Observation of optically stimulated reorientation of dipolar defects in Pr$^{3+}$ doped strontium fluoride.

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ABSTRACT

We have performed optical and dielectric measurements on the reorientation of $C_{4v}$ ($F^-$) dipolar defects found in SrF$_2$ doped with Pr$^{3+}$. By monitoring the polarization of fluorescence from optically excited Pr$^{3+}$ ions in these defect sites, we have observed the movement of the adjacent interstitial $F^-$. We have also observed the motion of these $F^-$ ions by measuring the thermally stimulated depolarization current. These two procedures yield significantly different results. We propose an optically driven mechanism for interstitial $F^-$ motion that may explain this disparity.

Keywords: thermally stimulated depolarization; ionic thermocurrent; dielectric relaxation; site-selective spectroscopy; calcium fluoride; strontium fluoride; praseodymium


PACS codes: 77.22.Ej, 63.20.Mt, 78.55.-m
I. INTRODUCTION

Fluorite crystals (such as CaF$_2$ and SrF$_2$) readily accept trivalent rare earth ions into their structure. These ions occupy substitutional sites replacing divalent host cations. An interstitial F$^-$ ion provides charge compensation for the trivalent rare earth. For crystals containing Pr$^{3+}$ and Eu$^{3+}$ rare earth dopants, this compensating F$^-$ ion most often resides in a nearest-neighbor (nn) interstitial site, thus producing a dipolar defect with tetragonal ($C_{4v}$) symmetry.$^{1,2,3}$ (See Fig. 1.)

![Diagram of C$_{4v}$ defect]({Fig. 1. Tetragonal or C$_{4v}$ defect found in CaF$_2$ and SrF$_2$ doped with trivalent rare earth ions. Thermal stimulation permits the nearest-neighbor interstitial F$^-$ to hop among the six available nearest-neighbor interstitial sites. This interstitial F$^-$ can thermally hop to adjacent nn sites, thereby changing the orientation of the defect. This interstitial movement has been traditionally studied using dielectric methods such as dielectric relaxation$^4$ and thermally stimulated depolarization current$^5$ (TSDC, also known as ionic thermocurrent or ITC). These techniques monitor the electrical polarization of the material. Recently, some researchers have observed this}
interstitial motion by monitoring the changing optical polarization of laser stimulated fluorescence.\textsuperscript{6,7}

For samples doped with Pr\textsuperscript{3+}, most of the optical data contains an anomaly not seen in the dielectric measurements. In this work, we have used both methods to tackle this anomaly.

**II. FLUORESCENCE DEPOLARIZATION RESULTS**

We have optically observed the reorientation of C\textsubscript{4v} defects in Pr\textsuperscript{3+} doped SrF\textsubscript{2} using the method described by Voron’ko \textit{et al.}\textsuperscript{6} and Jamison and Reeves.\textsuperscript{7} SrF\textsubscript{2} doped with 0.1 molar percent Pr\textsuperscript{3+} was obtained from Optovac. We cut a sample along its \textlangle 100\textrangle planes and controlled its temperature with an ADP Cryogenics closed cycle helium refrigerator. The sample was illuminated with 476.5 nm light from a Coherent Innova 300 argon ion laser; this wavelength happens to correspond with the $^3\text{H}_4 \rightarrow ^3\text{P}_0$ excitation for Pr\textsuperscript{3+} in SrF\textsubscript{2} (Ref. 7). The laser light was polarized in the \textlangle 010\textrangle crystal direction and traveled in the \textlangle 100\textrangle direction. The fluorescent light emitted in the \textlangle 001\textrangle direction was directed through a polarizer to a Spex 1680A monochromator. An Ortec 265 photomultiplier tube captured the light from the monochromator. We placed a mechanical chopper in the laser’s path and measured the output of the PMT with a Stanford Research 830 digital lock-in amplifier using the chopper as a frequency reference.

