# ITC STUDIES OF RELAXATION PHENOMENA IN CaF$_2$:Gd$^{3+}$ CRYSTALS

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**Abstract**—The thermally stimulated depolarization current (TSDC) method was used to study relaxation phenomena of low symmetry complexes in CaF$_2$:Gd$^{3+}$ crystals. During successive TSDC scans under exactly the same experimental conditions the shape of certain peaks was observed to change in a manner indicating conversions of tetragonal (type I) to trigonal (type II) Gd$^{3+}$–F$_i^-$ complexes. In a first attempt to interpret the phenomenon, the transformation of type I to type II dipoles, which are considered as two distinctive configurations of the Gd$^{3+}$–F$_i^-$ structure, is tentatively ascribed to the influence of the applied external electric field in the relaxation processes involved.

## INTRODUCTION

Alkaline earth fluorides with trivalent impurities have been the subject of many investigations in the last 30 years because of the importance of the relaxation phenomena of the complexes formed for the properties of ionic crystals.

When a trivalent impurity is introduced into an alkaline earth fluoride lattice, different kinds of complexes may be formed, depending on the relative position between the impurity and the compensating atoms. Principally, there are two types of complexes in CaF$_2$:Gd$^{3+}$ crystals [1]. A type I complex has tetragonal symmetry ($C_{4v}$) with the fluoride interstitial compensator in a nearest neighbour position (nnn) to the trivalent impurity.

For the study of the orientation of such dipoles the most accurate experimental technique is the TSDC (or ITC) method [2, 3]. According to this technique an electric field is applied to the crystal at room temperature (where the relaxation time of the existed complexes is generally short) to orient the dipoles. Afterwards, the sample is cooled down usually to liquid nitrogen temperature (where the relaxation time becomes much longer). The electric field is then switched off and the sample is warmed up at a constant rate. As the dipoles lose their orientation a depolarization current (TSDC) is generated which obeys the following expression:

$$i(T) = \frac{AP_0}{\tau_0} \exp\left(-\frac{h^m}{kT}\right)$$
$$\times \exp\left[\frac{1}{b\tau_0} \int_{T_0}^{T} \exp\left(-\frac{h^m}{kT'}\right) dT'\right],$$

where $A$ is the surface area of the sample, $b$ the constant temperature rate, $P_0$ the initial polarization, $\tau_0$ the usual pre-exponential factor in the Arrhenius relation $\tau(T) = \tau_0 \exp(h^m/kT)$, $h^m$ the migration enthalpy of the complexes and $k$ the Boltzmann constant. For every kind of dipole the current first increases, reaches exponentially a maximum and then drops to zero. Thus a corresponding peak appears in the spectra.

The aim of the present note is to report on some very interesting changes observed on the TSDC spectra of the CaF$_2$:Gd$^{3+}$ crystals successively recorded under the same experimental conditions. These changes indicate transformations of tetragonal to trigonal complexes which might be caused by the application of the electric field.

## EXPERIMENTAL DETAILS

The crystals used were made at the University of Kazan (U.S.S.R.) with the Bridgman–Stocbarger method. The concentration of the Gd$^{3+}$ impurity was either 0.07% or 0.1% mole. The samples were cut and prepared to have typical dimensions of area $S = 50$ mm$^2$ and $d = 1$–1.5 mm. A vibrating reed electrometer was used for the measurement of the TSDC current and the samples were placed between platinum electrodes in a vacuum of 10$^{-3}$ Torr. The temperature varied between liquid nitrogen and room temperature at a constant rate of $b = 0.17$ K s$^{-1}$. The polarization electric field was $E_p \approx 21$ kV cm$^{-1}$ and applied at room temperature ($\approx 295$ K) for 5 min. Afterwards the samples were cooled down to $\approx 80$ K

and then the electric field removed. Then the samples were short-circuited through a $R = 10^8$ $\Omega$ resistance for about 30 min for the background to decrease significantly. After each scanning the samples were kept at room temperature for about 1 h before the beginning of the procedure for the next experiment.

## RESULTS AND DISCUSSION

Figure 1a depicts the TSDC spectra received from our measurements for $CaF_2:Gd^{3+}$. Three peaks labeled A, B and C were observed. Migration enthalpies $h^m$ and pre-exponential factors $\tau_0$ from the corresponding Arrhenius plots of the above peaks are provided in Table 1.

From the values of the energy parameters, the position on the temperature axis and comparisons with results cited in the literature, peak A is attributed to the tetragonal centres $Gd^{3+}-F_i^-$ ($C_{4v}$) of type I (nn) complexes [1, 4–6]. Similarly peak B is attributed to the trigonal centres ($C_{3v}$) of type II complexes (nnn) [1]. It is worth noticing that peak B has also been attributed to a small complex or cluster possessing a residual moment [7]. Regarding peak C, there is not, to the best of our knowledge, any conclusively established assignment to a certain dipole structure so far. We can speculate about some kind of clusters which are known to be formed in this material [8, 9].

