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Effect of the Ce^{3+} concentration on the reorientation of dipoles in $SrF_2:Ce^{3+}$

W. van Weperen, B. P. M. Lenting, E. J. Bijvank, and H. W. den Hartog
Solid State Physics Laboratory, 1 Melkweg, Groningen, The Netherlands

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The effect of the impurity concentration on the reorientation of dipolar complexes in SrF_2, consisting of a trivalent cerium ion and a neighboring interstitial fluorine ion, has been investigated. It was found in an earlier paper that the width of the reorientation band as measured by the ionic-thermocurrents technique (ITC) increases with increasing concentration. This can be understood when it is assumed that the activation energy associated with the reorienting dipoles is modified by dipole-dipole interaction. In the present paper we propose that there is a Gaussian distribution of values for the activation energy. The width p of this distribution has been calculated on the basis of a crude electrostatic interaction model. It will be shown in this paper that p increases with increasing concentration of Ce^{3+}. In addition, we shall see that in the interpretation given in this paper the average activation energy is independent of the Ce^{3+} concentration, whereas in earlier treatments of the ITC bands several authors have found that the activation energy decreases with increasing concentration.

I. INTRODUCTION

Charge compensation in ionic crystals has been studied for some decades by means of dielectric techniques and spectroscopic methods such as electron spin resonance (ESR) and electron-nuclear double resonance (ENDOR). Alkaline-earth fluoride crystals doped with trivalent rare-earth impurities (R^{3+}) have been investigated by several research groups.[1-4] In a recent paper on electric dipoles in SrF_2: R^{3+},[5] we have observed that the relaxation behavior of dipolar complexes is influenced significantly by dipole-dipole interaction, even at moderate dipole concentrations.

As a result of the dipole-dipole interaction the experimentally observed reorientation curve as measured by the ionic-thermocurrents technique (ITC; see also, Bucci *et al.*[6,7]) cannot be explained successfully with the theoretically calculated one,

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

where

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

In (1), E is the activation energy associated with the reorienting dipoles; τ_0 is the characteristic relaxation time; and $f'(T)$ is the reciprocal heating rate which is a function of the temperature. In (2), A is the effective surface area of the sample; N_d is the concentration of the dipoles; V is the voltage applied to the sample; d is the thickness of the crystal; 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 (see also Lenting *et al.*[5]), and a correction factor necessary when the polarization has not reached its equilibrium value (see Refs. 5 and 8).

Changes in the ITC curves as a function of the dipole concentration have been observed by Shelley and Miller[9] for the system $CaF_2:Na^+$. These authors have calculated the shape of the ITC curve in the presence of dipole-dipole interaction. Unfortunately, the concentration of the dipoles was chosen as high as (2–2.5)%. At this concentration, appreciable clustering of defects is expected to take place, which casts doubts on the results.

Royce and Mascarenhas[10] have observed that with increasing dipole concentration the activation energy decreases; at the same time, τ_0 increases in magnitude. This was ascribed by Royce and Mascarenhas to elastic interactions similar to those suggested by Lüty.[11] Johnson *et al.*[12] studied dielectric and anelastic losses in $CaF_2:Na^+$; they observed that the width of the Debye peak increases with increasing Na^+ concentrations. The increasing width was associated by Johnson *et al.* with dipole-dipole interactions.

The interaction among the dipoles leads to a broadening of the dipole reorientation curve. For increasing concentrations, the halfwidth of the ITC peak increases. The position of maximum depolarization current, on the other hand, is not affected by dipole-dipole interactions. In order to explain these features, we propose that the activation energy associated with the jumping dipoles is modified by dipole-dipole interactions. The activation energy is no longer equal to one fixed value, but we have a distribution of values scattered about a value E_0. In this paper we shall assume that the distribution is Gaussian, i.e.,