Electronic and magnetic dipole transitions will only occur for certain orientations of the defect. Likewise, the polarization of the emitted photon will depend on defect orientation.\textsuperscript{6,7,8} When the excited ions decay at low temperatures (less than 140 K in our work), the polarization of the excited defects is preserved in the polarization of the
fluorescent photons. However, if the interstitial F ions have enough thermal energy to hop to other \( nn \) sites before the ions decay, the emitted photons will have a random polarization. Assuming the reorientation is a thermally driven Arrhenius process, the polarization of the fluorescence is given by

\[
P_{\sigma\pi}(T) = \frac{1/\tau_f}{2\nu \exp(-E/k_B T) + 1/\tau_f},
\]

for processes involving \( \sigma \) electric dipole absorption and \( \pi \) electric dipole fluorescence. Here, \( \nu \) is the attack frequency, \( \tau_f \) is the lifetime of the fluorescence, and \( E \) is the enthalpy of activation.

We observed fluorescence at three wavelengths: 637.5 nm, 638.7 nm, and 603.1 nm. These correspond to transitions coming from the \( ^3P_0 (\gamma_1) \) level to the \( ^3F_2 (W_3, \gamma_5), ^3F_2 (W_2, \gamma_1), \) and \( ^3H_6 (X_3, \gamma_1) \) levels respectively as identified by Reeves, Jones, and Syme. While the 638.7 nm line received the most study, similar activation parameters were found for each line. We measured the fluorescence lifetime of these transitions as \( 115.6 \pm 2.3 \) \( \mu s \), somewhat shorter than the 140 \( \mu s \) found by Jamison and Reeves. Typical results of the fluorescence depolarization are shown in Fig. 2. Fitted parameters are shown in Table I.
Curiously, a single Arrhenius relaxation inadequately described the polarization of the fluorescence. However, if we add a slower secondary relaxation, we can fit the observations nicely. It seems that at least two hopping mechanisms are available to the F\(^{-}\): a high-energy path with an attack frequency on the order of the Debye frequency, and a low-energy path with an extraordinarily low attack frequency.

In their study of both SrF\(_2\) and CaF\(_2\) doped with Pr\(^{3+}\), Jamison and Reeves found similar results. They also performed such experiments on CaF\(_2\) and SrF\(_2\) doped with Eu\(^{3+}\). For those materials they found that a single Arrhenius relaxation was sufficient to explain the polarization of the fluorescence.
Voron’ko et al.\textsuperscript{6} studied CaF\textsubscript{2} doped with both Eu\textsuperscript{3+} and Pr\textsuperscript{3+}. In each case, they found that a single Arrhenius relaxation adequately explained the results. Why their results differed from the CaF\textsubscript{2}:Pr\textsuperscript{3+} results of Jamison and Reeves is unknown, but it may be related to the different excitation and luminescence transitions observed by Voron’ko et al.

### Table I. Fit parameters of our optical data assuming the case of a single defect species with one or two reorientation paths available.

<table>
<thead>
<tr>
<th></th>
<th>Activation energy</th>
<th>Attack frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single path model</td>
<td>0.407 ± 0.006 eV</td>
<td>$10^{13.0}$ Hz\textsuperscript{a}</td>
</tr>
<tr>
<td>Two path model</td>
<td>0.416 ± 0.005 eV</td>
<td>$10^{13.0}$ Hz\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td>0.0629 ± 0.0053 eV</td>
<td>$10^{4.56 ± 0.14}$ Hz</td>
</tr>
</tbody>
</table>

\textsuperscript{a}To reduce the number of fitted parameters, this value was taken from the TSDC fits. (See below.)

### III. DIELECTRIC MEASUREMENTS

Previous measurements using TSDC\textsuperscript{9,3} and dielectric relaxation\textsuperscript{10,3} have found an activation energy and an attack frequency similar to the high energy path found above; however, no one has ever observed a low energy path using these methods (see Tables II & III). (For an introduction to both dielectric relaxation [also known as Debye relaxation] and TSDC, see Agullo-Lopez, Catlow, and Townsend.\textsuperscript{11})
### Table II. Reorientation parameters for $C_{4v}$ defects in CaF$_2$:Pr$^{3+}$.

