POINT DEFECT INTERACTIONS IN CaF_2 : GdF_3

A. Franklin, J. Crissman, K. Young

► To cite this version:

A. Franklin, J. Crissman, K. Young. POINT DEFECT INTERACTIONS IN CaF_2 : GdF_3 . Journal de Physique Colloques, 1973, 34 (C9), pp.C9-179-C9-183. 10.1051/jphyscol:1973934 . jpa-00215409

HAL Id: jpa-00215409

<https://hal.science/jpa-00215409>

Submitted on 1 Jan 1973

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

POINT DEFECT INTERACTIONS IN $\text{CaF}_2 : \text{GdF}_3$

A. D. FRANKLIN, J. CRISSMAN and K. F. YOUNG

Institute for Materials Research, National Bureau of Standards,
Washington, DC 20234, USA

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 ERPE 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 $\text{CaF}_2 : \text{GdF}_3$ 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 $\text{CaF}_2 : \text{GdF}_3$. 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 %. 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 $\text{CaF}_2 : \text{GdF}_3$ 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 SrF_2 crystals containing only GdF_3 and also containing CeF_3 as well. Additional GdF_3 and also the addition of CeF_3 to a fixed concentration of GdF_3 reduced the intensity of Gd^{3+} pair spectra relative to that from unpaired Gd^{3+} ions. Their results led them to suggest that the « unpaired » spectrum actually arises from a complex clustering of RE^{3+} ions and compensating F^- interstitials that maintain a cubic symmetry as seen by the RE^{3+} ions.

1.2 PAIR RELAXATION. — This uncertainty in the interactions among the point defects in rare-earth doped CaF_2 made it attractive to attempt to « calibrate » the EPR intensities from $\text{CaF}_2 : \text{GdF}_3$ 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 thermocurrent (ITC) technique (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_I .

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 $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, but not in the $\langle 100 \rangle$ 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_{II} .

Stott and Crawford suggested that R_I and R_{II} arose from two separate sets of pairs, R_I from those with nearest-neighbor (1n) fluorine interstitials and

R_{II} 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_I and R_{II} 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 CaF_2 containing GdF_3 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 $\langle 110 \rangle$ CaF_2 crystal containing nominally 0.05 mole percent GdF_3 , 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 Gd^{3+} ions was monitored after each anneal. Three well-defined peaks are seen in the anelastic spectrum for this $\langle 110 \rangle$ specimen. The large peak at the lowest temperature corresponds to R_{II} and the middle one to R_I . The high temperature peak, here designated as R_{III} , corresponds approximately to the peaks seen earlier in $\text{CaF}_2 : \text{YF}_3$ by Southgate (1966). All three peaks are strongly diminished in intensity by annealing at 870 K and increased

FIG. 1. — Anelastic relaxation for $\langle 110 \rangle$ crystal of CaF_2 with nominally 0.05 mole percent GdF_3 .

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 $\langle 100 \rangle$ and $\langle 111 \rangle$ orientations. These results are summarized in table I.

TABLE I

Anelastic relaxation in $\text{CaF}_2 : \text{GdF}_3$, nominal 0.05 mole %

Orientation	Freq. kHz	Peak Obs. T K	Calc. T K	Relaxation
$\langle 110 \rangle$	32	100	~ 115	R_{II}
	32	238	244	R_I
	32	560		R_{III}
$\langle 100 \rangle$	40	238	244	R_I
	40	560		R_{III}
$\langle 111 \rangle$	26	100	~ 115	R_{II}
	26	560		R_{III}

Note that R_I is missing from the $\langle 111 \rangle$ spectrum, and R_{II} from the $\langle 100 \rangle$ while $\langle 110 \rangle$ 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_2 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, ϵ'' , vs real, ϵ' , 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} .

FIG. 2. — Composite Cole-Cole plot for dielectric relaxation of CaF_2 crystal with 0.08 mole percent GdF_3 , annealed at 1070 K.

