

Dipoles in solid solutions Sr_{1-x}Gd_xF_{2+x}

Citation for published version (APA):

Hartog, den, H. W., & Meuldijk, J. (1984). Dipoles in solid solutions Sr_{1-x}Gd_xF_{2+x}. *Physical Review B: Condensed Matter*, 29(4), 2210-2215. <https://doi.org/10.1103/PhysRevB.29.2210>

DOI:

[10.1103/PhysRevB.29.2210](https://doi.org/10.1103/PhysRevB.29.2210)

Document status and date:

Published: 01/01/1984

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Dipoles in solid solutions $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$

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(Received 1 August 1983)

In this paper we present new results on the dielectric relaxation behavior of solid solutions of the type $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$. Attention will be paid to dipole relaxation peaks associated with two different complexes: (a) the nearest-neighbor (NN) $\text{Gd}^{3+}\text{-F}_i^-$ dipole and (b) the next-nearest-neighbor (NNN) $\text{Gd}^{3+}\text{-F}_i^-$ center. The experiments have been carried out in the frequency range from 100 to 3×10^4 Hz. From the behavior of the NN and NNN dipole relaxation bands as a function of the excitation frequency, we have determined the energy difference between the two different dipole configurations to be about 0.050 eV. In addition, we have studied the intensity of the dipole bands as a function of the concentration (x) of Gd^{3+} ions. It is possible to explain the observed behavior of the intensity of the dipole relaxation peaks as a function of x without the need of assuming that there is extensive clustering of Gd^{3+} impurities. We propose to divide the dipoles into two different groups: The first one contains dipoles that are not disturbed severely by extremely close dipoles, contributing to the dipole relaxation peak; the second group of dipoles, which are at close distances from at least a second dipole, contributes significantly to the dc-ionic-conduction process.

I. INTRODUCTION

Solid solutions of the type $M_{1-x}R_x\text{F}_{2+x}$, where M is a divalent cation Ca, Sr, or Ba, and R is a rare-earth ion, have been studied extensively during the last few years by means of numerous experimental techniques.¹⁻⁸ These experiments have provided us with detailed information about the structure and the dynamical properties of the defects in the materials under consideration. Apart from the very powerful spectroscopic methods such as electron spin resonance (ESR), electron-nuclear double resonance (ENDOR), and site-selective high-resolution spectroscopy, a significant number of papers employing the ionic conductivity, the ionic thermocurrents (ITC), and dielectric-loss techniques have been published.

The present paper deals with solid solutions $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$, which have been studied earlier in our laboratory by means of ESR, electric field effect in ESR, and ITC.⁹⁻¹¹ The techniques employed in this investigation are the dielectric-loss technique (the frequency range of the investigations is from 100 to 3×10^4 Hz) and ESR. We shall concentrate in this paper on the behavior of the dipole relaxation peaks of two types of dipoles, which are often present in alkaline-earth fluoride crystals containing trivalent lanthanide impurities: (a) the dipole consisting of a Gd^{3+} impurity and the nearest-neighbor (NN) interstitial fluoride ion (NN dipole), and (b) the dipole consisting of a Gd^{3+} impurity and a next-nearest-neighbor (NNN) interstitial fluoride ion (NNN dipole).

The relaxation parameters obtained from the dipole relaxation peaks are in good agreement with those found in our earlier papers,^{9,10} in which we have employed the ITC method. Special attention has been paid to the behavior of the ratio of the intensities of the dipole peaks associated with NN and NNN dipoles as a function of the excitation frequency. We know that the loss peaks shift towards

higher temperatures if the frequency is increased. This means that the equilibrium between the two types of dipole configurations may be probed as a function of the temperature. We will show in this paper that the results of these experiments may be interpreted by assuming that the NN configuration has a formation energy which is approximately 0.050 eV lower than the NNN configuration. This result is in fair agreement with those obtained earlier by Matthews and Crawford,¹² and Aalbers and den Hartog.¹¹