<table>
<thead>
<tr>
<th>Path</th>
<th>Activation Energy (eV)</th>
<th>Attack Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jamison and Reeves$^7$,</td>
<td>0.42</td>
<td>$1 \times 10^{13}$</td>
</tr>
<tr>
<td>(fluorescence depolarization)</td>
<td>High energy</td>
<td></td>
</tr>
<tr>
<td>Low energy path</td>
<td>0.04</td>
<td>900</td>
</tr>
<tr>
<td>Voron’ko et. al (fluorescence depolarization)</td>
<td>0.4 ± 0.03</td>
<td>$(2.5 ± 2) \times 10^{12}$</td>
</tr>
<tr>
<td>Andeen, Link, and Fontanella$^9$ (dielectric relaxation)</td>
<td>0.432</td>
<td>$7.75 \times 10^{13}$</td>
</tr>
<tr>
<td>Wagner and Mascarenhas$^8$ (TSDC)</td>
<td>0.47</td>
<td>$5 \times 10^{14}$</td>
</tr>
</tbody>
</table>

### Table III. Reorientation parameters for $C_{4v}$ defects in SrF$_2$:Pr$^{3+}$.

<table>
<thead>
<tr>
<th>Path</th>
<th>Activation Energy (eV)</th>
<th>Attack Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jamison and Reeves$^7$</td>
<td>0.46</td>
<td>$1 \times 10^{13}$</td>
</tr>
<tr>
<td>(fluorescence depolarization)</td>
<td>High energy path</td>
<td></td>
</tr>
<tr>
<td>from $^1D_2$ state</td>
<td>0.07</td>
<td>7000</td>
</tr>
<tr>
<td>Low energy path</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jamison and Reeves$^7$</td>
<td>0.45</td>
<td>$1 \times 10^{13}$</td>
</tr>
<tr>
<td>(fluorescence depolarization)</td>
<td>High energy path</td>
<td></td>
</tr>
<tr>
<td>from $^3P_0$ state</td>
<td>0.06</td>
<td>12000</td>
</tr>
<tr>
<td>path</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meuldijk, der Meulen, and</td>
<td>0.46 ± 0.01</td>
<td>$10^{13.5 \pm 0.2}$</td>
</tr>
<tr>
<td>Den Hartog$^3$ (TSDC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study (TSDC)</td>
<td>0.453 ± 0.010</td>
<td>$10^{13.0 \pm 0.3}$</td>
</tr>
</tbody>
</table>

Andeen, Link, and Fontanella$^9$ and Meuldijk, der Meulen, and den Hartog$^3$ have performed dielectric relaxation measurements on CaF$_2$:Pr$^{3+}$ and SrF$_2$:Pr$^{3+}$ respectively.
They found a single \( mn \) relaxation with an activation energy and attack frequency similar to the high-energy path found in the fluorescence depolarization results. If the low energy path was available, the dielectric relaxation curve would be considerably broadened (for CaF\(_2\):Pr\(^{3+}\), a width at half-height of 36 K vs. the observed 19 K) and no longer have the characteristic shape of a single depolarization path. (See Fig. 3.)

Fig. 3. Simulations of dielectric relaxation results for CaF\(_2\):Pr\(^{3+}\). The simulation with the solid line assumes only one mechanism is available: one with a 0.45 eV activation energy and a \( 10^{13} \) Hz attack frequency. A very similar result was found by Andeen, Link, and Fontanella\(^{10}\).

The simulation with the dashed line assumes that two mechanisms are available for relaxation (as seen in our fluorescence depolarization results): one with a 0.42 eV activation energy and a \( 10^{13} \) Hz attack frequency and a second mechanism with a 0.063 eV activation energy and a \( 10^{4.56} \) Hz attack frequency.