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_3 concentration (0.3 mole percent). Table II summarizes the relaxation parameters from this specimen, where τ_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, $\text{CaF}_2 : \text{GdF}_3$, 0.3 mole %

Relaxation	Anneal K	τ_0 s	Q eV
R_I	1070	1.31×10^{-14}	0.42
	920	—	0.42
R_{II}	1070	3.8×10^{-15}	0.21
	920	—	—

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^- interstitial in the In position and the relaxation time of R_I . This connection is confirmed by the correlation between the intensity, $\Delta\epsilon_I$, of R_I and the ratio R of the intensities of EPR spectra from paired and unpaired Gd^{3+} ions shown in figure 3. It was shown (Franklin, 1972) that if n_0 is the mole fraction of dipoles derived from

FIG. 3. — Correlation between ratio of mole fraction M of total GdF_3 in CaF_2 crystals to concentration, n_0 , of dipoles and ratio of intensities of EPR spectra of paired and unpaired Gd^{3+} ions. Circles correspond to estimated experimental error.

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

$$\frac{M}{n_0} = f + \frac{f}{K} R^{-1}. \quad (1)$$

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

$$\tau_{\text{EPR}}^{-1} = 4(W_{11} + W_{12} + W_{13}),$$

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

Franklin and Crissman (1971) linked R_I and R_{II} as two relaxation modes from the same center, the $\text{Gd}^{3+}\text{-F}^-$ 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 shell under the same assumption, together with the assumption that W_{13} and W_{23} are negligibly small, the modes shown in table III are found.

The modes corresponding to R_{II} and R_I have already been discussed (Franklin and Crissman, 1971). If excursions to 3n sites are allowed, and if $3 W_{33}$ is taken as smaller than $W_{31} + 2 W_{32}$, consis-

tent with the model in which the binding energies take the order $1n > 2n > 3n$, then three new anelastic modes, with similar relaxation rates, appear. Experimentally, their relaxation rates could be indistinguishable, and would produce essentially the same relaxation for each direction of the stress, exactly in correspondence with R_{III} .

The relaxation parameters in table II were used in the expressions for the relaxation rates in table III to calculate the peak temperatures for anelastic relaxations R_I and R_{II} listed in table I. Good agreement is obtained between the observed and calculated peak temperatures, as noted already by Franklin and Crissman (1971) for earlier data. This correspondence between the dielectric and anelastic relaxations makes it very reasonable to suppose that they refer to the same mechanisms, and makes it tempting to assign all modes to the same center, the $\text{Gd}^{3+}\text{-F}^-$ interstitial pair.

However, difficulties are encountered with the intensities. Stott and Crawford (1971a, 1971b) report that the heights of the peaks in their ITC data corresponding to R_I and R_{II} could be varied independently, and it is very noticeable in figure 1 that the annealing affects the intensity of R_{II} more than it does that of R_I and R_{III} . It is possible that R_{II} 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_I and R_{II} in the dielectric spectrum may be estimated from the observed activation energies. Since R_I 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_{II} 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

$$\frac{W_{12}}{W_{21}} \approx \exp\left(-\frac{\Delta E}{kT}\right) \quad (2)$$

where ΔE 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 $\text{Gd}^{3+}\text{-F}^-$ interstitial pair

Mode	λ relaxation rate	Appearance	Relaxation
—	—	—	—
T_{1u}	$3 W_{21} + (4/3) W_{12}$	Dielectric	R_{II}
T_{2g}	$3 W_{21}$	Anelastic, $\langle 111 \rangle$, $\langle 110 \rangle$	R_{II}
T_{1u}	$4 W_{11} + (8/3) W_{12}$	Dielectric	R_I
E_g	$6 W_{11} + 4 W_{12}$	Anelastic, $\langle 100 \rangle$, $\langle 110 \rangle$	R_I
T_{1u}	$W_{31} + 2 W_{32} + 2(1 \pm \sqrt{2}) W_{33}$	Dielectric	R_{III}
T_{2g}	$W_{31} + 2 W_{32} + 2 W_{33}$	Anelastic, $\langle 111 \rangle$, $\langle 110 \rangle$	R_{III}
E_g	$W_{31} + 2 W_{32} + (3 \pm \sqrt{3}) W_{33}$	Anelastic, $\langle 100 \rangle$, $\langle 110 \rangle$	R_{III}

circumstances, the ratio of the intensities, $\Delta\epsilon$, of the two dielectric relaxations is

$$\frac{\Delta\epsilon_{\text{II}}}{\Delta\epsilon_{\text{I}}} \approx \frac{16}{9} \frac{T_{\text{I}}}{T_{\text{II}}} \exp\left(-\frac{\Delta E}{kT_{\text{II}}}\right) \quad (3)$$

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 ΔE , the ratio is about 2.5×10^{-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_{III} with R_{I} alone, and at the moment there is no overwhelming reason to link them together. R_{III} may therefore represent a third center.