$$N(E)=(N_d/p\sqrt{\pi})e^{-(E-E_0)^2/p^2}, \quad (3)$$

where p is a measure of the width of the distribu-

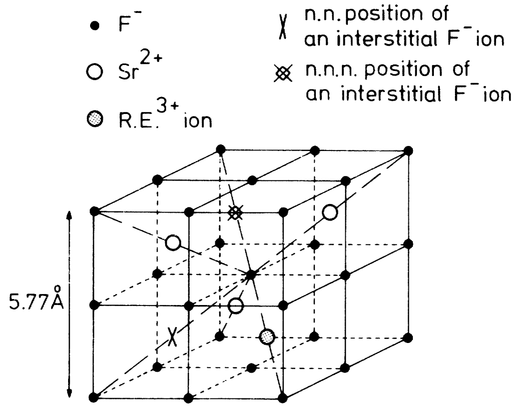

FIG. 1. Three-dimensional schematic representation of a $\mathrm{SrF_2}$ crystal showing the structure of tetragonal (type-I) and trigonal (type-II) R^{3+}-$\bar{\mathrm{F}}_i$- complexes.

tion. According to this model, p will increase with increasing dipole concentrations.

In order to demonstrate the effect of dipole-dipole interactions, we shall study in this paper the dipole reorientation of $\mathrm{SrF_2:Ce^{3+}}$ at various impurity concentrations (a three-dimensional representation of these dipoles has been given in Fig. 1). From the model used in the present paper, we can determine the following parameters: C, τ_0, E_0, and the width of the distribution of activation energies p. It will be shown that the central value of the distribution of activation energies E_0 is equal to the activation energy observed at low concentrations. Also, the value of τ_0 is approximately the same for samples doped with different concentrations of $\mathrm{Ce^{3+}}$. Variations are observed in the value of C, which depend linearly upon the concentration and p, which is a measure of the dipole-dipole interaction strength.

From the results presented in this paper, we shall conclude that the dipole reorientation curves observed in $\mathrm{SrF_2}$ crystals doped with 10^{18}–10^{19} $\mathrm{Ce^{3+}}$ ions/cm^3 can be explained rather well when dipole-dipole interaction is included. Good agreement between theory and experiment is obtained for the halfwidths of the ITC curves; also, the general curve fitting on the basis of the model proposed in the present paper is much better than for the conventional theory used elsewhere.[5] The computer fits allowed us to estimate the average strength of the dipole-dipole interaction. As expected, we have found that the average dipole-dipole interaction varies linearly with the concentration of the dipoles.

II. EXPERIMENTAL PROCEDURES

The crystals used in this investigation were prepared in very pure carbon crucibles by means of a Bridgman method using high-frequency induction heating. Details of the preparation techniques employed have been described in a previous paper.[5] Also, the setup for the ITC experiments has been given in that publication.

The depolarization peaks were fitted by theoretically calculated curves using a CDC Cyber 74-16 computer. The fittings were obtained by employing the Marquardt method and providing best values for the characteristic relaxation time τ_0, the average activation energy E_0, and the value of p.

III. THEORY

A. Distribution of activation energies

For the calculation of the distribution of activation energies we shall apply the rigid point ion lattice model. It is assumed, that the $\mathrm{Ce^{3+}}$-F_i^- complexes have a dipole moment $P=\frac{1}{2}ed$, which is directed along the crystallographic $\langle 100\rangle$ directions (d is the lattice parameter of $\mathrm{SrF_2}$). We have to correct this dipole moment, because P is embedded in a dielectric with a large static dielectric constant $\epsilon = 7.69$. The effective dipole moment $\mu_e = [3\epsilon/(2\epsilon+1)]P = 1.41P$; here, $3\epsilon/(2\epsilon+1)$ is the so-called amplification factor.[5]

