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Effect of clustering on the space-charge relaxation phenomena in fluorite-type solid solutions $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$

J. Meuldijk, G. Kiers, and H. W. den Hartog

Solid State Physics Laboratory, 1 Melkweg, 9718-EP Groningen, The Netherlands

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In this paper we present the results of ionic thermocurrent (ITC) and dielectric loss experiments on two systems of solid solutions: $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$. The materials investigated have the fluorite structure, and the value of x has been varied in the range $0 \leq x \leq 0.4$. In contrast with results published in earlier papers on solid solutions $Sr_{1-x}La_xF_{2+x}$, we find, for the above-mentioned materials, that clustering plays an important role. It appears that clustering becomes more and more important with decreasing ionic radius of the trivalent lanthanide. We have observed that for Yb-, Er-, and Dy-doped crystals the concentration of next-nearest-neighbor (NNN) dipoles decreases for RF_3 concentrations higher than 0.4, 0.6, and 1.0 mol %, respectively. The ITC peak associated with space-charge relaxation shows a complicated behavior as a function of the RF_3 concentration ($R=$ Dy or Er). For low concentrations the space-charge relaxation peak shifts to lower temperatures with increasing concentration until a minimum value for the temperature is reached. For $Sr_{1-x}Er_xF_{2+x}$ and $Sr_{1-x}Dy_xF_{2+x}$ the concentrations for which this minimum occurs are 0.6 and 1.0 mol %, respectively; i.e., the same concentrations as those mentioned above, where the NNN dipole concentration has its maximum value. The position of the high-temperature (HT) band turns out to be related to the concentration of dipoles in the low-concentration range. In heavily doped materials the position of the HT band probably depends upon the number of clusters present. It will be concluded that clustering is very complex and that it is not possible to draw unambiguous conclusions from our experimental results concerning the defect structure of heavily doped materials. In spite of this we have presented a few possible descriptions which may be applicable.

I. INTRODUCTION

In recent investigations carried out in this laboratory we have studied charge-transport properties of solid solutions $A_{1-x}R_xF_{2+x}$ (Refs. 1—3) (A is an alkaline earth and R is a rare-earth ion), which turn out to have a cubic lattice structure for large values of x ($0 \leq x \leq 0.40$). The lattice structure is the same as the one observed for pure CaF_2 (the fluorite structure), which consists of two sublattices; the sublattice of fluoride ions is a simple cubic lattice with fluoride ions at each of the corners of the cubes and the sublattice of the remaining positive ions which is such that the centers of alternating cubes of fluoride ions are occupied by divalent cations (see Fig. 1). The trivalent impurities are located at substitutional A^{2+} sites; at the same time empty cubes of fluoride ions are filled with interstitial fluoride ions in order to preserve electroneutrality.

For very low R^{3+} concentration the majority of the impurities is compensated locally by nearest-neighbor (NN) or next-nearest-neighbor (NNN) interstitial fluoride ions; in this way NN or NNN dipoles are produced. The existence of these complexes has been established by means of various techniques.[4−6] In some solid solutions, particularly the CaF_2-based ones, clustering has been observed even for relatively low R^{3+} concentrations.[7−9] It appears that in the clustering process the formation of 2:2:2 complexes and 4:3:2 clusters is important.[10−15] Another group

of clusters has been introduced by Figueroa et al.[16] These authors have suggested that one trivalent impurity ion may form aggregates with two interstitial fluoride ions, giving rise to linear or L-shaped clusters. Consequently, there should be also cubic R^{3+} ions in order to maintain electroneutrality. Indeed EPR experiments carried out by Brown et al.[17] have shown that in $Sr_{1-x}Er_xF_{2+x}$ cubic erbium ions are present.
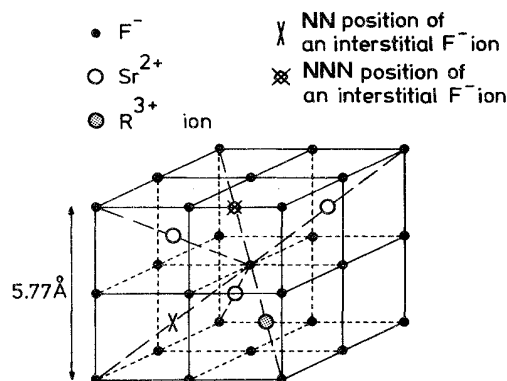

FIG. 1. Three-dimensional schematic representation of the fluorite-type lattice structure of SrF_2 containing an NN and an NNN dipole consisting of an R^{3+} impurity and an interstitial F^- ion.