R_{I} definitely arises from the $\text{Gd}^{3+}\text{-F}^-$ interstitial pair and its relaxation rate corresponds to the frequency of the fastest jump away from the In 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 there is much less than in the In site. The relaxation rate in R_{I} is probably determined by W_{11} , 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 $\text{Gd}^{3+}\text{-F}^-$ 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_{III} . It appears here only in the anelastic spectrum, and anneals very like the $\text{Gd}^{3+}\text{-F}^-$ interstitial pair. It appears in all three orientations, most strongly in $\langle 100 \rangle$. Southgate (1966) observed very similar relaxations under $\langle 100 \rangle$ and $\langle 111 \rangle$ stresses in YF_3 -doped CaF_2 (he did not study $\langle 110 \rangle$).

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_{III} with R_{I} suggests that one or other or both may arise from the empty trap, which would disappear as the $\text{Gd}^{3+}\text{-F}^-$ interstitial pairs disappeared.

References

- BAKER, J. M., DAVIES, E. R. and HURRELL, J. P., *Phys. Lett.* **26A** (1968a) 352; *Proc. R. Soc. A* **308** (1968b) 403.
 BONTINCK, W., *Physica* **24** (1958) 650.
 CHEETHAM, A. K., FENDER, B. E. F., STEELE, D., TAYLOR, R. J. and WILLIS, B. T. M., *Solid State Commun.* **8** (1970) 171.
 CHEETHAM, A. K., FENDER, B. E. F. and COOPER, M. J., *J. Phys. C* **4** (1971) 3107.
 COLE, K. S. and COLE, R. H., *J. Chem. Phys.* **10** (1942) 98.
 FRANKLIN, A. D., *J. Nonmetals* **1** (1972) 27, in *Sintering and Related Phenomena*, ed. G. C. Kuczynski (Plenum, NY) 1973.
 FRANKLIN, A. D. and CRISSMAN, J., *J. Phys. C* **4** (1971) L 239.
 FRANKLIN, A. D. and MARZULLO, S., *J. Phys. C* **3** (1970) L 171.
 FRANKLIN, A. D. and MARZULLO, S., *Proc. Brit. Ceram. Soc.* **19** (1971) 135.
 FRANKLIN, A. D., SHORB, A. and WACHTMAN, J. B., Jr., *J. Res. Nat. Bur. Stand.* **68A** (1964) 425.
 FRIEDMAN, E. and LOW, W., *J. Chem. Phys.* **33** (1960) 1275.
 GILFANOV, F. Z., DOBKINA, Zh. S., STOLOV, A. L. and LIVANOVA, L. D., *Optics and Spectroscopy (USSR)* **20** (1966) 152.
 KUNZE, I. and MÜLLER, P., *Phys. Stat. Sol. (A)* **13** (1972) 197.
 LOH, E., *Phys. Rev.* **154** (1967a) 270; *Phys. Rev.* **158** (1967b) 273.
 MAKOVSKY, J., *Proc. Conf. on Phys. Quantum Electronics*, San Juan (McGraw Hill) (1966a), p. 340; *Phys. Lett.* **19** (1966b) 647.
 MINER, G. K., GRAHAM, T. P. and JOHNSTON, G. T., *J. Chem. Phys.* **57** (1972) 1263.
 PIMENTEL, G. C. and MCCLELLAN, A. L., *The Hydrogen Bond* (Freeman and Co., San Francisco) 1960.
 ROYCE, B. S. H. and MASCARENHAS, S., *Phys. Rev. Lett.* **24** (1970) 98.
 SOUTHGATE, P. D., *J. Phys. Chem. Solids* **27** (1966) 1623.
 STIEFBOLD, D. R. and HUGGINS, R. A., *J. Sol. State Chem.* **5** (1972) 15.
 STOTT, J. P. and CRAWFORD H. H., Jr., *Phys. Rev. Lett.* **26** (1971a) 384; *Phys. Rev. B* **4** (1971b) 668.
 WAGNER, J. and MASCARENHAS, S., *Phys. Rev. B* **6** (1972) 4867.
 WATKINS, G. D., *Phys. Rev.* **113** (1959) 91.