The dipole-dipole interaction between two $\mathrm{Ce^{3+}}$-F_i^- complexes associated with dipoles $\vec{\mu}_1$ and $\vec{\mu}_2$ can be written

$$U=\frac{1}{4\pi\epsilon\epsilon_0}\left(\frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r_{12}^3}-\frac{3(\vec{\mu}_1\cdot\vec{\mathrm{r}}_{12})(\vec{\mu}_2\cdot\vec{\mathrm{r}}_{12})}{r_{12}^5}\right), \qquad (4)$$

where $\vec{\mathrm{r}}_{12}$ is the vector connecting the position of dipoles $\vec{\mu}_1$ and $\vec{\mu}_2$. In the present calculations we shall assume that the dipoles $\vec{\mu}_1$ and $\vec{\mu}_2$ are located at the $\mathrm{Ce^{3+}}$ impurity positions. From an inspection of the nearest-neighbor complexes we find that there are six possible directions for each of the dipoles.

In order to calculate the variations in the activation energy, we should determine the differences in the dipole-dipole interaction for two different orientations of the central reorienting electrical dipole. The first position is the one corresponding with minimum potential energy; the second one is associated with maximum potential energy found for the reorienting dipole. Because the exact configuration corresponding with maximum potential energy is unknown, we approximate the changes of the activation energy by the dipole-dipole interaction energy for equilibrium configurations.

Interaction of the central dipole with two or more dipoles in the neighborhood has been neglected because we only consider dilute systems (10^{18}–10^{19} dipoles per cm^3). We have taken into account the effects associated with at least 1000 $\mathrm{Ce^{3+}}$ sites.

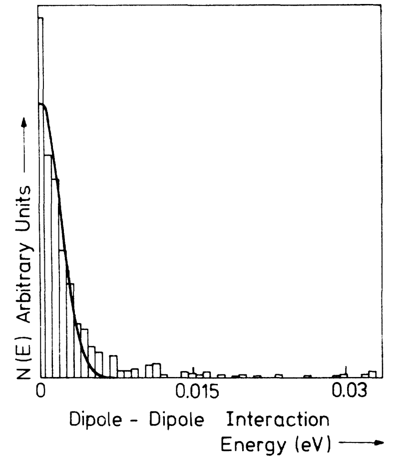

FIG. 2. $SrF_2{:}R^{3+}$ nearest-neighbor dipole-dipole interaction energy spectrum. $N_d = 2 \times 10^{19}$ dipoles per cm^3; halfwidth of the fitted Gaussian energy-distribution function $p = 0.0026$ eV.

From the results of our calculations we have constructed a histogram in which the deviation of the activation energy with respect to the average value E_0 (see Fig. 2). The histogram indicates that the distribution of activation energies is not Gaussian; some local maxima far from $E = E_0$ are found. The histogram, however, gives an indication about the importance of the effect of dipole-dipole interaction. The shape of the histogram can be fitted by a Gaussian distribution function. The width of the distribution function depends upon the concentration of the dipoles; a plot showing the relation between the width of the energy distribution and the dipole concentration has been given in Fig. 3. When on the other hand the broadening of the ITC peak is caused by interaction between reorienting dipoles and monopoles which may be present as a result of nonlocal charge compensation (see also Sec. V), a treatment similar to the one presented above should be given. The strength of the interaction will be appreciably larger, because the interaction energy now decreases with $1/r^2$, instead of $1/r^3$ (r is the distance between the monopole and the reorienting dipole). This implies that the fluctuations of the activation energy will be larger for monopole-dipole than for dipole-dipole interactions, when the concentrations of monopoles and dipoles are equal.

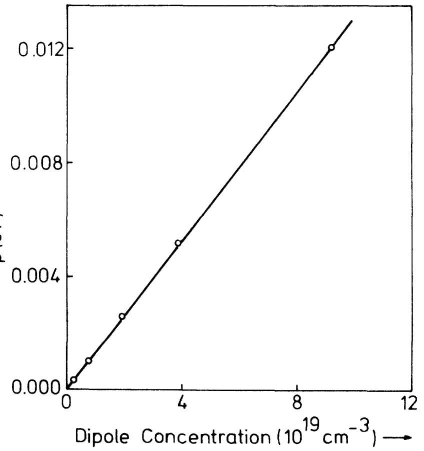

FIG. 3. Plot of the calculated width of the dipole-dipole interaction energy distribution as a function of the dipole concentration. The model used has been explained in the text.

