak by 25%. After holding the sample at 300 K for 10 min, the loss was substantially restored. This behavior would be expected if the Er^{3+} component of the complex captures an electron. An extended complex would present a greater electron-capture cross section than a compact one, and hence a complex with the F_i^- in the nnn site might be expected to suffer more from exposure of the sample to ionizing radiation than one with it in the nn site. The increase in dipole destruction with increasing temperature can be explained by a decrease in the effectiveness of the competing traps. Irradiation at 80 K followed by warming to 200 K resulted in a considerable reduction in the 54-K peak, which supports this hypothesis. Twidell¹¹ found that x irradiation at room temperature decreased the concentration of the Er^{3+} centers with cubic symmetry and left the tetragonal centers unaffected. Other work¹⁸⁻²¹ has also shown that low doses of radiation at either 77 or 300 K convert RE^{3+} on cubic sites to RE^{2+} and leave that on other sites unaffected. We were unable to monitor the isolated Er^{3+} but the absence of radiolysis of the bound state at either of these temperatures is consistent with our results. The loss of cubic RE^{3+} evidently stems from the

conversion of isolated RE^{3+} to RE^{2+} by capture of an electron, and isolated RE^{2+} is quite stable at room temperature. The population of dipolar centers is restored quite rapidly at room temperature, suggesting that the presence of a nearby F_i^- reduces the binding of the trapped electron sufficiently to permit it to escape at room temperature.

The extremely low activation energy and high entropy factor for rotation of the dipole responsible for the 54-K peak are rather curious. The activation energy for motion of the free F_i^- has not been definitely established, but the published values²² are considerably higher than the reorientation energy of the tetragonal complex. ENDOR results⁸ suggest that the lattice distortion in the tetragonal complex is probably slight and mainly due to the F_i^- . It is difficult to predict the magnitudes, or even the signs, of the lattice relaxations in the trigonal complex in the absence of any experimental information about them, but it is clear that the electrostatic effects due to the Er^{3+} will be more marked with the compensating F_i^- more distant. It is possible that the effects might be large enough to lead to the anomalous values for the parameters for reorientation, either by direct motion of the F_i^- or by a replacement sequence, and to the large barrier (~ 1 eV) for conversion to the nn complex.

It seems reasonable to suggest that the 54-K peak is due to relaxation of the nnn $Er^{3+}-F_i^-$ complex, but without more definite information about the populations of the various possible complexes⁴ and about the lattice relaxations this identification must remain rather tentative. It is apparent that a systematic study of the lattice relaxations in the vicinity of these defects would be most valuable. ENDOR would clearly be the most direct technique, although interpretation of the results is complicated by covalent bonding. Study of the dipolar relaxation phenomena for various RE^{3+} and host lattices by means of ITC would clearly be worthwhile.

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