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Reorientation of dipoles in SrF_2: R^{3+}

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Measurements of dipole relaxation of two types of R^{3+}-interstitial complexes in SrF_2:R^{3+} single crystals using the ionic-thermocurrents method are reported. For the light elements in the series of lanthanides we have found relaxations due to tetragonal complexes, whereas in crystals doped with heavy R^{3+} ions such as Dy^{3+}, Ho^{3+}, etc., the predominant defects have trigonal symmetry. The variation of the activation energy as a function of the R^{3+} radius is discussed. In addition, the effect of the impurity concentration on the relaxation parameters is studied.

I. INTRODUCTION

When trivalent lanthanide impurities are substituted for divalent cations in alkaline-earth fluorides, one may observe effects from local charge compensation. In crystals which are pure apart from the contamination with trivalent ions, the charge compensation can be provided by nearby interstitial anions. The resulting complexes can be considered as permanent dipoles embedded in a dielectric and can be polarized by applying an external electric field.

Relaxation effects of the orientational polarization can be studied by means of dielectric loss experiments, but today many investigators prefer the elegant method of ionic thermocurrents (ITC), which was introduced about a decade ago by Bucci *et al.*[1,2]

ITC experiments on doped alkaline-earth fluorides have revealed a lot of information about the defect structure in these materials. Unfortunately, there have been very few systematic ITC studies on alkaline-earth fluorides. It is the purpose of this paper to report about an investigation involving SrF_2 crystals, doped with all rare-earth (R) ions except the unstable ion Pm^{3+}.

We shall discuss the variation of the important relaxation parameters as a function of R^{3+} dopant, which can be observed by means of the ITC method. In addition, we have investigated the effect of the concentration upon the calculated values of the activation energy and characteristic relaxation time τ_0.

It is well known that in general the relaxation phenomena studied by means of the ITC method can be described by the following formula[3-5]

$$I(T) = \frac{C}{\tau_0} e^{-E/kT} \exp\left(-\int_0^T \frac{f'(T')}{\tau_0} e^{-E/kT'}\, dT'\right), \tag{1}$$

where

$$C = A(N_d \mu_e^2 V / 3dkT_{p,\mathrm{eff}})(1 - e^{-t_p/\tau(T_p)}). \tag{2}$$

In (1), E is the activation energy associated with the jumping dipoles; τ_0 is the relaxation time of the dipole for temperature $T=\infty$; $f'(T)$ is the reciprocal heating rate which is a function of the temperature T; $f'(T)$ is not a constant because in our experiments we increase the thermocouple voltage, indicating the temperature of the sample, linearly with time; and $f'(T)$ is approximated by a polynomial in T of the seventh degree.

In (2), A is the effective surface area of the crystal; N_d is the concentration of the dipoles; V is the voltage across the sample during the polarization stage; d is the thickness of the sample; μ_e, $T_{p,\mathrm{eff}}$, and the factor $1 - e^{-t_p/\tau(T_p)}$ are the effective dipole moment, the effective polarization temperature, and a correction factor necessary when the polarization has not reached its equilibrium value.[4,5] It is easy to show that the total charge removed from the electrodes attached to the crystal is equal to

$$\int I\, dT = C. \tag{3}$$

Therefore the integral in (3) is a measure for the concentration of the dipoles.

II. EXPERIMENTAL PROCEDURE

The crystals used in this investigation were grown by our crystal-growing facility from Merck Suprapur SrF_2 powder. Approximately 1-wt.% PbF_2 was added prior to crystal growth to act as a scavenger, especially to reduce the O^{2-} content. The crystal growth took place under high vacuum (10^{-4} Torr). The lanthanide impurities were added as fluorides (nominally 300–3000 ppm) before crystal growth. After terminating the crystal growth the resulting boules were cooled down slowly to room temperature in order to avoid cracks. In this way cylindrical crystal boules 3

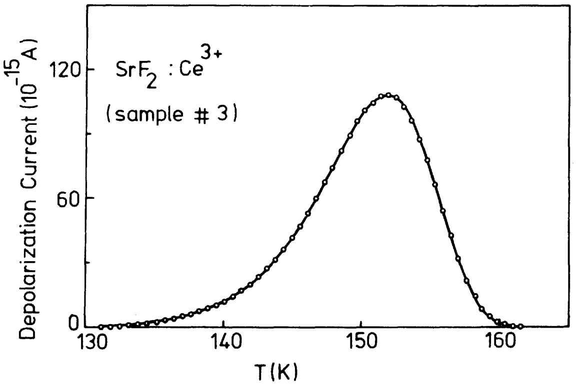

FIG. 1. Result of an ITC experiment on SrF$_2$:Ce^{3+} (sample No. 3, see Table I). The experimental points are indicated; the drawn curve is the computer fit; the result shown here is typical for samples with low dipole concentrations.

cm long with a diameter of about 1 cm were obtained.