For monopole-dipole interactions, we have constructed histograms similar to the one shown in Fig. 2 and we have found that the broadening due to this interaction is indeed larger than for dipole-dipole interaction. In addition, one should realize that both the effective positive charges (i.e., the Ce^{3+} impurities) and the negative charges contribute to the broadening of the ITC curves. The monopole-dipole interaction produces a broadening of the ITC curve which is, for concentrations of about 10^{19} cm^{-3}, 14–15 times as large as that of dipole-dipole interaction at the same concentration. As will be discussed in Sec. V, we have found from the broadening of our experimental peaks that the concentration of monopoles is very small and does not contribute significantly to the broadening of the ITC bands.

B. Dipole reorientation

When a sample with a frozen polarization is allowed to warm up slowly, the total polarization P will decrease. This decreasing polarization can be monitored by measuring the depolarization current. In the present paper we shall consider, as discussed in Sec. III A, a Gaussian distribution of activation energies; therefore, the jump rate of different dipoles will not be the same. This implies that we have many overlapping ITC curves described by the differential equation

$$\frac{dP(E,T)}{dt} = -\frac{1}{\tau_0} e^{-E/kT} P(E,T) . \tag{5}$$

At $t = 0$ we have $P(E, 0) = P_0 \exp[-(E - E_0)^2/p^2]$, being the contribution to the total polarization due to dipoles with activation energies E. From (5) we can derive an ITC formula, which is similar to (1); however, there is a modification due to the Gaussian distribution of activation energies.

It is possible to factorize the result obtained for the depolarization current as a function of temperature in such a way that the first factor contains E_0, τ_0, C, and T only; this factor has the same form as the unperturbed ITC formula (1). The second factor contains an integral over E and can be considered as a correction factor

$$\begin{aligned} I(T) &= \left[\frac{C}{\tau_0} e^{-E_0 kT} \exp\left(-\int_0^T \frac{f'(T')}{\tau_0} e^{-E_0/kT'} dT'\right)\right] \\ &\times \left[\frac{1}{p\sqrt{\pi}} \int_0^\infty dE \exp\left(\frac{-(E-E_0)}{kT} - \frac{(E-E_0)^2}{p^2} - \int_0^T \frac{f'(T')}{\tau_0}\left(e^{-E/kT'} - e^{-E_0/kT'}\right) dT'\right)\right] \\ &= I^*(T) \cdot F(E_0, \tau_0, p, T) . \end{aligned} \qquad (6)$$

Calculations have shown that below T_m, F deviates, at most, 15% from unity; above T_m we found that F increases rapidly with T (see Fig. 4). Usually, the sample is heated approximately linearly with time; therefore, it is allowed to replace $f'(T')$ in F by a constant value a, which is equal to the average reciprocal heating rate. With an additional approximation

$$-\int_0^T \frac{a}{\tau_0}\left(e^{-E/kT'} - e^{-E_0/kT'}\right) dT' \simeq \frac{aT}{\tau_0}\left(\frac{e^{-E_0/kT}}{(E_0/kT)+2} - \frac{e^{-E/kT}}{(E/kT)+2}\right), \qquad (7)$$

which holds for $\frac{1}{2}E_0 < E < \frac{3}{2}E_0$, we can approximate

$$F \simeq \frac{1}{p\sqrt{\pi}} \int_{E_0/2}^{3/2E_0} dE \exp\left(\frac{-(E-E_0)}{kT} - \frac{(E-E_0)^2}{p^2}\right) \times \exp\left[-\frac{aT}{\tau_0}\left(\frac{e^{-E/kT}}{(E/kT)+2} - \frac{e^{-E_0/kT}}{(E_0/kT)+2}\right)\right]. \qquad (8)$$