In this paper we will pay some attention to the following question: Are there dipoles in heavily doped samples? From ESR and the dielectric-loss experiments we conclude that there are real dipoles for GdF_3 concentrations up to about 4 mol %. It appears, however, that the number of dipoles, as measured with the dielectric-loss method decreases with increasing GdF_3 concentrations for $x \geq 0.01$. In order to explain these observations we shall develop a model, in which we discriminate between two different types of dipoles: (a) the relatively unperturbed ones that contribute to the dipole relaxation peak, and (b) a second group of dipoles, which are at close distances from at least one other dipole and do not contribute to the dielectric-loss peaks associated with dipoles. These two different groups of dipoles can be observed in ESR and we have found no differences between the signals associated with these two dipole groups. In addition we conclude from our ESR results that in the concentration range $0 \leq x \leq 0.05$, clustering, if present, only plays a minor role; we have not observed any trace of signals which should be associated with clusters and we did not find any signals showing cubic symmetry either. This latter observation would indicate that in the samples there are no gettered 2:2:2 clusters, which are supposed to trap an extra interstitial F^- ion, and there are no L -shaped or linear clusters as described by Figueroa *et al.*^{13,14}

II. EXPERIMENTAL PROCEDURES

The crystals employed in this investigation have been prepared in our crystal-growth facility with a modified Bridgman setup employing an rf heater. The procedures carried out during the preparation of the crystalline materials have been described in some detail earlier.¹⁵ The cylindrical crystal boules were cut with a slide-wire saw to obtain cylindrical disks approximately 1.5 mm thick for the dielectric-loss experiments. The crystals used for the ESR experiments were cleaved from the boules because it is necessary to orient the crystal carefully in the magnetic field. This is usually done by making use of the presence of well-defined cleavage planes, which are obtained for samples containing less than 6 mol% GdF_3 ($\{111\}$ planes).

The dielectric-loss experiments are carried out with a General Radio capacitance bridge of the type 1615-A in combination with a Princeton Applied Research (PAR) type-128 lock-in amplifier. The ESR experiments were performed with a Varian E-line Century Series electron-paramagnetic-resonance (EPR) spectrometer operating at about 9.2 GHz.

III. EXPERIMENTAL RESULTS

A dielectric-loss spectrum of samples $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$, in general, shows two dipole relaxation bands, the NN

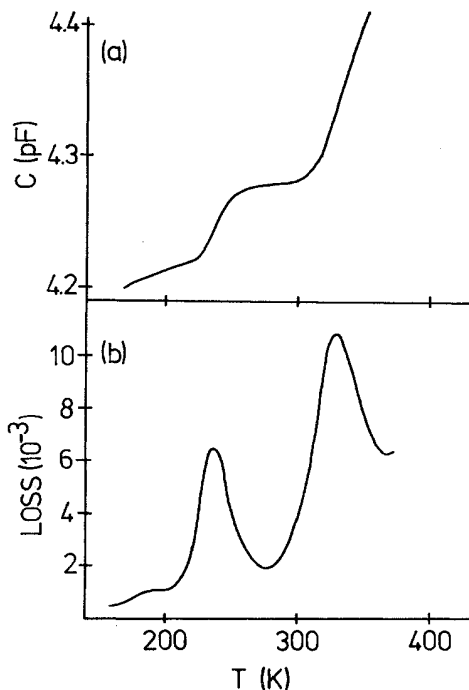


FIG. 1. Results of dielectric relaxation experiments on an SrF_2 crystal doped with 0.5 mol% GdF_3 . The measurements have been carried out at an excitation frequency of 1000 Hz. From a comparison of the curves in (a) and (b) we see that a peak in the dielectric loss coincides with a sharp increase of the capacitance, as expected from the Kramers-Kronig relations, which hold between ϵ' and ϵ'' . The increasing background of (most clearly) the loss as a function of T is due to the relaxation of space charges. This can be deduced from a comparison of this figure with Fig. 2.

band, which is located at low temperatures, and an NNN band at higher temperatures. We have investigated the behavior in a wide range of Gd concentrations employing frequencies between 100 and 30 000 Hz. Apart from the two main loss peaks mentioned we observed a weak bump at very low temperatures for some of the samples. A typical result of a measurement on a relatively heavily doped sample has been shown in Fig. 1. In this figure we have also plotted the behavior of the capacitance of the system as a function of the temperature; combining the results of the dielectric loss and the capacitance we observed a clear relationship, as may be expected from the Kramers-Kronig relations between ϵ' and ϵ'' . In addition to the well-defined relaxation peaks, we observe in Fig. 1 that there is a continuously increasing background; this background appears to be stronger for larger values of x . More detailed experiments, carried out in our laboratory have shown that the background is related with space-charge effects.¹⁶ In Fig. 2 we show a set of plots similar to the ones for the sample measured in Fig. 1 with only 0.2 mol% GdF_3 . A comparison of these two figures shows the difference in the high-temperature region, which should be associated with space-charge relaxation effects. In Fig. 3 we have plotted three dielectric-loss spectra of a sample containing 0.2 mol% GdF_3 measured at frequencies of 100, 1000, and 10 000 Hz. We observe first that the relaxation peaks shift to higher temperature with increasing frequency as expected from a Debye-type relaxation behavior. From these shifts we can derive the activation energies associated with the above-mentioned