Another group of solid solutions, however, does not show clustering at an extensive scale. Typical examples of this group are $Sr_{1-x}La_xF_{2+x}$ and $Ba_{1-x}La_xF_{2+x}$; these materials have been investigated in detail by Meuldijk and den Hartog,[18] den Hartog and Langevoort,[2] and den Hartog, Pen, and Meuldijk.[19] In the materials of this group the predominant defects are dipolar complexes consisting of an R^{3+} impurity and a nearby interstitial fluoride ion (NN or NNN dipoles). The results obtained until now suggest that the tendency towards clustering depends strongly upon the relative sizes of the host and impurity ions.

In this paper we present new results on solid solutions $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$. The impurity ions are elements of the second part of the series of lanthanide ions. These ions are smaller than the ones of the first part of this series (i.e., La, Ce, Pr, and Nd). It will be shown that the results of the dielectric experiments carried out in this investigation deviate very strongly from those obtained earlier for the solid solutions $Sr_{1-x}La_xF_{2+x}$, $Sr_{1-x}Nd_xF_{2+x}$, and $Ba_{1-x}La_xF_{2+x}$.[18,3,2] Whereas in the latter materials the ionic thermocurrent (ITC) peak associated with space-charge relaxation processes could be analyzed in terms of the percolation conduction proposed by den Hartog and Langevoort,[2] the materials studied in this paper need an approach where clustering plays an important role. This result is in agreement with spectroscopic data of Brown et al.[17] for solid solutions $Sr_{1-x}Er_xF_{2+x}$. Brown et al. have concluded from their results that solid solutions $Sr_{1-x}R_xF_{2+x}$ containing the ions of the final part of the series of lanthanides are different from those containing ions of the first part of that series (e.g., Ce^{3+}). The results of the ITC and dielectric loss experiments presented in this paper lead us to the conclusion that the solid solutions $Sr_{1-x}R_xF_{2+x}$ have a defect structure, which depends upon the choice of the R^{3+} ion. The small-sized R^{3+} impurities give rise to clusters, while the large ones will form predominantly dipolar defects.

From earlier results of ITC experiments, where clustering does not play an important role (Refs. 2, 3, and 15), we have seen that the space-charge relaxation band [high-temperature (HT) band] shifts gradually to lower temperatures with increasing R^{3+} concentrations, until the position approximately coincides with one of the dipole relaxation bands (very often the NNN dipole peak). In contrast with this we observe for the materials studied in this paper that for moderate concentrations $(0.01 < x < 0.07)$ the position of the HT band shifts to higher temperatures *with increasing* R^{3+} *concentrations*. At very high concentrations $x > 0.10$ the value of T_{max} of this peak decreases again, but this decrease is far less drastic than in the materials mentioned above. For very large Dy^{3+} and Er^{3+} concentrations the value of T_{max} is approximately 280 and 300 K, respectively, which should be compared with the corresponding values between 150 and 190 K observed for $Sr_{1-x}La_xF_{2+x}$, $Sr_{1-x}Ce_xF_{2+x}$, and $Sr_{1-x}Nd_xF_{2+x}$.[18,20,3] The observed behavior of the position of the space-charge relaxation peak as a function of the Dy^{3+} or the Er^{3+} concentration will be discussed and it will be shown that both the peculiar behavior of T_{max} in the concentration

range $0.01 < x < 0.07$ and the large values for T_{max} for very heavily doped materials are due to the presence of clusters in the materials studied in this paper.

II. EXPERIMENTAL PROCEDURES

The experimental setup and procedures for the growth of the single-crystal materials have been described elsewhere.[2,3] The cryostat which has been used to carry out the ITC experiments has been discussed in detail by Lenting et al.[21] For the ITC experiments the samples (cylindrical disks with a diameter of 8 mm and thickness of about 2 mm) were polarized by means of a high voltage of about 4 kV. The polarization temperature was chosen well above the temperature T_{max}, which is the temperature for which the space-charge relaxation peak has its maximum depolarization current. The polarization time was always 5 min.

