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POINT DEFECT INTERACTIONS IN CaF$_2$ : GdF$_3$

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Résumé. — La réorientation de la paire Gd$^{3+}$ substitutionnel-F$^-$ interstitiel dans CaF$_2$ a été étudiée à l'aide de mesures d'élargissement de durée de vie EPR et des études de relaxation diélectrique et anélastique entre la température ambiante et l'azote liquide. La fraction molaire GdF$_3$ varie de 0,01 à 0,3 %. Les cristaux ont été recuits dans une atmosphère de He et HF entre 600 et 800 °C puis refroidis rapidement. Trois relaxations principales sont observées dans le spectre anélastique, les deux à basse température correspondant bien aux deux relaxations principales observées dans le spectre diélectrique.

Abstract. — The reorientation of the point-defect pair formed in CaF$_2$ crystals by substitutional Gd$^{3+}$ and interstitial F$^-$ ions has been studied using EPR lifetime broadening measurements and dielectric and anelastic relaxation studies at temperatures between liquid N$_2$ and room. The GdF$_3$ concentration ranged from 0.01 to 0.3 mole percent. The crystals were annealed in an atmosphere of He and HF at temperatures from 600° to 800°C and quickly cooled. Three major relaxations were observed in the anelastic spectrum, the two at lowest temperatures corresponding well to two major relaxations observed in the dielectric spectrum. The most important of these correlated both in relaxation parameters and intensity changes upon annealing and/or changing concentration of GdF$_3$ with the lifetime broadening and intensity of the EPR spectrum from the nearest-neighbor pair. The entire pattern has the proper symmetry for the pair with relaxation modes generated by excursions of the F$^-$ interstitial out to third-neighbor positions, assuming that the most stable positions are closest to the Gd$^{3+}$ ions. However, this model is inconsistent with the relative intensities of the dielectric relaxations, and it is concluded that at least two distinct centers must be present.

1. Introduction. — 1.1 Point defects in CaF$_2$ doped with trivalent cations. — The point defect population in alkaline-earth fluoride crystals containing trivalent rare-earth and similar ions is often assumed to be represented by the simple model in which the trivalent cations substitute for the alkaline-earth cations and the excess fluorine ions go into interstitial sites. At high temperatures, these defects are assumed to be uncorrelated, and the experiments of Friedman and Low (1960) on CaF$_2$: GdF$_3$ suggest that rapid cooling can at least partially quench in this state. At low temperatures, it is supposed that the aliovalent cations and interstitial fluorines associate into pairs, and again Friedman and Low observed an increase in the pair signal in the Gd$^{3+}$ EPR spectrum upon slowly cooling the crystal from elevated temperatures.

However, more detailed studies have revealed very anomalous behavior. The ratio of pairs to unpaired trivalent cations is expected to increase with increasing rare-earth concentration, but the optical studies of Makovsky (1966a, 1966b) and Gilfanov et al. (1966) showed that just the opposite occurred in CaF$_2$: GdF$_3$. At concentrations of about 2 mole percent the pair spectrum is not observable but the unpaired is. Loh (1967) has observed an apparent decrease in the intensity of absorption spectra from Ce$^{3+}$ and Pr$^{3+}$ ions assumed paired with F$^-$ interstitials as the concentration increased above about 0.1 mole %.$^\circ$ He has attributed this decrease to the loss of pairs through the formation of clusters of trivalent cations with their interstitial fluorine ions.

In a previous study (Franklin and Marzullo (1971)) on small crystals of CaF$_2$: GdF$_3$ annealed and rapidly cooled, we also noted a strong decrease in the ratio of the EPR spectrum from paired to that from unpaired Gd$^{3+}$ ions as the concentration increased from about 0.01 to 0.5 mole percent. We also found that low-temperature (below about 800°C) annealing tended to remove the pair spectrum, a removal that could be reversed by reannealing the crystal at higher temperatures.
Miner et al. (1972) have also noted the apparent suppression of the pair spectrum with increasing concentration, in SrF₂ crystals containing only GdF₃ and also containing CeF₃ as well. Additional GdF₃ and also the addition of CeF₃ to a fixed concentration of GdF₃ reduced the intensity of Gd³⁺ pair spectra relative to that from unpaired Gd³⁺ ions. Their results led them to suggest that the «unpaired» spectrum actually arises from a complex clustering of RE³⁺ ions and compensating F⁻ interstitials that maintain a cubic symmetry as seen by the RE³⁺ ions.