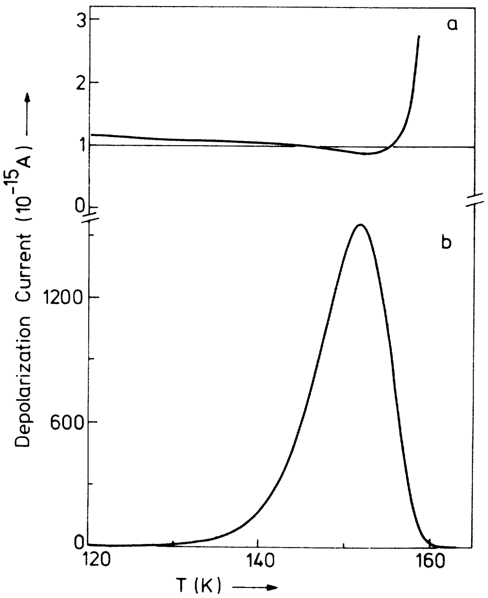

FIG. 4. (a) Plot of the factor F, which accounts for the broadening of the ITC curve, caused by dipole-dipole interactions. (b) Uncorrected ITC curve for the sample of Fig. 5 (sample No. 9).

IV. RESULTS

To demonstrate the difference in quality of the fits of the curves represented by formulas (1) and (6), we have shown the best fits obtained by the two methods for an ITC experiment on $SrF_2:Ce^{3+}$ in Fig. 5. It can be seen that the experimental points cannot be fitted in a reasonable way by a curve given by Eq. (1). Serious discrepancies between the theoretical and experimental ITC curves are observed, also in that temperature region where the depolarization current is large.

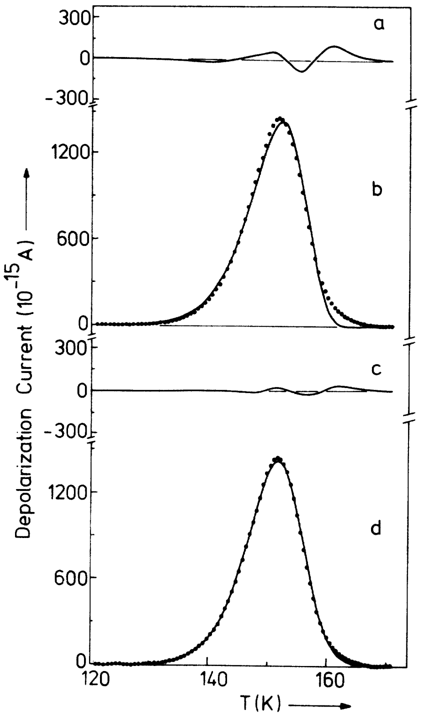

FIG. 5. Example of the improvement that is achieved when dipole-dipole interactions are taken into account. (b) Experimental points and the best fit by a three-parameter ITC formula; results: $E = 0.42$ eV, $\tau_0 = 10^{-12}$sec (d) Same points fitted by a four-parameter formula: results: $E_0 = 0.48$ eV; $p = 0.007$ eV, $\tau_0 = 10^{-14}$ sec. (a) and (c) give the vertical distance between the experimental points and the fitted curve. Experimental points have been taken from the results of sample No. 9.

Also we observe that the fitted parameters E and τ_0 depend strongly upon the dipole concentration.

The agreement between the experimental points and the curve given by Eq. (6) is reasonable. There is a discrepancy between theory and experiment in the high-temperature tail of the ITC peak. It is possible that this discrepancy can be explained by deviations of the energy distribution from the Gaussian line shape. We have observed in Sec. III A, that local maxima exist for the distribution function of activation energies relatively far from $E=E_0$. An interesting feature of the fit of the new theoretical ITC curve derived in Sec. III B to the experimentally observed reorientation band is that the increasing half width with increasing dipole concentration, which has been observed by several authors in the literature, can be understood.

