

between the lowest band and the group of bands emerging from the $\Gamma_{25'}$ level; the peak at 8.1 eV involves the bands originating in Γ_{12} . Although transitions between these states are forbidden at Γ , a substantial contribution results from the mixing of states of different symmetries away from the zone center.

We conclude from these results that band theory enables a reasonably satisfactory description of the low-energy optical conductivity of potassium. There appears to be little need to invoke many-body effects to explain the essential features of the experimental results in the 1–10-eV region.

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Reorientation Kinetics of Fluoride- and Oxygen-Compensated Dipoles in Gadolinium-Doped Calcium Fluoride

E. L. Kitts, Jr., and J. H. Crawford, Jr.

Physics Department, University of North Carolina, Chapel Hill, North Carolina 27514

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A study of the thermal depolarization spectra for crystals of calcium fluoride containing trivalent gadolinium has been made before and after oxygen contamination. In the oxygen-contaminated crystals, a new ionic thermocurrent peak, with an activation energy of 0.49 eV and a reciprocal frequency factor of 5×10^{-14} sec, is attributed to the relaxation of $\text{Gd}^{3+}\text{-F}^-$ dipoles in the T_1 complex ($\text{Gd}^{3+}\text{O}_4^{2-}\text{F}^-$).

Although numerous applications of the ionic thermocurrent (ITC) technique¹ to simple impurity-defect dipoles in ionic solids are quite familiar, no relaxations specifically attributable to more complex structures have been reported. We report here for the first time a study of the relaxation of such a complex center, namely, $\text{Gd}^{3+}\text{O}_4^{2-}\text{F}^-$ in calcium fluoride. In addition, earlier work² on the relaxation behavior of the tetragonal Gd^{3+} -fluoride interstitial dipolar complex has been confirmed by higher-precision measurements.

ITC refers to the displacement current which results from the thermal release of "frozen-in" polarization as the crystal is warmed at a linear rate. The experimental procedure is to polarize at a temperature T_p at which the dipolar complex of interest can readily reorient, to then cool, with the polarizing field ϵ applied, to a temperature T_0 low enough to "freeze in" the polarization, and then to measure the depolarization current

as the crystal is warmed with the field removed. The ITC equation, which gives the form of the ITC curve for a single type of dipole, is

$$j(T) = \frac{N\mu^2\epsilon}{3kT_p\tau_0} \exp\left(\frac{-E}{kT}\right) \times \exp\left[-\frac{1}{b\tau_0} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dt'\right], \quad (1)$$

where N is the dipole concentration, μ is the dipole moment, τ_0 is the reciprocal frequency factor, E is the activation energy, and b is the heating rate.

In alkaline-earth fluoride crystals containing trivalent lanthanide ions (RE^{3+}), the extra positive charge is usually compensated either by interstitial fluoride ions (F_i^-) or by substitutional O^{2-} . If $\text{CaF}_2:RE^{3+}$ crystals are grown in reducing conditions with an excess of fluorine, then the predominant dipolar complex is one of tetragonal (C_{4v}) symmetry in which the F_i^- occupies a near-

est-neighbor interstitial site. This has been well established by EPR^{3,4} and electron-nuclear double-resonance (ENDOR)^{5,6} studies. Compensation by O^{2-} is readily achieved by heating $CaF_2:RE^{3+}$ in the presence of water vapor.⁷⁻⁹ The introduction of oxygen proceeds particularly efficiently in a hydrogen atmosphere contained in a quartz tube.⁸ Two trigonal EPR spectra are characteristic of $CaF_2:RE^{3+}$ having oxygen compensation. Siervo⁹ attributed these two spectra to the substitution of O^{2-} and OH^- , respectively, at a nearest-neighbor anion site. A recent ENDOR study by Reddy *et al.*¹⁰ has shown this assignment to be incorrect. Instead, the two trigonal spectra, designated T_1 and T_2 , are due to $RE^{3+}O_4^{2-}F^-$ and $RE^{3+}O^{2-}F_7^-$, respectively. These configurations are shown in Fig. 1.