The samples were cleaved at the following dimensions: thickness 0.1–0.2 cm; the surface area varied between 0.1–0.4 cm^2. Polarization of the crystals was obtained by applying 1500–2400 V under vacuum. In order to prevent charge carriers from entering the sample, blocked electrodes were used. The crystal was mounted on a cold finger; a good thermal contact was provided by a platelet of In metal between the sample and the cold finger. In this way we could reach cooling rates of 0.3 K/sec.

After freezing in the polarization, the sample was warmed up approximately linearly with time (usually 0.04 K/sec), employing a temperature controller similar to the one designed by Van Overbeeke.[6] As a temperature sensor we used a Cu-Constantan thermocouple. The depolarization currents were detected with a Cary Vibrating Reed electrometer capable of measuring currents as small as 10^{-17} A. In order to avoid errors introduced by long *RC* times, we employed the relatively low resistance of 10^{10} instead of 10^{12} Ω to detect the depolarization currents ranging from 5×10^{-15} to 10^{-12} A.

Each of the experimentally observed ITC peaks was fitted to a theoretically expected shape with a CDC Cyber 74-16 computer, providing the activation energy (E) and the characteristic relaxation time (τ_0) associated with reorienting dipoles.

III. EXPERIMENTAL RESULTS

In SrF$_2$:R^{3+} two different types of ITC peaks can be observed: the peaks of type I are located at about 150 K, whereas the peaks of type II are found at approximately 205 K. Relaxation phenomena producing the ITC peak I are predominant in the first part of the series of lanthanides; on the other hand, relaxations of type II are found for the heaviest R^{3+} ions. In samples doped with GD^{3+}, Tb^{3+}, and Dy^{3+} we have observed both types of relaxation simultaneously. Kitts, Ikeya, and Crawford[3] have investigated SrF$_2$:Gd^{3+} by means of combined ITC and EPR experiments, and they have concluded that the relaxation effects of type I are due to reorientation of dipoles with tetragonal symmetry (C_{4v}). The most obvious system responsible for these relaxations are permanent electric dipoles formed by the substitutional R^{3+} impurity and an interstitial F^- ion in a nearest-neighbor position. The ITC peaks of type II were found to be due to dipoles of trigonal (C_{3v}) symmetry. Here the reorienting entity consists of a R^{3+} ion and an interstitial F^- ion in a next-nearest-neighbor position. Our experimental results on SrF$_2$:Gd^{3+} agree well with those published by Kitts *et al.*[3]; for complexes of type I we have found for the activation energy (E), the characteristic relaxation time (τ_0), and the temperature corresponding with the maximum depolarization current the following values: 0.47 eV, 1.8×10^{-14} sec, and 151 K, respectively. The corresponding values obtained by Kitts *et al.*[3] are 0.45 eV, 10^{-14} sec, and 143 K. The significant parameters, associated with complexes of type II deduced from our depolarization peak, are 0.64 eV, 3.7×10^{-14} sec, and 206 K, which should be compared with the results published by Kitts *et al.*[3]: 0.62 eV, 4×10^{-14} sec, and 206 K.

In Fig. 1 we show the ITC peak due to C_{4v} dipoles in SrF$_2$:Ce^{3+}. The experimental points are indi-

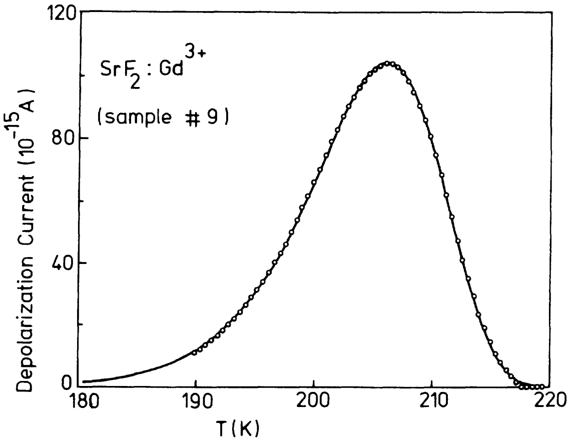

FIG. 2. Depolarization peak of type-II dipoles in SrF$_2$:Gd^{3+} (sample No. 9, see Table II). The fitted curve agrees well with the experimental points as expected for samples with low dipole concentrations.