1.2 Pair Relaxation. — This uncertainty in the interactions among the point defects in rare-earth doped CaF₂ made it attractive to attempt to «calibrate» the EPR intensities from CaF₂ : GdF₃ by measuring some of the concentrations by independent means. Since the pairs possess electrical dipoles, it should be possible to measure their concentrations by means of dielectric relaxation. However, it was first necessary to identify which relaxation in the dielectric spectrum arises from the pairs. For this purpose, comparison was made with lifetime broadening of the EPR pair spectrum and with anelastic relaxation.

A relaxation in the dielectric spectrum that has been studied using the ionic technique (ITC) (Bucci and Fieschi, 1964) by several groups (Royce and Mascarenhas, 1970; Stott and Crawford, 1971a and 1971b; Stiefbold and Huggins, 1972; Kunze and Müller, 1972; Wagner and Mascarenhas, 1972) was shown by Franklin and Marzullo (1970) to correspond closely in relaxation parameters to the relaxation giving rise to lifetime broadening (Watkins, 1959) of the pair EPR spectrum. This spectrum in turn has been firmly tied by ENDOR measurements (Baker, Davies and Hurrell, 1968a and 1968b) to the pair formed by the substitutional trivalent cation and a nearest-neighbor interstitial fluorine. In addition, Franklin and Crissman (1971) found a relaxation in the anelastic spectrum at the expected temperature and frequency and with the correct symmetry properties to correspond to this same pair relaxation. This relaxation will be designated in this paper as $R_{11}$.

Both the ITC measurements of Stott and Crawford (1971a, 1971b) and the anelastic relaxation data of Franklin and Crissman (1971) exhibited a second relaxation with a much lower activation energy (0.16 eV as compared to 0.4 eV). This relaxation appeared in the anelastic spectrum with the stress in $<110>$ and $<111>$ directions, but not in the $<100>$ direction, suggesting a defect with the same symmetry as the set of interstitial sites next nearest the trivalent impurity cation. We will designate this second relaxation as $R_{11}$.

Stott and Crawford suggested that $R_4$ and $R_{11}$ arose from two separate sets of pairs, $R_4$ from those with nearest-neighbor (1n) fluorine interstitials and $R_{11}$ from those with next-nearest-neighbor (2n) fluorine interstitials. The implication is that during relaxation interstitials do not move between 1n and 2n sites. In this case, the intensities of the two relaxations might be expected to vary independently, and Stott and Crawford found evidence that this does happen. Franklin and Crissman (1971), on the other hand, suggested that $R_4$ and $R_{11}$ were two relaxation modes arising from the same pair, with the fluorine interstitial jumps between 1n and 2n sites playing an important role. This model, however, requires that a constant ratio be maintained between the intensities of the two relaxations as heat treatment or other influences are used to vary the number of centers, a prediction that appears to be at variance with the observations of Stott and Crawford.

2. Experimental. — In the present paper we report additional dielectric and anelastic relaxation measurements on CaF₂ containing GdF₃ in amounts from 0.01 to 0.3 mole percent. All anneals were performed in an atmosphere of He plus HF, as described by Franklin and Marzullo (1971) and the presence of oxygen checked by optical absorption measurements at a wavelength of 200 nm (Bontinck, 1958).

Figure 1 shows anelastic relaxation data for a $<110>$ CaF₂ crystal containing nominally 0.05 mole percent GdF₃, annealed at 1070 K for about 5 h or at 870 K for about 70 h, and rapidly cooled to below 600 K in about 1-1.5 min and to room temperature in less than 5 min. The ratio of the intensities of the room-temperature EPR spectra from the paired and unpaired Gd³⁺ ions was monitored after each anneal. Three well-defined peaks are seen in the anelastic spectrum for this $<110>$ specimen. The large peak at the lowest temperature corresponds to $R_{11}$ and the middle one to $R_4$. The high temperature peak, here designated as $R_{11}$, corresponds approximately to the peaks seen earlier in CaF₂ : YF₃ by Southgate (1966). All three peaks are strongly diminished in intensity by annealing at 870 K and increased.