The "as-received" crystals used in this study were grown by Optovac Inc., and contained a nominal doping level of 0.1 mol% trivalent gadolinium. An EPR assay¹¹ of the crystal revealed 68% of the Gd^{3+} at sites of tetragonal symmetry, 27% at cubic sites, 5% at trigonal sites, and a few very weak lines corresponding to unidentified Gd^{3+} sites. The solid line in Fig. 2 shows the ITC spectrum above 100 K for the "as-received" crystal, using a heating rate of 0.1 K sec^{-1} . The principal ITC peak was observed at 131 K, and is attributed to the relaxation of the tetragonal $Gd^{3+}-F_i^-$ dipolar complex. An excellent computed fit of the ITC peak with the first-order dipolar-relaxation relation (ITC equation) yielded an activation energy (E) of $0.42 \pm 0.01 \text{ eV}$ and a reciprocal frequency factor (τ_0) of $10^{-14.6 \pm 0.5} \text{ sec}$. This value for activation energy agrees fairly well with the value obtained earlier by Stott and Crawford.² Because of the use of an exchange gas, which was not used in the earlier study,² the temperature of the sample was known with more pre-

cision in this study, and the value obtained for τ_0 seems to be more reasonable. A second peak of substantial size was observed at 221 K. A good computed fit with the ITC equation was obtained, yielding the following values for the relaxation parameters: $E = 0.69 \pm 0.02 \text{ eV}$ and $\tau_0 = 10^{-14.0 \pm 0.7} \text{ sec}$. The 221-K peak has been tentatively attributed¹² to the trigonal $Gd^{3+}-F_i^-$ complex, where the F_i^- is in a next-nearest-neighbor position. This identification conflicts with an earlier assignment² of a 60-K ITC peak to this complex.

The oxygen-contaminated samples were prepared by annealing the "as-received" crystal at 800°C for about 24 h in a quartz tube through which hydrogen was flowing. EPR assays¹¹ of these samples so treated revealed only the two trigonal spectra characteristic of oxygen-contaminated $CaF_2:Gd^{3+}$. In particular, the EPR measurement detected no Gd^{3+} with local compensation by either hydride or fluoride ions. A typical ITC spectrum for one of these oxygen-contaminated samples is presented by the dashed-curve segments in Fig. 2. Only a very small fraction of the 131-K peak remains, and the 221-K peak has disappeared. Instead, a large, well-behaved peak at 166 K dominates the ITC spectrum. A good computed fit of this new peak with the ITC equation yielded the following values for the relaxation parameters: $E = 0.49 \pm 0.01 \text{ eV}$ and $\tau_0 = 10^{-13.3 \pm 0.5} \text{ sec}$. The $Gd^{3+}-O^{2-}$ dipoles assigned to the T_2 EPR spectrum would not be expected to reorient thermally so as to produce an ITC peak. On the other hand, the $Gd^{3+}-F^-$ dipole in the $Gd^{3+}O_4^{2-}F^-$ complex assigned to the T_1 EPR spectrum could reorient by an interchange of the fluo-

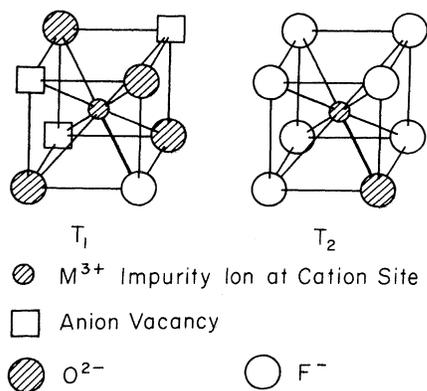


FIG. 1. Models assigned to T_1 and T_2 EPR spectra.