Wagner and Mascarenhas\(^9\) and Meuldijk, der Meulen, and den Hartog\(^3\) have performed TSDC on CaF\(_2\):Pr\(^{3+}\) and SrF\(_2\):Pr\(^{3+}\) respectively. We report here new TSDC
results for SrF$_2$:Pr$^{3+}$. As in the dielectric relaxation measurements, each study found a *nn* reorientation path with parameters comparable to the high-energy path seen in the fluorescence depolarization results. However, neither measurement revealed any indication of a low-energy path. If such a low-energy path were present, it would have completely dominated the depolarization process under TSDC. (See Fig. 4).

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**Fig. 4.** TSDC results for SrF$_2$:Pr$^{3+}$. The dashed line is a simulated TSDC curve which assumes that two mechanisms are available for relaxation (as seen in our fluorescence depolarization results): one with a 0.42 eV activation energy and a $10^{13}$ Hz attack frequency, and a second mechanism with a 0.063 eV activation energy and a $10^{4.56}$ Hz attack frequency. Here, the low energy mechanism completely dominates the depolarization process.

However, the fit of our experimental data reveals only one available mechanism with a 0.45 eV activation energy and a $10^{13}$ Hz attack frequency.
IV. OUR THERMALLY STIMULATED DEPOLARIZATION RESULTS

Our TSDC measurements were performed as follows. A 1 mm thick wafer was cleaved from the same boule used in our optical measurements. Silver electrodes were painted onto the <111> surfaces of the wafer and then placed into a helium filled cryostat. At room temperature, a 410 V potential was placed across the sample. We then plunged the cryostat into a Dewar of liquid nitrogen, let the sample reach thermal equilibrium, and then removed the applied voltage. We connected the leads of the electrodes to a Cary 401 vibrating reed electrometer. The cryostat was removed from the Dewar and allowed to warm while the electrometer monitored the current from the sample. The resulting current vs. temperature data were fit using the TSDC equation:  

\[ i(T) = \frac{A P_0}{\tau_0} e^{\frac{-E_0}{kT}} \exp \left[ \frac{1}{\tau_0} \int_{T_0}^{T} \frac{dt}{dT'} e^{\frac{-E_0}{kT'}} dT' \right] \]

(Here, A is the area of the sample, P_0 is the initial polarization of the sample, and T_0 is the temperature from which the sample is warmed.) The results are shown in Fig. 4. This clearly shows a single Arrhenius relaxation with a 0.45 eV activation energy and an attack frequency on the order of the Debye frequency.

To search for any minor reorientations that were overwhelmed by the strong 0.45 eV reorientation in the above experiment, we used the following technique. We held the cryostat temperature at 121 K for up to 7 hours while we applied 410 V across the sample; this selectively polarizes those defects with lower activation energies. We then cooled the sample to liquid nitrogen temperature, removed the polarizing voltage and
warmed as above. Results are shown in Fig. 5. This reveals two more Arrhenius relaxations with activation energies of 0.35 eV and 0.41 eV.

Fig. 5. TSDC spectrum obtained by peak cleaning. The sample was held at 110 K and polarized for several hours before the measurements were taken. This selectively polarized those defects with low activation energies (0.41 eV or less); thus, the primary process (with an activation energy of 0.45 eV) did not completely dominate the results.

These weak relaxations are most likely due to trace impurities in the sample. We can estimate the relative population of these other defects as follows. The time constant for reorientation is given by

\[ \tau = \frac{1}{v_0} e^{-E/kT} \]

Thus, for a given defect species, the number of polarized dipoles is
where \( t \) is the annealing period, and \( T \) is the annealing temperature. If we assume that the dipole moment of the 0.41 eV defect is the same as that of the 0.45 eV defect, the population of the 0.41 eV defect is only 3% the population of the 0.45 eV defect. Similarly, the 0.35 eV defect has only 1% the population of the 0.45 eV defect. (Since we are dealing with a nearest-neighbor defect, other dipolar defects would most likely have the same or larger dipole moment; so, this is probably an underestimate of their populations.)