![Fig. 1. — Anelastic relaxation for $<110>$ crystal of CaF₂ with nominally 0.05 mole percent GdF₃.](image-url)
by the 1070 K anneal, effects that were apparently reversible and could be repeated on the same crystal. Measurements were made also on crystals with \(<100>\) and \(<111>\) orientations. These results are summarized in Table I.

**Table I**

Anelastic relaxation in CaF<sub>2</sub> : GdF<sub>3</sub>, nominal 0.05 mole %

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Freq. kHz</th>
<th>Peak T K</th>
<th>Obs.</th>
<th>Calc.</th>
<th>Relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;110&gt;)</td>
<td>32</td>
<td>100</td>
<td>(~115)</td>
<td>(R_{II})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>238</td>
<td>244</td>
<td>(R_I)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>560</td>
<td></td>
<td>(R_{III})</td>
<td></td>
</tr>
<tr>
<td>(&lt;100&gt;)</td>
<td>40</td>
<td>238</td>
<td>244</td>
<td>(R_I)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>560</td>
<td></td>
<td>(R_{III})</td>
<td></td>
</tr>
<tr>
<td>(&lt;111&gt;)</td>
<td>26</td>
<td>100</td>
<td>(~115)</td>
<td>(R_{II})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>560</td>
<td></td>
<td>(R_{III})</td>
<td></td>
</tr>
</tbody>
</table>

Note that \(R_I\) is missing from the \(<111>\) spectrum, and \(R_{II}\) from the \(<100>\) while \(<110>\) shows both and all three orientations exhibit \(R_{III}\). In all three, \(R_I\) and \(R_{III}\) are decreased in intensity by annealing by about the same proportion, while \(R_{II}\) is much more strongly affected. The calculated values for the peak temperatures were obtained using the dielectric data to be discussed next.

Dielectric relaxation measurements were made in the frequency range from 50 Hz to about 100 kHz and at temperatures from about 80 K to room temperature on CaF<sub>2</sub> crystals containing 0.01 to 0.3 mole percent, subject to similar heat treatments (the lower anneal temperature was 650 K and because of the much smaller specimen size the cooling was more rapid). EPR intensities were measured for these crystals as well. Figure 2 illustrates the data taken. This is presented in the form of superimposed Cole-Cole plots (imaginary, \(\epsilon''\), vs real, \(\epsilon'\), component of the complex dielectric constant, \(\epsilon'' = \epsilon' - i\epsilon''\), as suggested by Cole and Cole, 1942), representing measurements in the same frequency interval taken at the various temperatures shown. These data show that whereas a well-defined relaxation occurs in the region of \(R_I\), there may be several partially overlapping relaxations in the region of \(R_{II}\).

For all concentrations and anneals, \(R_I\) exhibited essentially the same relaxation parameters. Among the several occurring in the region of \(R_{II}\), one appeared to correlate best with \(R_I\) and has been designated specifically as \(R_{II}\). It could best be seen with the specimen with the highest GdF<sub>3</sub> concentration (0.3 mole percent). Table II summarizes the relaxation parameters from this specimen, where \(\tau_0\) and \(Q\) are defined in terms of the Arrhenius equation for the relaxation time,

\[
\tau = \tau_0 \exp \left(\frac{Q}{kT}\right),
\]

**Table II**

Dielectric relaxation parameters, CaF<sub>2</sub> : GdF<sub>3</sub>, 0.3 mole %

<table>
<thead>
<tr>
<th>Relaxation</th>
<th>Anneal K</th>
<th>(\tau_0) s</th>
<th>(Q) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_I)</td>
<td>1070</td>
<td>1.31 \times 10^{-14}</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>(R_{II})</td>
<td>1070</td>
<td>3.8 \times 10^{-15}</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

The dc conductivity at higher temperatures made it impossible to detect a relaxation in the dielectric spectrum corresponding to \(R_{III}\).