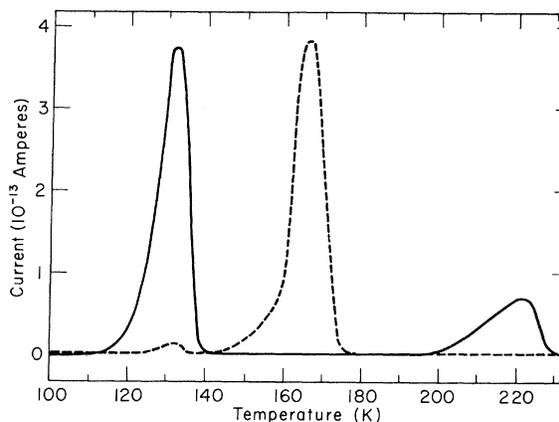


FIG. 2. ITC spectra for $CaF_2:Gd^{3+}$ at a heating rate of 0.1 K sec^{-1} . Solid curve for "as-received" crystal; dashed-curve segments for oxygen-contaminated crystals.

TABLE I. Relaxation parameters for dipoles in CaF_2 .

Crystal	Dipolar complex	E (eV)	$\log_{10}\tau_0$ (sec) *	Method (Ref.)
$\text{CaF}_2:\text{Gd}^{3+}$	$\text{Gd}^{3+}-\text{F}_i^-$ (C_{4v})	0.42 ± 0.01	-14.7 ± 0.5	ITC (this work)
		0.38	-13.1	EPR/diel. relax. (16)
		0.395 ± 0.01	-12.9 ± 0.3	ITC (2)
$\text{CaF}_2:\text{Gd}^{3+}$	$\text{Gd}^{3+}\text{O}_4^{2-}\text{F}^-$ (T_1)	0.50 ± 0.03	-15.8 ± 1.5	ITC (15)
$\text{CaF}_2:\text{Na}^+$	$\text{Na}^+ - \text{V}_\text{F}$	0.49 ± 0.01	-13.4 ± 0.5	ITC (this work)
		0.52	-14.2	ITC (13)
		0.48	-12.8	ITC (14)

ride ion with one of the three anion vacancies. Thus the new ITC peak at 166 K is assigned to the T_1 center, and is thought to be the first ITC peak to be identified with a center of such complexity. In addition to inherent interest in the T_1 center itself, this identification is important because the center forms so readily under conditions favorable for hydrolysis. Thus its incidental appearance during various thermal treatments utilized in the study of other centers in $\text{CaF}_2:\text{RE}^{3+}$ can lead to confusion. The values obtained for the relaxation parameters of the T_1 center agree well with those obtained by Shelly and Miller¹³ and by Kunze and Müller¹⁴ for relaxation of the Na^+ -anion vacancy dipole in $\text{CaF}_2:\text{Na}^+$, where, as in the T_1 center, reorientation would occur by the interchange of a fluoride ion with an anion vacancy.

Table I presents a summary of measurements of the relaxation parameters for dipoles in calcium fluoride. The list is by no means exhaustive, but rather was selected as being particularly appropriate for comparison with the results of this study. With the exception of the values reported by Stiefbold and Huggins,¹⁵ the results agree very well.

To the degree that the dipole moment is known, the area under the ITC peak provides a measure of the dipole concentration. Using the dipole moment consistent with the undistorted point-ion model (UPIM), namely, 4.37×10^{-27} C cm, the tetragonal $\text{Gd}^{3+}-\text{F}_i^-$ dipole concentration was determined to be 7×10^{18} cm^{-3} in the "as-received" crystal. Assuming the crystal actually contains the nominal doping level added in the melt, the total Gd^{3+} concentration would be 2.5×10^{19} cm^{-3} . The EPR assay¹¹ indicates that the tetragonal $\text{Gd}^{3+}-\text{F}_i^-$ dipoles account for 68% of the detectable Gd^{3+} . Thus about 65% of the Gd^{3+} added to the melt is unaccounted for in the "as-received" crystals, perhaps being present in aggregates

not detected by either ITC or EPR. After oxygen contamination during the 800°C anneal, the total Gd^{3+} concentration in solution appears to have increased. EPR assays¹¹ of two oxygen-contaminated samples show almost all of the detectable Gd^{3+} to be in either T_1 or T_2 centers, with relative T_1 -center concentrations of 37% and 57%. The UPIM moment for the T_1 center (3.78×10^{-27} C cm) yields T_1 -center concentrations of 8×10^{18} cm^{-3} and 1.2×10^{19} cm^{-3} , respectively. Hence, assuming these UPIM dipole moments are accurate, more than 80% of the Gd^{3+} added in the melt appears to be in solution following the 24-h hydrolysis at 800°C.