V. DISCUSSION

Dielectric relaxation and TSDC show no evidence of a second depolarization path in CaF\(_2\):Pr\(^{3+}\) or SrF\(_2\):Pr\(^{3+}\), whereas the optical measurements do. Perhaps the second relaxation path appears only when the sample is exposed to light. TSDC and dielectric relaxation are performed in darkness; site-selective spectroscopy requires resonant photons. If an incident photon has an effect on the lattice surrounding the Pr\(^{3+}\), this may result in a second reorientation process with a different attack frequency.

Researchers studying spectral hole burning have reported optically stimulated reorientation of \( C_5 \) centers in SrF\(_2\):Pr\(^{3+}\) and CaF\(_2\):Pr\(^{3+}\) doped with H\(^-\), D\(^-\), and T\(^-\).\(^{12,13,14}\) For each of these, optically stimulated local mode vibrations were found to be the likely cause. Also, there is evidence that Pr\(^{3+}\) ions interact more strongly with the lattice than Eu\(^{3+}\) ions. Ellens et al.\(^{15}\) report electron-phonon coupling constants for these ions in several different crystal lattices (not including CaF\(_2\) or SrF\(_2\)). The coupling constant for Pr\(^{3+}\) is consistently larger than that of Eu\(^{3+}\) (probably due to praseodymium’s larger ion size). This effect is in
the right direction to explain the difference in Jamison and Reeves' optical measurements of Pr\(^{3+}\) and Eu\(^{3+}\) doped materials.

If there is an optical effect on defect orientation, two possibilities exist. In case I, a second reorientation path persists as long as the Pr\(^{3+}\) ion is in the excited state. Since optical measurements detect only photons coming from excited ions, an observer would only see the depolarization of defect clusters having two relaxation paths available. However, the attack frequency is usually on the order of the Debye frequency of the crystal (roughly \(10^{13}\) Hz in SrF\(_2\)); an attack frequency smaller by 10 orders of magnitude would be extraordinary.

Yet, this low attack frequency may be deceptive. Consider the following mechanism, case II: the Pr\(^{3+}\) ion absorbs an incident photon; the ion suddenly expands and during this expansion moves the surrounding ions and opens a path of lower activation energy (around 0.063 eV, as observed in our optical work). The actual attack frequency would not change radically; however, if this low-energy path were available for only a fraction of the fluorescence lifetime, it would have the appearance of a second relaxation process with a very low attack frequency.

In SrF\(_2\), we measured the fluorescence lifetime \(\tau_f\) as 116 \(\mu\)s. If we assume the actual attack frequency \(v_0\) of the F is constant at \(10^{13}\) Hz, we can calculate the duration of the low energy path \(\tau_{\text{lowE}}\) from the effective attack frequency found in the fluorescence depolarization measurements (\(v_{\text{eff}} = 42000\) Hz):
This is remarkably close to the inverse of the vibrational frequency of the interstitial F\(^-\) (10\(^{13}\) Hz), about what one would expect for the duration of coherent movement of the ions surrounding the defect after excitation. Such analysis of Jamison and Reeves’ optical measurements on CaF\(_2\):Pr\(^{3+}\) and SrF\(_2\):Pr\(^{3+}\) yields similar results (see Table IV).