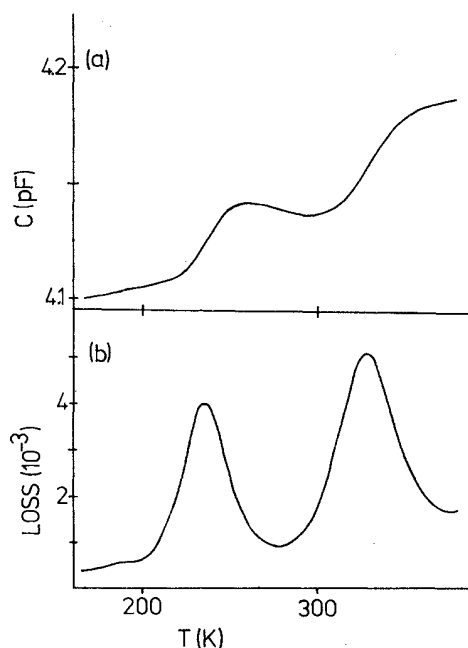


FIG. 2. Results of dielectric relaxation experiments on an SrF_2 crystal doped with 0.2 mol% GdF_3 . The excitation frequency is 1000 Hz. The relationship between the dielectric-loss results and those for the capacitance, which have been indicated in Fig. 1, is clearly shown. The background due to the space-charge relaxation effects in the present case is weaker than for the sample measured in Fig. 1.

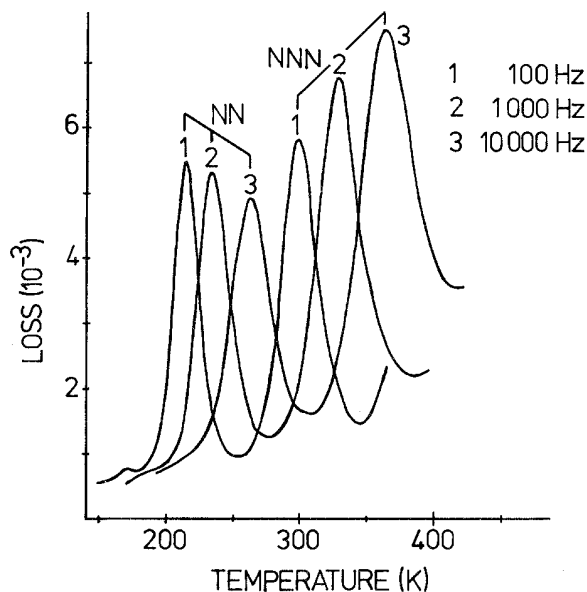


FIG. 3. Dielectric-loss "spectra" of an SrF_2 sample containing 0.2 mol % GdF_3 measured at three different excitation frequencies: 100, 10^3 , and 10^4 Hz. The loss peaks shift to higher temperatures with increasing frequency and the ratio of the NN and the NNN peak intensities decrease with increasing excitation frequency.

jumping dipoles. The corresponding Arrhenius plots have been given in Fig. 4. From these plots we can determine the relaxation parameters occurring in the expression for the relaxation time

$$\tau^i = \tau_0^i \exp(E_i/kT). \quad (1)$$

Here τ_0^i is the characteristic relaxation time of the complex of type i (NN or NNN) and E_i is the corresponding activation energy. The results have been compiled in Table I. They agree quite well with those obtained from ITC experiments carried out in our laboratory.^{9,10}

Another interesting feature that can be observed from the results given in Fig. 3 is that with increasing excitation frequency the ratio of the NN and NNN peak intensity decreases significantly; the NN peak intensity decreases, whereas the NNN peak intensity increases. This indicates that there is an easy exchange between the two possible dipole configurations (NN and NNN). In Fig. 5 we have plotted the behavior of the concentration ratio of the NN and NNN dipoles as a function of the NN peak position (which depends upon the excitation frequency f). The curve in this figure is the best fit of a theoretical relationship derived for these concentration ratios and the corresponding loss peak intensity ratios