Because of lattice distortion, the dipole moments may be substantially different from those predicted by the UPIM. This effect has not been studied quantitatively, but it is expected that taking account of distortions would reduce to some degree the discrepancy observed between the $\text{Gd}^{3+}-\text{F}_i^-$ and the T_1 -center concentrations. For a given area under the ITC peak, the dipole concentration is proportional to the inverse square of the dipole moment. Hence small changes in the $\text{Ge}^{3+}-\text{F}^-$ separation can significantly change the indicated dipole concentration. For the tetragonal $\text{Gd}^{3+}-\text{F}^-$ dipole, the electrostatic attraction between the F_i^- and small (relative to Ca^{2+}) trivalent impurity ion would be expected to reduce the dipole separation from that expected in the UPIM. Applying such a correction would increase the indicated $\text{Gd}^{3+}-\text{F}_i^-$ dipole concentration. In the T_1 center, on the other hand, one expects a distortion with the four O^{2-} ions relaxing radially inward toward the Gd^{3+} , and with the three anion vacancies and the F^- moving outward radially from the Gd^{3+} . This would increase the dipole moment, causing the estimate of dipole concentration based upon the UPIM to be somewhat high.

A detailed study of the formation kinetics of

the T_1 center has not been done, but it seems clear that with hydrolysis, the formation proceeds in time as $Gd^{3+}-F_i^- \rightarrow T_2 \rightarrow T_1$, indicating that the T_1 center is particularly stable. This stability might account for part of the apparent increase in the concentration of dissolved Gd^{3+} . A study of these formation kinetics would be interesting in its own right and this work indicates that ITC would be a valuable experimental tool in such a study.

We are particularly indebted to G. D. Jones and A. Edgar of the University of Canterbury (Christchurch, New Zealand) for the EPR assays of our samples and for helpful discussions. Also, helpful assistance and discussions relating to the hydrogen annealing procedure were provided by R. Lambe. A more extensive study of electric dipole relaxation in alkaline-earth fluorides containing a variety of rare-earth impurities will be published elsewhere.

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V_{Al} and V^- Centers in MgO^\dagger

W. P. Unruh, Y. Chen, and M. M. Abraham

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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The center produced by ionizing radiation which has been generally accepted to be the intrinsic V^- center in nominally pure MgO is shown to be actually associated with an aluminum impurity. A stable center with identical g values is produced by irradiation with energetic particles and its properties are compatible with the intrinsic V^- center.

During the course of previous work in this laboratory on trapped-hole centers affiliated with the alkali impurities in the alkaline-earth oxides,¹⁻³ it became obvious that, in order to understand better the nature of these centers, it would be necessary to explore further the environment of the V^- center in MgO . The ESR properties of the V^- center (previous notations: H_1, V_1 centers) were first investigated by Wertz *et al.*⁴⁻⁶ and their results showed that the center, which can be produced in as-grown crystals by a short exposure to ionizing radiation, possessed tetragonal symmetry about a $\langle 100 \rangle$ direction with $g_{\parallel} = 2.0032$ and $g_{\perp} = 2.0385$. They proposed a model of a hole trapped on an oxygen ion, forming an

O^- ion adjacent to an Mg-ion vacancy. Related centers such as the V_F, V_{OH} , and V_{OD} , where an $F^-, OH^-,$ or OD^- ion replaces the O^{2-} ion adjacent to the positive-ion vacancy and opposite to the O^- ion, may also be produced by ionizing radiation, and these centers have been studied by both ESR^{7,8} and electron-nuclear double-resonance (ENDOR)⁹⁻¹⁰ techniques. Those ENDOR results unequivocally identified the axial interactions of the fluorine, hydrogen, and deuterium nuclei in these related centers, but shed little light on the detailed structure of the defects. In particular, no information about the nearest-neighbor magnesium interactions was reported. The relative concentrations of these centers are