### Table IV. Attack frequencies for reorientation paths with low activation energy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Excited multiplet</th>
<th>Fluorescence lifetime, (\tau_f)</th>
<th>Attack freq., (\nu_0)</th>
<th>Effective attack freq., (\nu_{\text{eff}})</th>
<th>Duration of local mode vibrations, (\tau_{\text{lm}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^a)SrF(_2):Pr(^{3+})</td>
<td>(^3)P(_0)</td>
<td>115.6 ± 2.3 (\mu)s</td>
<td>10(^{13}) Hz</td>
<td>42000 Hz</td>
<td>4.9 \times 10^{-13} s</td>
</tr>
<tr>
<td>(^b)SrF(_2):Pr(^{3+})</td>
<td>(^1)D(_2)</td>
<td>1.0 ms</td>
<td>10(^{13}) Hz</td>
<td>7000 Hz</td>
<td>7 \times 10^{-13} s</td>
</tr>
<tr>
<td>(^b)SrF(_2):Pr(^{3+})</td>
<td>(^3)P(_0)</td>
<td>0.140 ms</td>
<td>10(^{13}) Hz</td>
<td>12000 Hz</td>
<td>1.7 \times 10^{-13} s</td>
</tr>
<tr>
<td>(^b)CaF(_2):Pr(^{3+})</td>
<td>(^1)D(_2)</td>
<td>0.850 ms</td>
<td>10(^{13}) Hz</td>
<td>900 Hz</td>
<td>7.6 \times 10^{-13} s</td>
</tr>
</tbody>
</table>

\(^a\)From our optical results. \(^b\)From Jamison and Reeves.

Using our above values for the lifetime of the fluorescence \(\tau_f\) and attack frequency \(\nu_{\text{eff}}\) for SrF\(_2\):Pr\(^{3+}\), we can calculate the probability of a single photon inducing a defect reorientation for case I:

\[
P_i = \tau_f \nu_{\text{eff}} \exp(-\Delta E / kT).
\]

We can also do the same for case II; just after the Pr\(^{3+}\) has been excited, the activation energy drops to a very low value for a period \(\tau_{\text{low}E}\) while the attack frequency \(\nu_0\) remains high. Here the probability \(P_{\text{II}}\) of a single photon causing a reorientation is
\[ P_{II} = \tau_{\text{low-E}} v_o \exp(-\Delta E/kT) \]
\[ = \frac{v_{\text{eff}}}{v_0} \tau_f v_o \exp(-\Delta E/kT) \]
\[ = v_{\text{eff}} \tau_f \exp(-\Delta E/kT) \]
\[ = P_f. \]

Hence, these two processes are indistinguishable.

VI. SEARCH FOR AN OPTICAL EFFECT ON DEFECT ORIENTATION USING DIELECTRIC METHODS

Using two different variations of TSDC, we explored the possibility of an optically induced relaxation path. This allowed us to directly compare the polarization of defects with or without the presence of light.

A. Optically Stimulated Dielectric Depolarization (OSDD)

We explored the possibility of an optically induced second relaxation path using a variation on TSDC. We polarized the sample and then cooled it to 115 K. At this temperature, the time constant for reorientation by the high energy path (0.45 eV) is

\[ \tau = \frac{1}{v_0} e^{E/kT} = 5.3 \times 10^7 \text{ s.} \]

This is far longer than the duration of the experiment; thus, the polarization lost by this mechanism is negligible. Our sample of SrF\(_2\):0.1%Pr\(^{3+}\) has approximately \(2 \times 10^{18}\) defects.

We illuminated the sample with 0.38 W of 476.5 nm light for 29 hrs; that is 39700 joules of light. (This wavelength happens to correspond with an absorption of Pr\(^{3+}\) ions in SrF\(_2\) and is the same wavelength used in the fluorescence depolarization experiments.) Due to
the geometry of the sample, only about half of the light can enter the crystal, and of that only 3% is actually absorbed. To capture on average one photon per defect, we need $1.3 \times 10^{20}$ photons or 54 joules of light. Thus, the crystal absorbed about 730 photons per defect. If there is an optical effect on defect polarization, then we would expect this light to deplete the polarization of the sample. As the sample was warmed, the usual TSDC signal should be diminished.