The depolarization currents were detected with a Cary 401 vibrating Reed electrometer. The complete setup is computer controlled. During the depolarization phase the temperature is increased linearly with time (0.05 K/s). The data consisting of values for the temperature and the depolarization current are collected at constant time intervals by a Hewlett-Packard HP-9835B desk-top computer (see also Ref. 20). With this computer the data are manipulated in such a way that they can be analyzed by our curve-fitting programs which are run by a Control Data Corporation Cyber-170/760 computer.

The dielectric loss experiments were carried out using a General Radio capacitance bridge (type 1615-A). The signals were detected with a Princeton Applied Research lock-in amplifier (type 128). The frequency of the ac signals could be adjusted at one of the following values: 100, 300, 1000, 3000, 10 000, or 30 000 Hz. For these measurements we employed a cryostat which is quite similar to the one used for the ITC experiments. Between the crystal and the electrodes we have inserted a thin foil of Teflon (0.1-mm thick).

The concentrations of the trivalent impurities have been determined with the x-ray fluorescence method. Below 1 mol % this method does not work because the sensitivity is too low. Therefore, we have employed here the nominal concentrations.

III. EXPERIMENTAL RESULTS

The results of the ITC and dielectric loss experiments of the solid solutions $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$ will be given in two separate sections. This will be done in order to show more clearly the differences between the two systems.

A. $Sr_{1-x}Er_xF_{2+x}$

The ITC curves observed for the systems $Sr_{1-x}Er_xF_{2+x}$ consist of two depolarization peaks (see curve *a* of Fig. 2). The first one is located at about 215 K; it does not shift as a function of the ErF_3 concentration. The only variation of this peak is shown by the intensity. At low concentrations the intensity of the peak increases with the ErF_3 concentration. For concentrations $x > 0.006$ the intensity
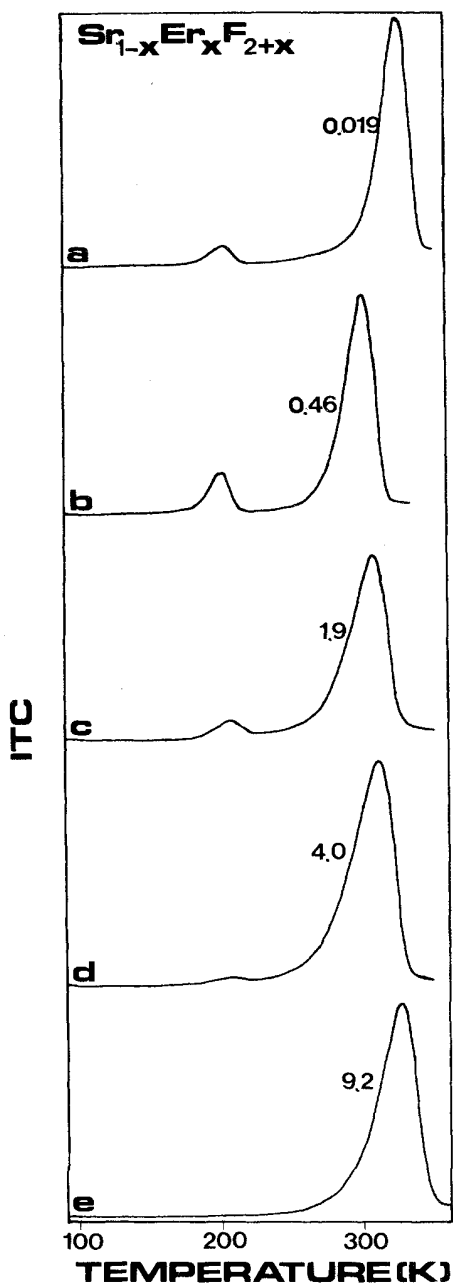
FIG. 2. Survey of the ITC "spectra" observed for various different $Sr_{1-x}Er_xF_{2+x}$ crystals. Different ITC curves a, b, c, d, and e are taken from samples containing 0.019, 0.46, 1.9, 4.0, and 9.2 mol % ErF_3, respectively.

of the peak at 215 K decreases with increasing concentration (see Fig. 3).