Interestingly enough, the peaks in the spectra exhibit characteristic changes in their amplitudes between successive TSDC experiments (Fig. 1). More specifically, the area under peak A decreases while that under peak B increases. This means that the relative stability of type II (nnn) complexes vs type I (nn) complexes gradually increases. What we have observed is a tendency for the conversion of type I to type II complexes, after a number of successive TSDC scannings.

Three experiments were carried out under the same conditions on three different samples and gave quite producible results pointing out that transformations occur between the two kinds of dipole generated peaks A and B.

The only external factor which acts on the crystal prior to TSDC scanning is the applied electric field. In a first attempt to interpret our results we consider type I and type II complexes as two configurations of the $Gd^{3+}-F_i^-$ structure. Obviously, the equilibrium



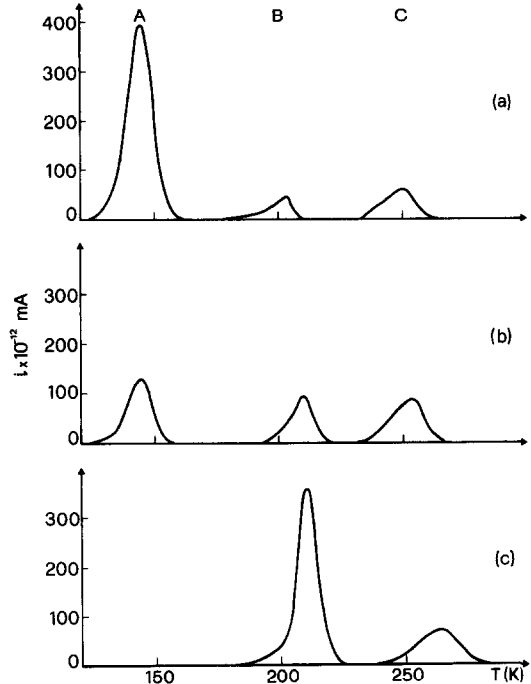Fig. 1. ITC results on $GaF_2:Gd^{3+}$ crystals. (a) Initial spectrum, (b) intermediate spectrum taken immediately after the first, (c) final spectrum, received generally as the fourth spectrum in a series of consecutive experiments carried out in one day.

between the two types of complexes depends upon the free energy of the crystal in the corresponding configuration. In other words, the complex type that prevails is that with the smaller free energy. The larger the difference between the two free energies the larger is the difference in the concentrations of the complexes. Figure 2 depicts $G = G(Q)$, the free energy $G$ of the crystal as a function of a configurational coordinate $Q$. Demonstrably, every curve comprises two energy wells at $Q_{nn}$ and $Q_{nnn}$ separated by a potential barrier.

Curve $\alpha$ (Fig. 2) corresponds to the first TSDC spectrum. The free energy is smaller for configuration

Table 1. Relaxation parameters of the observed dipole structures in $GaF_2:Gd^{3+}$ crystals

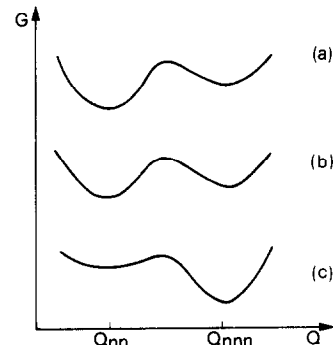| Peak | $h^m$ (eV) | $\tau_0$ (s) |
|------|-----------|-----------------------|
| A | 0.38 | $1.02 \times 10^{-12}$ |
| B | 0.62 | $4.80 \times 10^{-15}$ |
| C | 0.81 | $3.10 \times 10^{-15}$ |



Fig. 2. Configuration coordinate diagrams showing the conversion of type I (nn) to type II (nnn) dipoles.

$Q_{nn}$ and thus the concentration of type I complexes is larger. Supposing that the free energies in the two configurations are relatively equal and the energy barrier between them is small enough, a percentage of the complexes is in configuration $Q_{nnn}$. The ratio of the amplitudes of peaks A and B roughly reflects the ratio of the concentrations of the two types of complexes.

A repetition of the experiment implies a new application of the electric field. We envisage that this application has an effect on the migration processes of the type I (nn) and type II (nnn) dipoles of the $CaF_2:Gd^{3+}$ crystals in the following way. After the cooling-down procedure, as the temperature gradually increases the depolarization process occurs through the thermally activated jumping of the $F_i$ compensators. This may lead them to positions different from the initial ones they possessed prior to the application of the field. Microscopic calculations based on a quasimolecular model have shown [10] a significant influence of the external electric field on the local structure of the $Gd^{3+}-F_i^-$ (nn) dipoles. It is concluded that removal of the ions and therefore changes of the electrical dipoles should be expected. As a consequence, a new equilibrium inside the crystal is finally established. Within the picture of a configurational diagram these changes entail changes in the $G = G(Q)$ curves. The relative positions of the free energy minima and the separating barrier of the two configurations are changed (Fig. 2, curve b). Therefore, the corresponding populations of the two types of complexes are changed, a fact reflected in the changes in the amplitudes of peaks A and B in the spectra. The concentration of type I complexes decreases and that of the corresponding type II complexes increases. Thus, after a repetition of the experiment for a number of times we reach to a situation (Fig. 2, curve c) where all the complexes of type I have been transformed to type II complexes. Figure 2 (curve c) also explains why the reverse process, i.e. the conversion (type II → type I complexes) is unattainable since the potential barrier to be surpassed is high.