To calculate the expected loss of polarization, we can apply the theory developed in the previous section, i.e., extrapolate the Arrhenius behavior seen in the fluorescence depolarization measurements down to the temperature at which optically stimulated polarization was observed. The probability $P_t$ of a single photon causing a reorientation (using our above values for the lifetime of the fluorescence $\tau_f$ and attack frequency $\nu_{eff}$ for SrF$_2$:Pr$^{3+}$) is

\[
P_t(115K) = \tau_f \nu_{eff} \exp(-\Delta E / kT) \\
= 116\mu s \times 42000 \text{ Hz} \times e^{-0.063eV/kT} \\
= 0.00845.
\]

If an optical effect exists, the surviving polarization should be $(1 - 0.00845)^{730}$ or about 0.2% of the initial polarization. Admittedly, this is a very rough figure, but even if the number of photons per defect was off by an order of magnitude, the lost polarization should be an easily detected 54%. Nevertheless, after the sample was illuminated, no change in the depolarization current was detected.
B. Optically Stimulated Dielectric Polarization (OSDP)

The above experiment looked for a large change in a large signal. To look for a smaller effect, we altered the experiment to look for a small change in a small signal.

First, the temperature of the sample was held at 119 K while a polarizing voltage was applied for several hours; here, the time constant for reorientation is $1.1 \times 10^7$ s. The voltage was removed and the sample cooled to 77 K. We then warmed the sample while monitoring the depolarization current. As expected, we detected only the 0.35 eV depolarization since the sample was too cold to polarize the 0.41 eV and 0.45 eV defects. (See Fig. 6.)

![TSDC results for SrF$_2$:Pr$^{3+}$. The circles denote data acquired after the sample was polarized at 112 K while illuminated with 0.38 W of light for seven hours. The triangles denote data acquired after the sample was polarized at 119 K for seven hours without illumination.](image-url)
Next, we set the temperature of the sample to 112 K (time constant = $1.7 \times 10^8$ s) while polarizing the sample as above, but this time we illuminated the sample with 0.17 watts of 476.5 nm light from an argon ion laser. After seven hours, the voltage and light were removed; the sample was then cooled to 77 K and warmed as above. This time, despite the even longer time constant for reorientation, 0.36 eV and 0.45 eV relaxations do appear in the spectrum while the weak 0.41 eV relaxation remains absent. (See Fig. 6.) (The 0.36 eV relaxation has a barrier low enough to be explained by thermally stimulated polarization.)

Clearly, the presence of light induces polarization of the 0.45 eV defects. However, the amount of polarization induced in the sample is very low; we only aligned about 0.003 % of the defects in the sample. Again assuming that only half of the light enters the sample and that 3% of that light is absorbed, we have about one dipole alignment for every three million absorbed photons.

When repeating the experiment, the amount of polarization may change by as much as a factor three, probably due to small apparatus movements that change the amount of light entering the sample. If we repeat this experiment with lower annealing temperatures (down to 80 K), the 0.45 eV relaxation continues to appear while the 0.41 eV relaxation does not. Within the reproducibility of the experiment, the amount of polarization induced during this optical annealing process is not temperature dependent. There is certainly much less temperature dependence than would be expected for an Arrhenius process.

If we again apply the theory developed in section V, we would expect the probability of a single photon polarizing a defect to be approximated by $P_i$: 0.00712 at
112 K. Yet, the observed effect is independent of temperature and 20000 times weaker at 112 K.

VII. CONCLUSIONS

We have observed that the reorientation of defects in SrF$_2$:Pr$^{3+}$ may be driven optically as well as thermally. Standard dielectric techniques (TSDC and dielectric relaxation) reveal a dipolar defect with a 0.45 eV activation energy. This relaxation has been identified with C$_{4v}$ (Pr$^{3+}$, F$^-$) defects.\textsuperscript{1,3,9} With optically stimulated dielectric polarization (OSDP), we find that it is possible to polarize these defects by illuminating the sample with resonant light. This optical mechanism is independent of temperature.