The second peak in the ITC "spectrum" shows a completely different behavior. Firstly, the intensity of the peak does not vary significantly as a function of the concentration. Secondly, the position of the depolarization band varies drastically with the concentration. From this behavior we see that the bands must be associated with
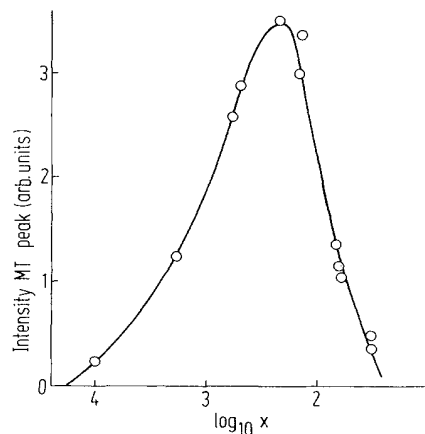

FIG. 3. Behavior of the intensity of the NNN dipole peak intensity as a function of the ErF_3 concentration.

two fundamentally different depolarization processes. The low-temperature peak is ascribed to the reorientation of permanent (NNN) Er^{3+}-F_i^- dipoles; this defect turns out to be the dominant one in $Sr_{1-x}Er_xF_{2+x}$ for small values of x ($x \leq 10^{-4}$). The peak at high temperatures ($300 \leq T \leq 340K$) has been associated with the development of space charges opposite to the electrodes. This implies that basically the HT peak provides us with information concerning the ionic conductivity processes in the solid solutions.

In Fig. 2 we show a survey of the various ITC results obtained for some different solid solutions of the type $Sr_{1-x}Er_xF_{2+x}$. From this figure we see that the position of the NNN dipole peak, if present, is the same for all crystals. On the other hand, we see the variations of the position of the HT band; starting at low ErF_3 concentrations we observe that the space-charge relaxation (or HT) band shifts toward lower temperatures with increasing ErF_3 concentrations. At about 1 mol % a minimum value for T_{max} is reached; for $x < 10^{-2}$ T_{max} increases with increasing values of x until at $x = 10^{-1}$ a maximum is reached. For $x > 10^{-1}$ the value of T_{max} decreases with increasing ErF_3 concentrations.

In Fig. 4 we show the behavior of T_{max} of the space-charge-relaxation peak as a function of the ErF_3 concen-
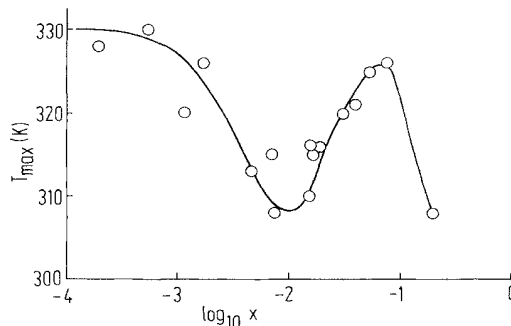

FIG. 4. Behavior of the position of the space-charge-relaxation (HT) peak as a function of the concentration of the Er^{3+} ions.

tration. This behavior appears to be quite similar to that observed for the system $Sr_{1-x}Yb_xF_{2+x}$, which has been investigated recently in our laboratory.[22] A detailed comparison of the results obtained for the systems $Sr_{1-x}Er_xF_{2+x}$ and $Sr_{1-x}Yb_xF_{2+x}$ shows that the fluctuations of T_{max} as a function of the RF_3 concentration are smaller for the solid solutions $Sr_{1-x}Er_xF_{2+x}$ than for $Sr_{1-x}Yb_xF_{2+x}$.