In a previous paper[5] we have found that the experimental values of τ_0 and E obtained for dipoles in $SrF_2:R^{3+}$ are correlated as

$$\tau_0=\tau_0^* e^{\alpha E}, \tag{9}$$

where τ_0^* is a proportionality factor and α is a constant. It should be noted that the same relation is observed for type-I dipoles (nearest-neighbor complexes) in $SrF_2:Ce^{3+}$ (see Fig. 6) when the concentration is varied. This effect can be understood on the basis of the model in which dipole-dipole interactions are taken into account. There exists a relationship between the temperature T_m at which the maximum depolarization current occurs and τ_0, E, and the reciprocal heating rate at T_m,

$$T_m^2=[E/kf'(T_m)]\tau_0 e^{E/kT_m}. \tag{10}$$

When T_m and $f'(T_m)$ are the same for the different samples, we obtain a relationship between E and τ_0 of the type (9).

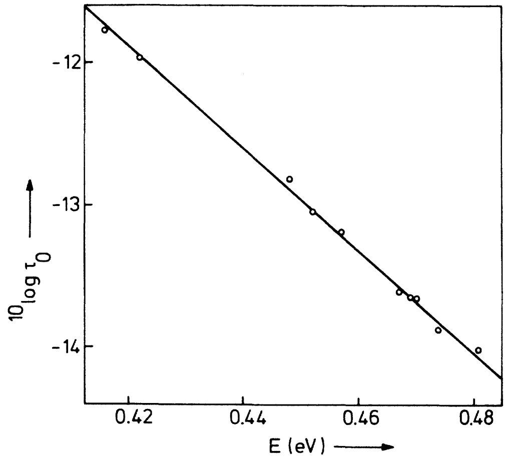

FIG. 6. Distribution of E and τ_0, found for various concentrations of the dopant, when dipole–dipole interactions are not taken into account.

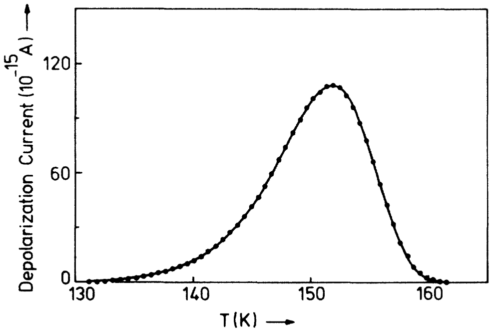

FIG. 7. Experimental points of a sample with low impurity concentration (sample No. 1). The drawn curve is the computer fit on the basis of Eq. (1). A fit using also the additional parameter p [Eq. (6)] gives only slight improvement.

The advantage of the new theoretical curve is that the results for E_0 and τ_0 are independent of the concentration of the dipoles. The experimental results shown in Fig. 5 are taken from a sample containing 10^{19} dipoles/cm^3. When the concentration is lowered to 10^{18}/cm^3 the fit on the basis of Eq. (1) becomes quite good (see Fig. 7); the fit using Eq. (6) is only slightly better. In Fig. 8, we show the relation between the width p of the activation energy distribution and the concentration of the dipoles. The results for E_0, τ_0, and p obtained for various Ce^{3+} concentrations have been compiled in Table I. For E_0 and τ_0, independent of the Ce^{3+} concentration we have found 0.48 ± 0.01 eV and $10^{-14.0\pm0.3}$ sec, respectively.

V. DISCUSSION

We have shown in this paper that the determination of the relaxation parameters E and τ_0 as ob-

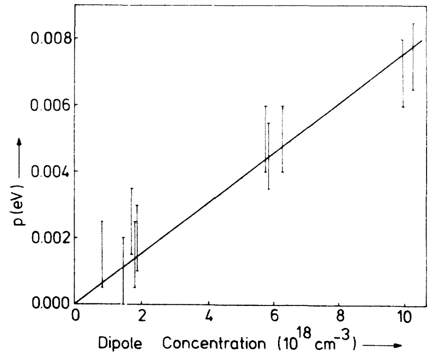

FIG. 8. Plot of the experimental width of the dipole-dipole interaction energy distribution as a function of the dipole concentration.