TABLE I. ITC data for dipole complexes of type I in $SrF_2:R^{3+}$.

Additional impurity	Sample No.	E (eV)	τ_0 (sec)	T_m (K)	Dipole concentration N_d (10^{18} cm^{-3})
La	1	0.44	4.68×10^{-13}	153.2	7.79
Ce	2	0.46	6.47×10^{-14}	151.8	5.53
Ce	3	0.48	9.81×10^{-15}	152.0	0.78
Ce	4	0.42	1.64×10^{-12}	152.0	10.00
Pr	5	0.44	3.38×10^{-13}	152.4	4.25
Nd	6	0.47	2.65×10^{-14}	152.7	3.74
Sm	7	0.38	5.64×10^{-12}	146.2	3.36
Eu	8	0.43	4.55×10^{-13}	152.8	4.26
Gd	9	0.47	1.77×10^{-14}	151.2	1.69
Tb	10	0.41	1.11×10^{-12}	148.0	3.19
Dy	11	0.44	1.31×10^{-13}	148.4	0.73

cated by circles; the drawn line is a least-squares computer fit, which gives us $E=0.48$ eV and $\tau_0=9.8\times10^{-15}$ sec. The quality of the fit is obvious; this is due to the fact that we are dealing here with rather low dipole concentrations (8.2×10^{17} dipoles/cm^3). The effect of the concentration on the line shape of the ITC curves will be discussed in Sec. IV.

In Fig. 2 the results obtained for dipolar relaxations of C_{3v} complexes in $SrF_2:Gd^{3+}$ are given. The parameters describing the reorientation process are $E=0.64$ eV and $\tau_0=3.7\times10^{-14}$ sec; in addition the concentration of the C_{3v} complexes in this particular sample is 2.9×10^{17} dipoles/cm^3. For these trigonal as well as for the tetragonal complexes, the intensity of the ITC peak depends linearly upon the applied voltage, which polarized the sample. This suggests that we are dealing with depolarization due to the reorientation of permanent dipoles.

Experiments as shown in Figs. 1 and 2 have been carried out for SrF_2 samples doped with all available R^{3+} impurities. The important parameters describing the reorientation processes have been compiled in Tables I and II. The relation between the various parameters given in Tables I and II is discussed in Sec. IV. Our experiments show that for a particular impurity ion the position of the ITC peak does not depend significantly upon the dipole concentration in contrast with the values of E and τ_0. For higher impurity concentrations the width of the ITC peak increases. This is demonstrated by the result given in Fig. 3; the half-width of this peak is 11.1 K. The width of the peak given in Fig. 1 is 9.7 K. As a result of the broadening of the ITC curves the parameter E decreases while τ_0 increases. In fact, there is an approximately exponential relationship between E and τ_0 found for one particular R^{3+} dopant at various concentrations. This implies that the parameters E and τ_0 obtained from the least-squares fits do not give a proper description of the relaxation phenomena when one is dealing with high impurity concentrations.

As compared to the large concentration-dependent variations, the differences between the values of E and τ_0 corresponding to the various R^{3+} impurities are rather small. This can be seen from Figs. 4 and 5, which summarize some of type-I dipoles.

In contrast with the large deviations of the relaxation parameters caused by differences of the

TABLE II. ITC data for dipole complexes of type II in $SrF_2:R^{3+}$.