Another parameter of the HT band which shows interesting variations as a function of the RF_3 concentration is the linewidth at half-height ($\Delta T_{1/2}$). The results for the series of solid solutions $Sr_{1-x}Er_xF_{2+x}$ have been presented in Fig. 5. For a concentration of about 3 mol % the linewidth reaches a maximum value; for higher concentrations the linewidth decreases slightly. Also this behavior is quite similar to that observed for $Sr_{1-x}Yb_xF_{2+x}$.[22] In both types of solid solution the width of the ITC peak observed for large values of x is significantly larger than the one found for very low values of x (i.e., $x < 10^{-3}$). This result is in contrast with the observations for the systems $Sr_{1-x}Nd_xF_{2+x}$ (Ref. 3); in the latter case the linewidth for large values of x is well below the one observed for samples with $x < 10^{-3}$. For completeness we have compiled the observed parameters of the HT band in Table I.

In order to obtain more information about the dipole-reorientation processes we have measured the behavior of the dielectric loss and the capacitance of various $Sr_{1-x}Er_xF_{2+x}$ samples as a function of the temperature. These experiments have been carried out at frequencies of 100, 300, 1000, 3000, 10000, and 30000 Hz. In Fig. 6 we show the loss results for a sample containing 0.019 mol % ErF_3. It shows a clear peak at about 325 K. The position of the peak does not shift significantly with the ErF_3 concentration. From a series of experiments employing the different frequencies available we are able to determine the activation energy. In Table II we have compiled the results for some different solid solutions. The value of the activation energy E_a obtained for the sample with a high ErF_3 concentration is slightly smaller than the other ones. This is probably due to the increasing background losses associated with conduction phenomena (space-charge relaxation).
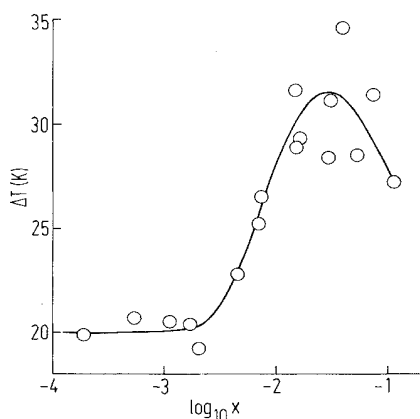
TABLE I. Experimental parameters of the HT band in $Sr_{1-x}Er_xF_{2+x}$.

x (mol %)	T_{max} (K)	$\Delta T_{1/2}$ (K)
0.02	328	20.0
0.05	330	20.7
0.11	320	20.5
0.17	326	20.4
0.20	324	19.2
0.46	313	22.8
0.68	315	25.2
0.72	308	26.5
1.5	316	28.9
1.5	310	31.6
1.6	315	29.3
2.9	328	30.4
2.9	320	28.4
3.1	314	31.4
3.9	321	33.6
5.2	325	28.5
7.5	326	31.4
11.2	324	27.2
19.3	308	27.2

B. $Sr_{1-x}Dy_xF_{2+x}$

In solid solutions consisting of SrF_2 and DyF_3 we find the relaxation peaks of two different dipoles; the NN or tetragonal dipoles and the NNN or trigonal dipoles (see curve a of Fig. 7). This observation is in agreement with earlier observations reported by Lenting et al.[21] and Van Weperen and den Hartog.[23] The NNN dipole is at very low concentrations the dominant defect; NN dipoles are present in relatively small concentrations. A typical example of the ITC curves observed at low DyF_3 concentrations has been shown in curve a of Fig. 7. In addition to the two dipole reorientation peaks we observe the space-charge-relaxation (HT) band.

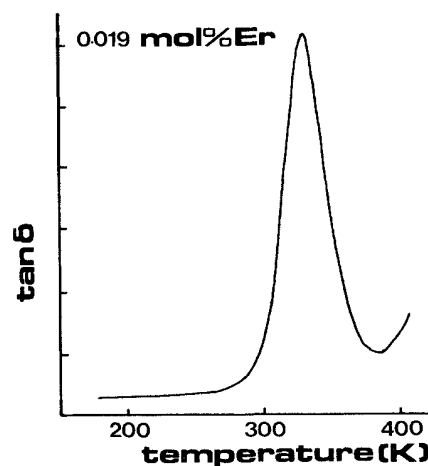FIG. 5. Behavior of the width of the space-charge-relaxation (HT) peak as a function of the ErF_3 concentration.

FIG. 6. Dielectric loss of an SrF_2 crystal doped with 0.019 mol % ErF_3 as a function of the measuring temperature. Excitation frequency in this experiment is 1000 Hz.