With the fluorescence depolarization measurements we find two apparently Arrhenius relaxations. The primary relaxation (activation energy = 0.42 eV; jump rate = $10^{13}$ Hz) matches well with the standard dielectric results. The secondary relaxation (activation energy = 0.063 eV; jump rate = 42000 Hz) is not seen with dielectric methods and is likely due to optical effects. Reeves, Jones, and Syme\textsuperscript{8} have previously identified the observed fluorescence transitions with the C$_{4v}$ (Pr$^{3+}$, F$^-$) defect. These results may be explained by the brief appearance of a lower energy path. As described in the discussion above, the optical stimulation of the Pr$^{3+}$ briefly lowers the barrier between adjacent nn sites to around 0.063 eV permitting reorientation to occur at a much lower temperature. (See Fig. 7.)
Unfortunately, we have been unable to build a theory that links the fluorescence depolarization results with the optical behavior seen in the dielectric measurements. Extrapolating the apparently Arrhenius behavior of the fluorescence depolarization results cannot account for the extreme weakness and non-Arrhenius behavior of the optical effects observed in the OSDD and OSDP measurements.

Nevertheless, the OSDP measurements definitively show the presence of an optical effect on the orientation of $C_{4v}$ ($F$) dipoles in SrF$_2$:Pr$^{3+}$. 

Fig. 7. The coherent motion of the ions surrounding the defect may lower the activation energy for movement of the interstitial $F^-$. 

[Diagram of barrier reduction due to coherent motion of surrounding F- ions]
Figure Captions

Fig. 1. Tetragonal or $C_4$ defect found in CaF$_2$ and SrF$_2$ doped with trivalent rare earth ions. Thermal stimulation permits the nearest-neighbor interstitial F to hop among the six available nearest-neighbor interstitial sites.

Fig. 2. Fluorescence depolarization results for SrF$_2$:Pr$^{3+}$. The dashed line is a least squares fit assuming only one reorientation path is available for the interstitial F. The solid line is a fit assuming that two paths are available. Fit parameters are found in Table III.

Fig. 3. Simulations of dielectric relaxation results for CaF$_2$:Pr$^{3+}$. The simulation with the solid line assumes only one mechanism is available: one with a 0.45 eV activation energy and a $10^{13}$ Hz attack frequency. A very similar result was found by Andeen, Link, and Fontanella$^{10}$.

The simulation with the dashed line assumes that two mechanisms are available for relaxation (as seen in our fluorescence depolarization results): one with a 0.42 eV activation energy and a $10^{13}$ Hz attack frequency and a second mechanism with a 0.063 eV activation energy and a $10^{4.56}$ Hz attack frequency.

Fig. 4. TSDC results for SrF$_2$:Pr$^{3+}$. The dashed line is a simulated TSDC curve which assumes that two mechanisms are available for relaxation (as seen in our fluorescence depolarization results): one with a 0.42 eV activation energy and a $10^{13}$ Hz attack frequency.
frequency, and a second mechanism with a 0.063 eV activation energy and a $10^{4.56}$ Hz attack frequency. Here, the low energy mechanism completely dominates the depolarization process.

However, the fit of our experimental data reveals only one available mechanism with a 0.45 eV activation energy and a $10^{13}$ Hz attack frequency.

Fig. 5. TSDC spectrum obtained by peak cleaning. The sample was held at 110 K and polarized for several hours before the measurements were taken. This selectively polarized those defects with low activation energies (0.41 eV or less); thus, the primary process (with an activation energy of 0.45 eV) did not completely dominate the results.

Fig. 6. TSDC results for SrF$_2$:Pr$^{3+}$. The circles denote data acquired after the sample was polarized at 112 K while illuminated with 0.38 W of light for seven hours. The triangles denote data acquired after the sample was polarized at 119 K for seven hours without illumination.

Fig. 7. The coherent motion of the ions surrounding the defect may lower the activation energy for movement of the interstitial F.


10 Carl Andeen, Donald Link and John Fontanella, Phys. Rev. B 16, 3762 (1977).