Additional impurity	Sample No.	E (eV)	τ_0 (sec)	T_m (K)	Dipole concentration N_d (10^{18} cm^{-3})
Gd	12	0.64	3.71×10^{-14}	206.2	0.28
Tb	13	0.52	2.88×10^{-11}	206.4	6.93
Dy	14	0.53	2.48×10^{-11}	209.0	9.92
Ho	15	0.57	5.92×10^{-12}	213.0	8.49
Er	16	0.59	2.45×10^{-12}	214.4	9.82
Tm	17	0.59	1.38×10^{-12}	209.7	6.87
Yb	18	0.58	1.53×10^{-12}	208.8	8.26
Lu	19	0.57	6.13×10^{-13}	201.4	6.34

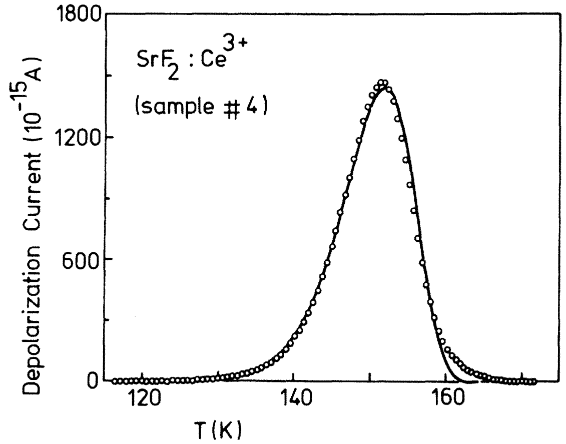

FIG. 3. Result of an ITC experiment on a heavily doped SrF_2:Ce^{3+} crystal (sample No. 4, see Table I). The quality of the fitted curve is less than that in Fig. 1.

dipole concentrations, the reproducibility of the experimental results (E and τ_0) for one particular concentration is very good. The maximum error in the activation energy E is 0.01 eV, while characteristic relaxation time can be determined with an accuracy of about 40%.

IV. THEORY

As it was shown that the relaxation properties depend upon the concentration of reorienting dipoles, it is useful to determine N_d very carefully. In order to do so, a discussion of the entities μ_e and $T_{p,\text{eff}}$ is necessary.

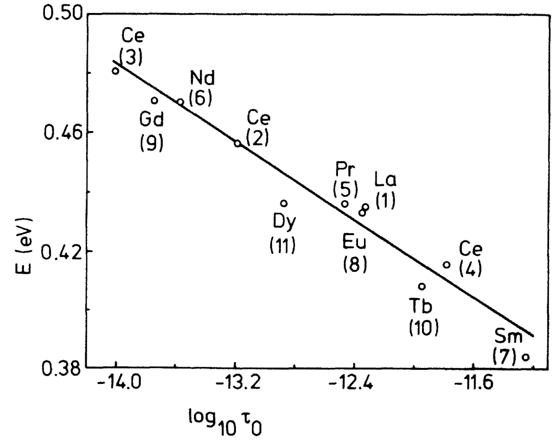

FIG. 4. Plot showing the correlation between E and $\log_{10}\tau_0$ for various ITC experiments on type-I dipoles in SrF_2 crystals doped with different R^{3+} impurities. For each of the experimental points the sample No. in Table I and dopant has been indicated.

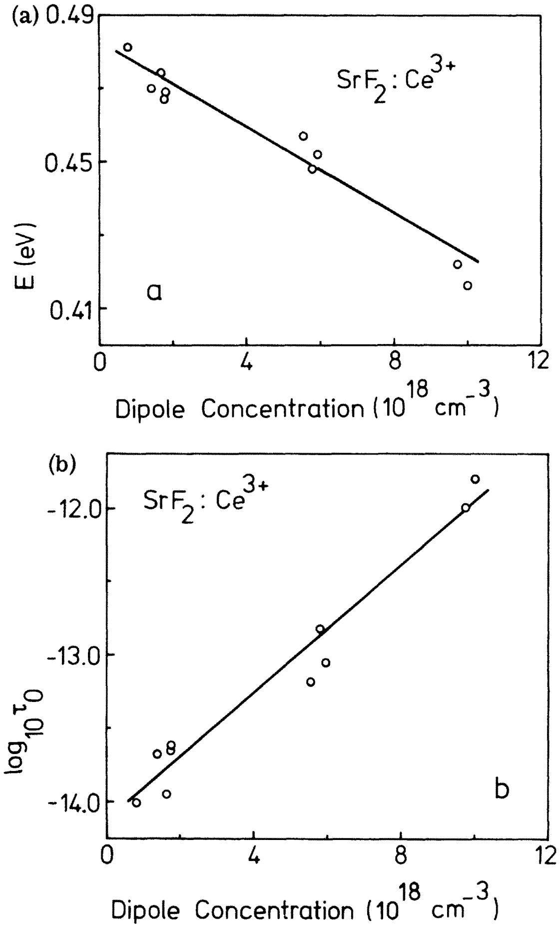

FIG. 5. (a) Behavior of the activation energy as a function of the dipole concentration for crystals of the type SrF_2:Ce^{3+}. (b) Behavior of the characteristic relaxation time τ_0 as a function of the dipole concentration for crystals of the type SrF_2:Ce^{3+}.