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

Sample No.	E_0 (eV)	τ_0 (10^{-14} sec)	p (eV)	N_d (10^{18} cm^{-3})
1	0.48	0.8	0.0015	0.9
2	0.47	2.1	0.0010	1.5
3	0.48	0.9	0.0025	1.8
4	0.47	2.1	0.0015	1.9
5	0.47	1.9	0.0020	1.9
6	0.49	0.6	0.0050	6.0
7	0.49	0.7	0.0045	6.1
8	0.47	1.6	0.0050	6.5
9	0.48	1.2	0.0070	10.3
10	0.48	1.5	0.0075	10.6

tained from an ITC experiment is ambiguous when Eq. (1) is used. It turns out that the shape of the dipole reorientation curve changes with the concentration of the dipoles even for fairly dilute systems. The broadening of the ITC bands is ascribed to interaction between the dipoles.

Kristianpoller and Kirsh[13] have suggested that the deviating shape of the ITC curve for samples with high impurity concentrations should be explained by second- or higher-order kinetics. It is, however, not possible in this way to connect the change in the line shape with the physical properties of the dipole system. In the model proposed in this paper the additional parameter p is easily translated in terms of dipole-dipole interaction.

In order to draw conclusions about the dipole-dipole interactions in $SrF_2:Ce^{3+}$, it is necessary to go into the defect structure of this material in some more detail. Association of defects with opposite effective charges can be regarded as a well established phenomenon. It appears, however, that many authors in the literature disagree about the answer to the question: To what extent is the charge compensation local and how many defects occur in nonlocal charge compensation situations?[14-17]

The present knowledge about the defect structure of alkaline earth fluoride crystals doped with trivalent cation impurities is only qualitative, but it suggests that the dipole-dipole interaction broadening is underestimated, if we take into account the effects of C_{4v} and C_{3v} dipoles only. When the values for the ratio of the concentration of dipoles and the total impurity concentration for $CaF_2:Gd^{3+}$ given by Stiefbold and Huggins[18] are similar to those for $SrF_2:Ce^{3+}$ we expect that the theoretically calculated dipole-dipole interaction strength is too small by a factor of five.

From a comparison of Figs. 3 and 8 we see that the discrepancy between the slopes can be explained satisfactorily by this factor. From this we can tentatively conclude that the concentration of the isolated trivalent rare-earth ions is very small as compared to that of the Ce^{3+} interstitial-fluorine complexes.

We should like to mention that the dipole-dipole interaction as treated in this paper may help to answer the question whether or not isolated trivalent impurities exist in alkaline earth fluoride single crystals. ESR (eventually ENDOR) or optical-spectroscopy experiments are needed in close connection with dipole reorientation experiments, because accurate knowledge about the concentration of the dipoles and eventual isolated impurity ions is necessary in order to draw sound conclusions.

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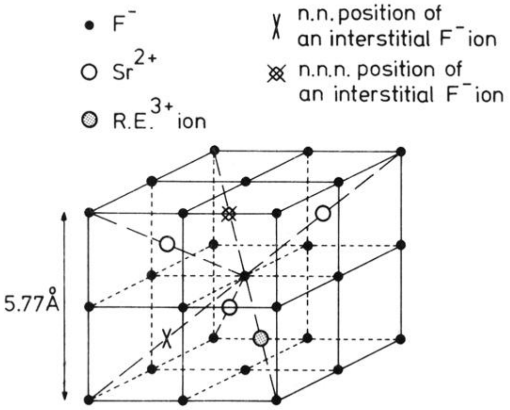

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