3. Discussion. — Data reported previously (Franklin and Marzullo, 1970) established a connection between the lifetime of the F<sup>-</sup> interstitial in the \(\langle 111 \rangle\) position and the relaxation time of \(R_I\). This connection is confirmed by the correlation between the intensity, \(\Delta \epsilon_{\text{rel}}\), of \(R_I\) and the ratio \(R\) of the intensities of EPR spectra from paired and unpaired Gd<sup>3+</sup> ions shown in figure 3. It was shown (Franklin, 1972) that if \(n_0\) is the mole fraction of dipoles derived from...
the intensity of the dielectric relaxation (assuming that the dipole moment is \((ea)\), where \(e\) is the magnitude of the electronic charge and \(a\) the distance from the cation to the ideal interstitial site), and if all Gd ions (total mole fraction \(M\)) appear as either paired or unpaired (i.e., no clusters or higher complexes), then

\[
\frac{M}{n_0} = f + \frac{f}{K} R^{-1}.
\]

The constants \(f\) and \(K\) have the following meaning: \((ea)^2/f\) is the true dipole moment, and \(KR\) is the ratio of concentrations of paired to unpaired Gd ions.

Figure 3 shows a plot of \(M/n_0\) from the dielectric data, against \(R^{-1}\), from the EPR data. The line is the least-squares fit, with \(K \approx 0.17\) and \(f \approx unity\). Departures from the line may arise from the clustering observed by Cheetham et al. (1970, 1971).

The correspondence between \(R_i\) and the EPR line-broadening makes it clear that the relaxation rate governing \(R_i\) is associated with jumps of the \(F^-\) interstitial ions away from the 1n sites. Using the convention that \(W_{ij}\) denotes the jump frequency from a site in the \(i\)th neighbor shell to one in the \(j\)th, and allowing only jumps between adjacent sites, the EPR lifetime should be given by

\[
\tau_{EPR} = 4(W_{11} + W_{12} + W_{13}),
\]

and the relaxation rate should be controlled by whichever of these is the largest.

Franklin and Crissman (1971) linked \(R_1\) and \(R_{11}\) as two relaxation modes from the same center, the Gd\(^{3+}\)-\(F^-\) interstitial pair with excursions of the \(F^-\) interstitial to the 2n sites. Their analysis of the relaxation modes was based on the assumption that \(W_{21}\) was larger than any other jump frequency. If the analysis is extended to allow excursions to the 3n sites, it is very noticeable in figure 1 that the annealing affects the intensity of \(R_{11}\) more than it does that of \(R_1\) and \(R_{11}\). It is possible that \(R_{11}\) consists of the superposition of several relaxations, but if so they all must have the same symmetry in the anelastic spectrum.

The relative intensities of \(R_1\) and \(R_{11}\) in the dielectric spectrum may be estimated from the observed activation energies. Since \(R_1\) is associated with the fastest jump away from the 1n site and exhibits an activation energy of about 0.4 eV, the activation energy for \(W_{12}\) must be at least this large. \(R_{11}\) is associated with \(W_{21}\), for which the activation energy is about 0.2 eV. Now the ratio of these two jump frequencies is approximately

\[
\frac{W_{12}}{W_{21}} \approx \exp\left(-\frac{\Delta E}{kT}\right)
\]

where \(\Delta E\) is the energy difference between the 2n and 1n sites. Hence, in this model the 2n sites must lie above the 1n sites by about 0.2 eV. Under these

### Table III

**Relaxation modes for Gd\(^{3+}\)-\(F^-\) interstitial pair**

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\lambda) relaxation rate</th>
<th>Appearance</th>
<th>Relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{1u})</td>
<td>(3 W_{21} + (4/3) W_{12})</td>
<td>Dielectric, (&lt; 111 &gt;, &lt; 110 &gt;)</td>
<td>(R_{11})</td>
</tr>
<tr>
<td>(T_{1g})</td>
<td>(3 W_{21})</td>
<td>Anelastic, (&lt; 111 &gt;, &lt; 110 &gt;)</td>
<td>(R_{11})</td>
</tr>
<tr>
<td>(T_{1u})</td>
<td>(4 W_{31} + (8/3) W_{12})</td>
<td>Dielectric, (&lt; 100 &gt;, &lt; 110 &gt;)</td>
<td>(R_1)</td>
</tr>
<tr>
<td>(E_g)</td>
<td>(6 W_{31} + 4 W_{12})</td>
<td>Anelastic, (&lt; 111 &gt;, &lt; 110 &gt;)</td>
<td>(R_{11})</td>
</tr>
<tr>
<td>(T_{1u})</td>
<td>(W_{31} + 2 W_{32} + 2(1 \pm \sqrt{2}) W_{33})</td>
<td>Dielectric</td>
<td>(R_{11})</td>
</tr>
<tr>
<td>(T_{1g})</td>
<td>(W_{31} + 2 W_{32} + 2 W_{33})</td>
<td>Anelastic, (&lt; 111 &gt;, &lt; 110 &gt;)</td>
<td>(R_{11})</td>
</tr>
<tr>
<td>(E_g)</td>
<td>(W_{31} + 2 W_{32} + (3 \pm \sqrt{3}) W_{33})</td>
<td>Anelastic, (&lt; 100 &gt;, &lt; 110 &gt;)</td>
<td>(R_{11})</td>
</tr>
</tbody>
</table>
circumstances, the ratio of the intensities, $\Delta e$, of the two dielectric relaxations is