A. μ_e

For a correct determination of μ_e we need to realize that the permanent dipoles are embedded in a dielectric with a rather large static dielectric constant ($\epsilon_{\text{stat}} = 7.69$). According to Böttcher[7] this leads to an increase of the dipole moment as compared to the corresponding dipole in vacuum. The amplification factor is $3\epsilon/(2\epsilon+1) = 1.41$. For the dipole moment in vacuum we apply the undistorted point-ion model. In this way we find for the tetragonal complexes an effective dipole moment of 0.68×10^{-28} C m, while the corresponding value for trigonal dipoles is 1.18×10^{-28} C m.

B. $T_{p,\text{eff}}$

Although after polarization during t_p seconds the sample is cooled down quickly, serious problems may still arise because the relaxation time $\tau(T) = \tau_0 e^{E/kT}$ is very short for temperatures a few tens of degrees higher than T_m. The cooling rate during "quenching" is about 0.32 K/sec, which should be compared with typical heating rates of 0.04 K/sec during the depolarization experiments. We have found that during the cooling process prior to the dipole relaxation experiment the equilibrium polarization is preserved until a temperature approximately 20 K above T_m is reached. At lower temperatures the polarization is frozen in. In accordance with Nunes de Oliveira and Leal Ferreira[8] we write for $T_{p,\mathrm{eff}}$

$$T_{p,\mathrm{eff}} \simeq \frac{T_m}{\beta^{1-\beta}\Gamma(\beta)} \quad (\text{when } T_p \gg T_m) \tag{4}$$

or

$$T_{p,\mathrm{eff}} \simeq \frac{T_m}{e^{-\beta} + \beta^{1-\beta}\gamma(\beta,\beta)} \quad (\text{when } T_p \simeq T_m). \tag{5}$$

In (4) and (5), $\beta \simeq (E+kT_m)/(2E+kT_m)$, in addition $\Gamma(\beta)$ and $\gamma(\beta,\beta)$ are the usual gamma and incomplete gamma functions, respectively.

The curve fitting of the ITC peaks to the behavior described by (1) was obtained by the Marquardt method. The experimental data, corresponding to the wings of the depolarization peaks, were weighted less than those in the central region, because of the smaller signal to noise ratio. In general, for the lowest concentrations of dipoles we have achieved the best curve fittings. As was shown in Sec. III, the position of the ITC peak does not depend significantly upon the dipole concentration. Also the fitted curves show peak positions, which agree well with the experimental ones. For maximum depolarization current the following relationship between E, τ_0, and T_m holds:

$$T_m^2 = [E/kf'(T_m)]\tau_0 e^{E/kT_m}. \tag{6}$$

Because experimentally as well as theoretically T_m is approximately constant, we expect that there is a strong correlation between E and τ_0. This correlation has been demonstrated in Fig. 4.

The broadening of the ITC peaks was found to depend upon the impurity concentration. Therefore, dipole-dipole interactions will probably be the origin of this broadening. These dipole-dipole interactions can give small fluctuations of the activation energy, which are of the order of μ_e^2/R^3. It can be shown that the probability of finding an additional dipole within a sphere of 5 Å is about 1% for dipole concentrations of 10^{19} cm^{-3}. This leads to dipolar interactions of the order of 0.01 eV, and therefore the measured ITC peak will be a superposition of many displaced depolarization peaks, of which the activation energies scatter about the average value. Probably also the monopole-dipole interaction affects the activation energy.

V. DISCUSSION

As discussed above, the depolarization effects giving rise to ITC peaks of type I are caused by tetragonal R^{3+}-interstitial complexes. The peaks of type II observed in SrF_2 crystals doped with the heaviest R^{3+} impurities are due to trigonal R^{3+}-interstitial complexes. A three-dimensional schematic representation of both kinds of defects has been visualized in Fig. 6.