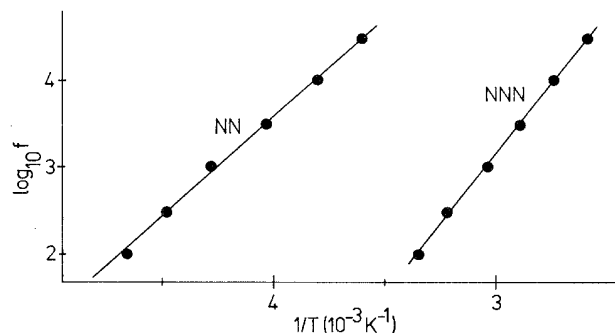


FIG. 4. Arrhenius plots of the loss-peak positions as a function of the excitation frequency. The slope of the lines is a measure for the activation energy of the jumps of the dipole under consideration.

$$\frac{(\tan\delta)_{\max, NN}}{(\tan\delta)_{\max, NNN}} = C \frac{\mu_{NN}^2 T_{NNN}}{\mu_{NNN}^2 T_{NN}} \times \left[\frac{1 + C(e^{\Delta E/kT} - T_{NN}/T_{NNN})}{C + e^{\Delta E/kT}} \right], \quad (2)$$

where μ_{NN} and μ_{NNN} are the dipole moments of the NN and NNN dipoles as determined by Aalbers and den Hartog.¹¹ T_{NN} and T_{NNN} are the temperatures of the maximum loss in the NN and NNN peak, respectively. C is a constant and ΔE is the energy difference of the two dipole configurations NN and NNN. From our experimental results we find that T_{NN}/T_{NNN} is about 0.72. With the use of the known parameters the best fit to the experimental results is obtained with $C = 0.53 \pm 0.04$ and $\Delta E = (0.050 \pm 0.002)$ eV for the sample doped with 0.2 mol % GdF_3 . For the sample containing 0.013 mol % GdF_3 we found for ΔE a value of (0.054 ± 0.002) eV.

In order to obtain additional information about the defect structure we have investigated a number of solid solution, of $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$, with different values of x in the range $0 < x < 0.05$. In Fig. 6 we have plotted the intensity of the dipole relaxation peaks as a function of the concentration of GdF_3 in the crystals. It appears that the dipole bands show a pronounced maximum at about 1 mol % or slightly below this value. Although there is a decreasing intensity of the loss peaks associated with dipolar complexes for $x > 0.01$, these complexes still give rise to considerable loss peaks for concentrations as high as ~ 3 mol %.

Gd^{3+} ions are very attractive probes for ESR investigations, because the signals obtained with this technique are readily observable at room temperature. In Fig. 7 we have given two spectra obtained for $\vec{H}_0 // [100]$. It is clear

TABLE I. Relaxation parameters of NN and NNN dipoles in solid solutions of $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$.

GdF ₃ concentration (mol %)	NN dipole		NNN dipole	
	E_{NN} (eV)	τ_0^{NN} (10^{-14} s)	E_{NNN} (eV)	τ_0^{NNN} (10^{-14} s)
0.013	0.460	2.3	0.642	1.7
0.201	0.460		0.648	
4.66	0.468			

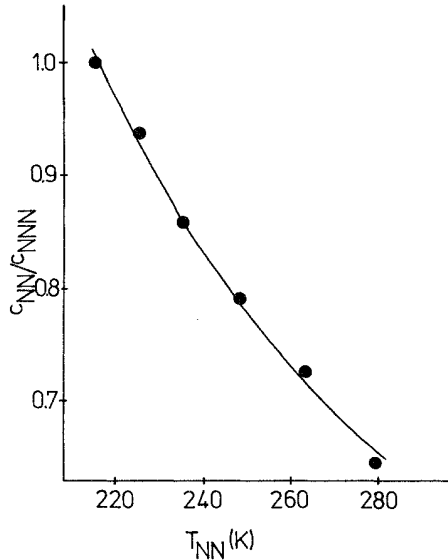


FIG. 5. Behavior of the ratio of the loss-peak intensities c_{NN} and c_{NNN} as a function of the position of the NN dipole relaxation peak (which depends upon the excitation frequency). The curve is the best fit of the relation given in Eq. (2) to the data points.

from a comparison of the two spectra that they are quite similar; the only differences between the spectra are the linewidths and the relative intensities of the peaks. The positions of the lines in the two spectra are approximately the same. The spectra given in Fig. 7 are in good agreement with the results given by Aalbers and den Hartog,¹¹ and using the results published by the latter authors it is possible to assign each of the lines to a particular type of dipole (NN or NNN). Because no extra lines are found, we conclude from the results given in Fig. 7 that in $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ there is no appreciable clustering of Gd ions.