$$\frac{\Delta e_i}{\Delta e_{ii}} \approx 16 \frac{T_i}{T_{ii}} \exp \left( - \frac{\Delta E}{kT_i} \right)$$  \hspace{1cm} (3)$$

where $T_i$ and $T_{ii}$ are the temperatures at which $R_i$ and $R_{ii}$ are observed. With 110 K and 220 K for $T_{ii}$ and $T_i$ and the value above 0.2 eV for $\Delta E$, the ratio is about $2.5 \times 10^{-9}$, i.e. given the observed relaxation parameters, the high-frequency mode should be unobservable. Thus, there appears to be a fatal inconsistency between the model and the data.

4. Conclusion. — It must be concluded that the model proposed earlier by Franklin and Crissman (1971) is untenable. $R_i$ and $R_{ii}$ cannot be from the same center, but must represent two separate centers. It is difficult to rationalize the symmetry of $R_{ii}$ with $R_i$ alone, and at the moment there is no overwhelming reason to link them together. $R_{ii}$ may therefore represent a third center.

$R_i$ definitely arises from the Gd$^{3+}$-F$^-$ interstitial pair and its relaxation rate corresponds to the frequency of the fastest jump away from the $I_n$ site. No EPR spectrum is observed corresponding to the F$^-$ interstitial in the $2n$ site, and it seems most reasonable to assume that the binding energy is much less than in the $I_n$ site. The relaxation rate in $R_i$ is probably determined by $W_{1i}$, but $W_{12}$ cannot definitely be excluded on the basis of present evidence.

$R_{ii}$ arises from a center that appears and disappears along with the Gd$^{3+}$-F$^-$ pair in our anneals (Franklin and Marzullo, 1971), although appearing to vary more independently in the experiments of Stott and Crawford (1971a, 1971b). This center has the same symmetry as the set of $2n$ sites. We have already suggested, on the basis of density measurements (Franklin, 1972) that an HF molecule may somehow accompany each GdF$_3$ unit in our crystals. If the HF molecule were lodged in an interstitial site the distance from the F atom to nearby lattice anions (2.36 Å) would be in the range for bifluoride ions in crystals (Pimentel and McClellan, 1960), and the symmetry would be that required for $R_{ii}$.

Very little information is available on $R_{ii}$. It appears here only in the anelastic spectrum, and anneals very like the Gd$^{3+}$-F$^-$ interstitial pair. It appears in all three orientations, most strongly in < 100 >. Southgate (1966) observed very similar relaxations under < 100 > and < 111 > stresses in YF$_3$-doped CaF$_3$ (he did not study < 110 >).

The decrease in the ratio of paired to unpaired Gd$^{3+}$ ions with low-temperature annealing and with increasing total GdF$_3$ concentration is not easy to understand on the basis of substitutional Gd$^{3+}$ ions and F$^-$ interstitials and their pairs or clusters of their pairs, even allowing for failure of the post-anneal quenches to freeze in all defects present at the anneal temperatures. Rather, it seems probable (Franklin, 1973) that F$^-$ interstitials are withdrawn at low temperatures, perhaps by going to traps deeper than the Gd$^{3+}$ ions and favored by increasing the GdF$_3$ concentration.

The similarity in behavior during annealing of $R_{ii}$ and $R_{ii}$ with $R_i$ suggests that one or other or both may arise from the empty trap, which would disappear as the Gd$^{3+}$-F$^-$ interstitial pairs disappeared.

References


Bonstain, W., Physica 24 (1958) 650.