The interstitial F^- ion neighboring the trivalent impurity moves in a potential well; its vibration frequency is assumed to be $1/2\pi\tau_0$, depending on the detailed shape of the potential well. This vibration frequency is usually related with that of the lattice vibrations (~10^{13} sec^{-1}). We have found that for complexes consisting of a trivalent impurity and an interstitial H^- ion in a nearest-neighbor position, the vibration frequency does not change significantly as a function of the ion size of the lanthanide impurity.[9] We therefore assume that also for interstitial F^- ions neighboring the impurity ion the shape of the potential well does not change drastically in going from La^{3+} to Lu^{3+}. Consequently, the characteristic relaxation time τ_0 does not vary strongly for the various lanthanide dopants.

Choosing a constant value for τ_0 and using the well determined value of the temperature at which the depolarization current reaches its maximum, we can calculate from (6) a corrected activation energy E^* which is independent of the concentration of the dipoles. In Figs. 7 and 8 we show the behavior of E^* as a function of the ionic radius

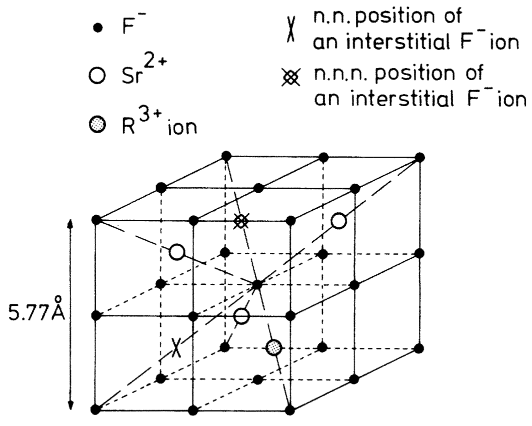

FIG. 6. Three-dimensional schematic representation of a SrF_2 crystal showing the structure of tetragonal and trigonal R^{3+}-F_i^- complexes.

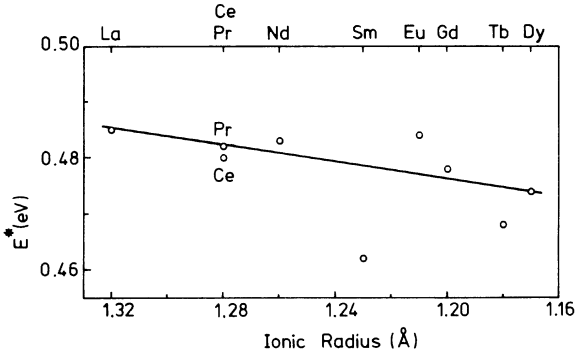

FIG. 7. Variation of the corrected activation energy (E^*) as a function of the R^{3+} radius for dipoles of type I.

of the trivalent impurity ions for tetragonal and trigonal dipoles, respectively. The radii of the various ions were taken from the work of Shannon and Prewitt.[10] The corrected E^* values for tetragonal dipoles show a slight decrease with decreasing lanthanide radii. On the other hand, E^* for trigonal dipoles reaches a maximum value for Er^{3+}.

Conforming to the model proposed by Bollmann *et al.*,[11] we shall assume that during reorientation of the tetragonal dipole the interstitial anion induces one of the neighboring substitutional F^- ions to move into another interstitial position, while the interstitial itself takes the empty substitutional site (interstitialcy mechanism). The activation energy corresponding to the motion of free interstitial anions in SrF_2, is 0.94 eV, which is appreciably larger than the values observed for our tetragonal complexes. It was suggested by Kitts and Crawford[12] that the lower value of the activation energy is due to the large binding energy of the dipolar complex. In addition, lattice relaxations in the vicinity of the defect could be a reason for the decreased value of E.