With regard to the small bump observed at the low-temperature side of the NN dipole peak we can say that it behaves as a dipole relaxation peak, i.e., it is located at a fixed position for the solid solutions $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$, as long as only the value of x is changed and the excitation frequency is kept constant. For $f = 1000$ Hz this bump is located at about 180 K and for GdF_3 concentration of 0.2 mol% the activation parameters $E = 0.39$ eV and

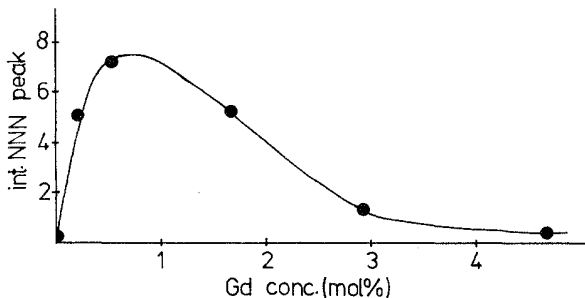


FIG. 6. Behavior of the NNN loss-peak intensity as a function of the GdF_3 concentration. The curve shows a pronounced maximum for GdF_3 concentrations of about 1 mol%.

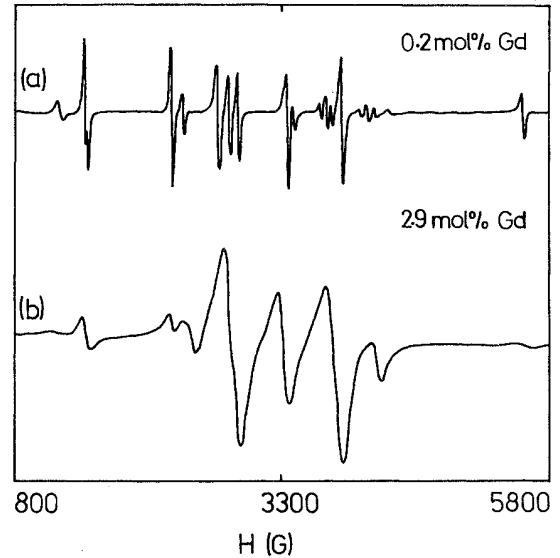


FIG. 7. X-band EPR spectra measured at room temperature of two SrF_2 samples for $\vec{H}_0 // [100]$. Curve *a* is taken from a sample containing 0.2 mol% GdF_3 and curve *b* corresponds to the sample containing 2.9 mol% GdF_3 .

$\tau_0 = 10^{-14}$ s. It should be noted that this small peak can be observed for values of $x < 0.09$.

IV. DISCUSSION

In this paper we focus our attention to the properties of the dipole peaks as observed by dielectric-loss experiments. From earlier work on solid solutions $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ we know that both NN and NNN dipoles exist.⁹⁻¹¹ The relaxation parameters which could be deduced from the Arrhenius plots are in good agreement with earlier ITC results published by our group.^{9,10}

From the behavior of the intensity ratio of the two loss peaks associated with NN and NNN dipoles in $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ we have determined the energy difference between these two dipole configurations (for a comparison of the theoretically calculated best fit [Eq. (2)], and the corresponding experimental results we refer to Fig. 5). The energy difference between the two dipole configurations agrees with the values determined earlier by Aalbers and den Hartog,¹¹ and Matthews and Crawford.¹² The proportionality factor C in Eq. (2), which is 0.53, should be compared with $6/8 = 0.75$. The latter value is expected on purely statistical grounds if we realize that in the neighborhood of a trivalent Gd ion there are six possible NN sites for the interstitial fluoride ion and eight NNN sites. In addition the ratio $c_{\text{NN}}/c_{\text{NNN}}$ is modified to some extent by vibrational entropy contributions, which are probably small. From this we conclude that there is qualitative agreement between the theoretical and experimental value of C .