Significantly enough, if we store the specimens at room temperature for a couple of weeks the initial TSDC (Fig. 1a) spectrum is observed. This means that in the short term the electric field can affect the equilibrium position of the two types of complexes, but in the long term, when no external electric field is applied, the system tends towards the initial equilibrium position. Invariably, a repetition of the experiment gives similar changes in the spectra to those previously mentioned. Within the context of the present model the electric field should be considered as an external factor which affects the equi-librium position of the two types of complexes. If this factor is removed the initial situation is gradually recovered and the transformation between the two types of complexes in both directions is valid according to the interconversion $Gd^{3+}-nn\ F_i^- \rightleftarrows Gd^{3+}-nnn\ F_i^-$, previously proposed [11] for the rare earth complexes.

Remarkably, such changes in the spectra have not been observed in similar experiments performed on $LiF:Be^{2+}$ crystals [12]. However, LiF crystals form a simple cubic lattice, in which type every anion is adjacent to a cation at normal lattice sites equivalently along the three crystallographic axes. When a divalent impurity substitutes for a monovalent ion the condition for electual neutrality requires that an equal number of positive ion vacancies (created by injection of ions to the surface) be present in the crystal. The impurities are associated with the vacancies forming complexes with permanent dipole moments. These (substitutional divalent impurity-cation vacancy) dipoles usually arrange themselves into nn and nnn structures. The depolarization procedure during an ITC experiment allows in the most part, interchange of the vacancies between equivalent neighbour sites mainly nn → nn transitions. On the other hand, in the $CaF_2$ structure the halide anions form a simple cubic sublattice whereas every cation is located in a body-centered position of a cube formed by eight anions. Since the number of cations is one half of the number of the available body-centered sites, the other half of these sites remain empty. When a trivalent impurity substitutes for a divalent ion the necessity of charge compensation requires incorporation of additional fluoride ions at interstitial sites within the lattice. The impurities are associated with interstitial anions to form complexes with dipole moments. These (substitutional trivalent impurities–interstitial anion) dipoles arrange themselves to nn or/and nnn structures. Obviously, due to the non-occupied lattice sites the possibility for nn → nnn transitions during the reorientation processes of the dipoles is enhanced in this lattice.

Preliminary experiments on $SrF_2:Gd^{3+}$ also showed three ITC peaks as in $GaF_2:Gd^{3+}$ but no evidence of the above-described phenomenon was observed. The two crystals have the same lattice structure but $SrF_2$ is much larger than $CaF_2$ as Sr is much larger than Ca: 1.39 and 1.26 Å. At present we do not wish to comment further on this point.

It is worth noticing at this point that in spite of numerous attempts no EPR evidence, to the best of our knowledge, of a trigonal center in $GaF_2:Gd^{3+}$ of the appropriate magnitude has been observed. Furthermore, previous reports on $GaF_2$ material [4, 13] doped with different rare earths provide

Table 2. Summary of relaxation parameters determined for type I complexes of $GaF_2:Gd^{3+}$ crystals

| $h^m$ (eV) | $\tau_0$ (s) | Ref. |
|---|---|---|
| 0.42 | $2.5 \times 10^{-15}$ | 4 |
| 0.377 | $2.8 \times 10^{-13}$ | 6 |
| 0.42 | $2.0 \times 10^{-15}$ | 14 |
| 0.51 | $1.4 \times 10^{-16}$ | 15 |
| 0.395 | $1.2 \times 10^{-13}$ | 16 |

evidence that the 0.62 eV peak is associated with a cluster of two or more rare earths. However, such an identification does not render the interpretation of our data any easier since interconversion of simple dipoles and clusters with the electric field applied below room temperature is rather unexpected.

Finally, we wish to comment on the large diversity of the reported values of the dipole reorientation parameters $h^m$ and $\tau_0$ cited in the literature (Table 2). One of the reasons is the dipole–dipole interaction [17, 18] which affects the relaxation processes and therefore could essentially change the above parameters. It seems to us that the external electric field should also be seriously considered as a cause of the above differences. In this respect, we believe that this new way to look at the relaxation phenomena of the dipoles could provide a better understanding of the migration processes in alkaline earth fluoride crystals.

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