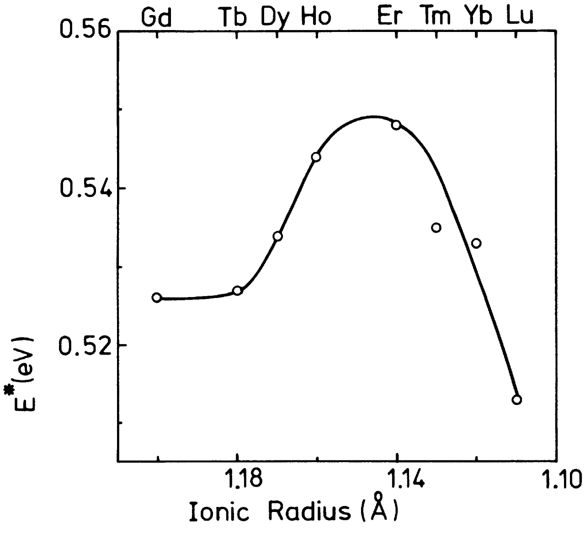

FIG. 8. Variation of the corrected activation energy (E^*) as a function of the R^{3+} radius for dipoles of type II.

A similar series of ITC experiments as reported here have been carried out by Kitts and Crawford[12] on the system CaF_2:R^{3+}. These authors found systematic changes in the activation energy and τ_0 as a function of the impurity-ion radius. As we have seen from our experiments on SrF_2:R^{3+}, E and τ_0 are strongly correlated; it was found useful to treat the results obtained by Kitts and Crawford in a similar way as ours. Again we define a corrected activation energy E^* and use a constant value of the characteristic relaxation time τ_0. The resulting corrected activation energy is found to decrease gradually and very slightly with decreasing radius of the R^{3+} impurity which is comparable to the behavior of the system SrF_2:R^{3+} shown in Fig. 7.

The present interpretation of our experimental results suggests that the activation energy associated with the reorientation of tetragonal dipoles changes only very slightly for the various R^{3+} dopants. This is not unexpected when it is realized that the variations of the ionic radius of the trivalent impurities for which tetragonal dipoles have been observed is less than 15%.

In view of the above discussion, we can understand why for the trigonal complexes the activation energy is significantly higher than for the tetragonal dipoles. The internuclear distance between the impurity and the interstitial anion is a factor of $\sqrt{3}$ larger for trigonal than for tetragonal defects. Consequently, the activation energy associated with trigonal dipoles will be closer to the corresponding value for free interstitial anions. The behavior of E^* of trigonal dipoles as a function of the R^{3+} radius can be understood as follows. For decreasing R^{3+} radii the neighboring F^- ions will move towards the impurity, implying that the excess positive charge will be screened more and more. Therefore, the interaction between the constituents becomes smaller, and the activation energy will increase as it approaches the activation energy of mobility of the free interstitial anions. The inward relaxation of the anions in the first coordination shell is limited by repulsive interactions between these anions. Owing to this effect, the activation energy reaches a maximum value. For still smaller impurity ions one may expect a relaxation of the "loose" R^{3+} ion within the cube of F^- ions towards the next-nearest-neighbor interstitial anion resulting in a decrease of the activation energy. This relaxation is also suggested by the results of EPR and electron-nuclear double resonance experiments.[13-16]

It can easily be seen that the reorientation mechanism of trigonal dipoles should be rather complicated. At least three anions are involved. We assume that during relaxation by an interstitialcy mechanism, the trigonal dipole is transformed into a tetragonal one. The relaxation time of these tetragonal dipoles is very short (approximately 30 msec) in the temperature range in which depolarization of trigonal dipoles occurs. It is obvious that during the relaxation process the concentration ratio of trigonal and tetragonal dipoles remains approximately constant, suggesting that simultaneously one of the tetragonal dipoles is transformed into a trigonal one. In this model the relaxation of trigonal dipoles is governed by the rate of the reaction

$$R^{3+}-\text{nn}\;F_i^- \rightleftarrows R^{3+}-\text{nnn}\;F_i^- . \qquad (7)$$

The ratio $\mathcal{R}$ of the concentrations of the tetragonal and trigonal complexes decreased drastically with decreasing R^{3+} radius for Gd^{3+}, Tb^{3+}, and Dy^{3+}. For $\mathcal{R}$ we have found 6.0, 0.5, and 0.07 for $SrF_2:Gd^{3+}$, $SrF_2:Tb^{3+}$, and $SrF_2:Dy^{3+}$, respectively. For smaller R^{3+} impurities the ITC peak due to tetragonal dipoles could not be detected. The present results show that the association energies for tetragonal and trigonal complexes do not differ strongly. Therefore even minor modifications such as a decreasing radius of the R^{3+} ion will be sufficient to have a great influence on the ratio $\mathcal{R}$.

ACKNOWLEDGMENT

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