We shall now discuss the general behavior of the strength of the dielectric-loss peaks due to the dipoles as a function of the total Gd^{3+} concentration. For this discussion we refer to the results presented in Fig. 6. We have

observed that on increasing the Gd^{3+} content the dipole relaxation peak associated with NNN dipoles increases until a maximum peak intensity is obtained for about 1 mol % GdF_3 . For higher concentrations the dipole peak decreases monotonically with increasing GdF_3 concentrations. This behavior can be due to clustering, which has been described by several authors in the recent literature.^{13,14,17-19} According to these authors solid solutions of the type $M_{1-x}R_xF_{2+x}$ often show considerable clustering at relatively low RF_3 concentrations. In some cases detailed models of the clusters involved have been given.^{13,14,20} It appears on the other hand, however, that there are also solid solutions $M_{1-x}R_xF_{2+x}$, in which clustering plays a minor or negligible role even for large values of x . Arguments for this have been given in a recent paper of our group.²¹ We also refer to the paper by Aalbers and den Hartog¹¹ on $Sr_{1-x}Gd_xF_{2+x}$ where it was shown that no additional EPR lines on top of those associated with NN and NNN dipoles could be observed up to Gd^{3+} concentrations of 0.5 mol %. Similar observations have been made for solid solutions of $Ba_{1-x}Gd_xF_{2+x}$ in the concentration range $0 \leq x \leq 0.05$.²² The investigations, employing the ESR techniques, for SrF_2 samples with 0–5 mol % GdF_3 (Fig. 7) show clearly that no additional ESR lines, which may be ascribed to clusters, occur. The results obtained with ESR also indicate that the dipoles could not be distinguished in our data.

In the following we shall propose a model to describe the observed behavior of the dipole relaxation band. We know from earlier investigations that the dipolar defects present in heavily doped materials may contribute considerably to the dc-ionic conduction.^{15,21,23} This suggests that some of the dipoles contribute to the ionic-conduction process and others do not; the latter ones contribute to dipole relaxation bands as observed in this paper. We shall try to distinguish between these two groups of dipolar systems, which cannot be separated with EPR. Dipolar complexes contributing to the dc-conduction process are probably located in the neighborhood of another dipole. On the other hand, a dipole contributing to the dipole relaxation band should be relatively far away from other dipoles. This means that we can define a sphere with the dipole under consideration at the center and a radius R , which is such that if there is not a second dipole within the sphere the central dipole contributes to the dipole peak. In those cases where a second dipole is found within the sphere the central dipole contributes to the dc-conduction process.

With the use of the model described above we can calculate the number of dipoles contributing to the dipole relaxation band, assuming that clustering is absent. If the number of cation positions in the sphere (excluding the central one, which is reserved for the central dipole), is equal to N and the concentration of dipolar complexes in the sample is x we find for the concentration of "unperturbed" dipolar complexes

$$y = x(1-x)^N. \quad (3)$$

In Fig. 8 we plotted three curves showing the behavior of the dipole relaxation peak intensity as a function of the RF_3 concentration for three values of N : 80, 100, and 120.

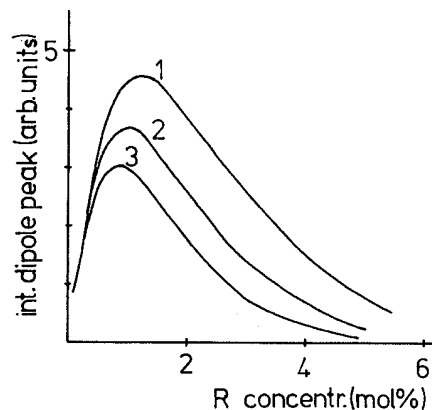


FIG. 8. Plots of the expected behavior of the NNN dipole peak intensity as a function of the GdF_3 concentration. For the calculations, Eq. (3) has been used. It has been assumed that within a sphere containing 80 (curve 1), 100 (curve 2), or 120 (curve 3) cation positions surrounding the central dipole there is not a second dipole.

Although these numbers may seem to be quite large, they are in fact shown to be very reasonable if we consider the plot in Fig. 9, giving the number of cations within a sphere as a function of the radius R . We see that the radius of the sphere containing approximately 100 cations is equal to approximately twice the dipole length of the NNN complex. Comparing the plot containing the experimental results and the theoretical results obtained from the above model described (Fig. 8), we see that the general agreement is remarkable. From this comparison we estimate that the number of cations within the sphere is approximately 100, indicating that the dipoles can be considered as real dipoles in the sense that they give rise to a dipolar relaxation peak if there is not a second dipole in the immediate neighborhood; i.e., within a distance of approximately $3.50d$, where d is the separation between two

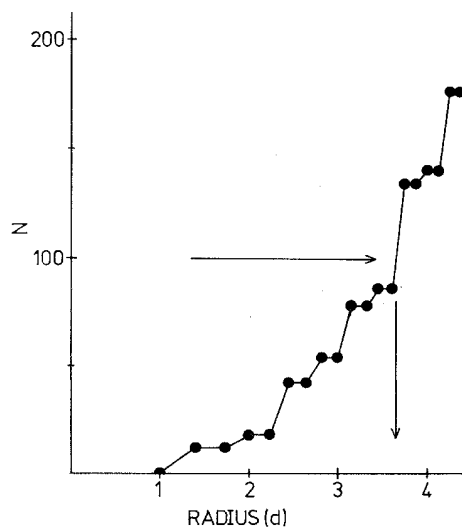


FIG. 9. Behavior of the number of cations within a sphere of radius R . It can be seen that in order to have approximately 100 cations within the sphere a radius of slightly larger than $3.50d$ should be chosen.

neighboring lattice F^- ions.

We have noted that in order to explain the behavior of the dipole relaxation band in $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ as a function of x we have to distinguish between two different types of dipolar complexes. We just described the properties of the ones contributing to the dipole relaxation band. We shall now concentrate on the properties of the complexes contributing to the dc-conduction process. den Hartog and Langevoort²³ recently proposed a dc-conduction mechanism in which dipolar complexes are involved. The conclusion reached was that with this model it is possible to understand the space-charge relaxation processes observed in various different cubic solid solutions of the type $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$.^{15,21,23} The relaxation time associated with space charges may be written as

$$1/\tau = (\alpha/\tau_D) + (1-\alpha)/\tau_F, \quad (4)$$

where τ_D is the relaxation time of the individual dipolar complexes and τ_F is the relaxation time connected with space charges in very diluted solid solutions. For a detailed description of the model we refer to our previous papers.^{15,21,23} According to the model the conductivity of concentrated solid solutions is governed by jumps of interstitial fluoride ions, which are in the neighborhood of a trivalent impurity. These fluoride ions may jump from one dipolar complex to another dipolar complex without net dissociation. A schematic representation of this (percolation-type) ionic-conduction process has been given in Fig. 10. We note that this conductivity model is completely in line with the ideas described above about the dipolar complexes, implying that they can be divided into two different groups. The first group of dipoles can only contribute to the dc-conduction process if they are dissociated, whereas the second group contributes to the conduction process via dipolelike jumps.

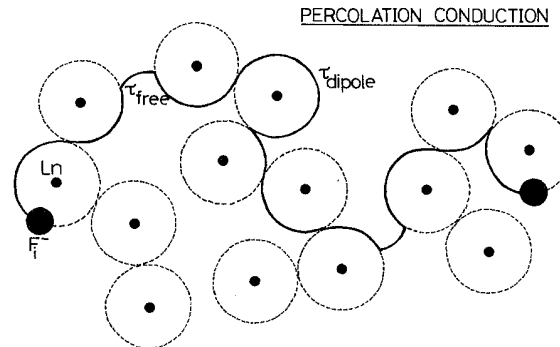


FIG. 10. Two-dimensional schematic representation of the percolation-conduction models proposed by den Hartog and Langevoort (Ref. 23). The crystalline background of the fluorite lattice has been left out. Only the dipoles consisting of a lanthanide impurity and an interstitial fluoride ion have been shown. In the figure it is suggested as indicated in Eq. (4) that two types of jumps contribute to the conduction process: (a) dipole jumps, and (b) jumps of free interstitial F^- ions.

ACKNOWLEDGMENTS

The authors wish to thank Mr. P. Wesseling for growing the crystals and technical assistance. We thank Mr. D. Last and Mr. R. W. Lof for carrying out part of the experiments. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie [Foundation for Fundamental Research on Matter (FOM)], and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek [Netherlands Organization for the Advancement of Pure Research (ZWO)].

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