TABLE II. Relaxation parameters of some solid solutions of the type $Sr_{1-x}Er_xF_{2+x}$.

x (mol %)	E_a (eV)	τ_0 (10^{-15} sec)
0.02	0.70±0.02	3.1
0.46	0.71±0.01	8.4
1.6	0.70±0.01	2.3
1.9	0.70±0.01	5.7
3.1	0.68±0.01	9.4

In Fig. 7 we present a collection of ITC curves for samples with different amounts of DyF_3. Although the ITC curves observed for the system $Sr_{1-x}Dy_xF_{2+x}$ deviate from those observed for $Sr_{1-x}Er_xF_{2+x}$, we have found that the behavior of the peak, associated with the reorientation of NNN dipoles, is quite similar to the NNN peak

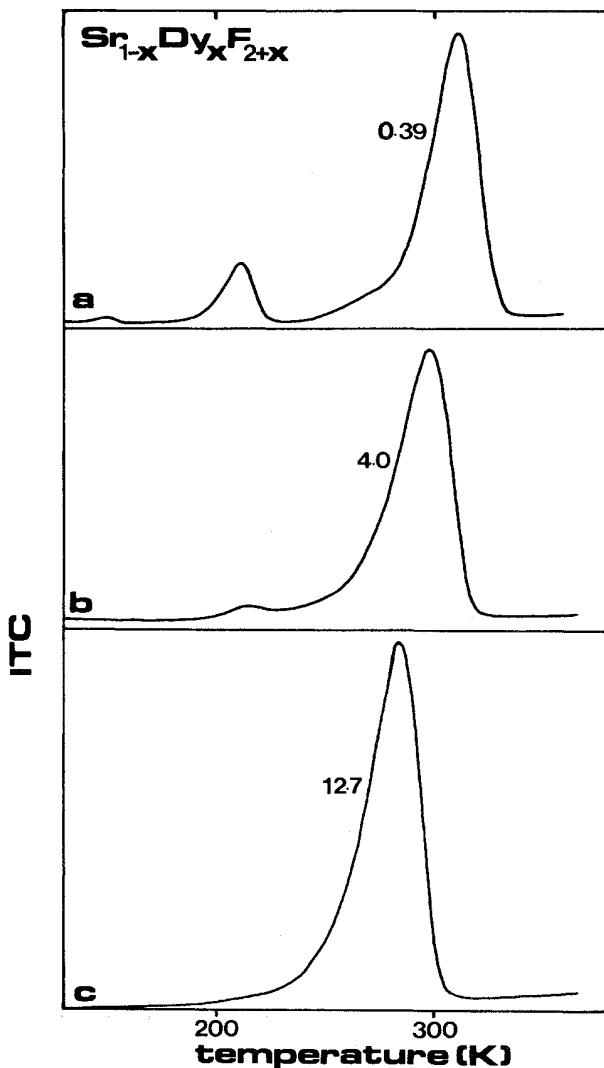FIG. 7. Survey of the ITC results obtained for some different $Sr_{1-x}Dy_xF_{2+x}$ crystals. Curves a, b, and c are taken from samples with 0.39, 4.0, and 12.7 mol % DyF_3, respectively.

in $Sr_{1-x}Er_xF_{2+x}$. At low concentrations the maximum intensity of the NNN dipole peak is reached for $x = 10^{-2}$, which should be compared with the value of $x = 5-6 \times 10^{-3}$ for the solid solutions $Sr_{1-x}Er_xF_{2+x}$.

Also the position of the HT band has been considered in some detail. In Fig. 8 we show the observed behavior of T_{max} vs $\log_{10}x$. We observe that the plot presented here is not very much different from the one given in Fig. 4. The fluctuations of T_{max} as a function of the concentration are smaller than in the system $Sr_{1-x}Er_xF_{2+x}$. For $Sr_{1-x}Dy_xF_{1+x}$ the value of T_{max} decreases in the low-concentration range. For $x \simeq 5 \times 10^{-3}$ T_{max} reaches a local minimum; for $5 \times 10^{-3} \leq x \leq 1.4 \times 10^{-2}$ T_{max} decreases with increasing values of x. It is interesting to note here that the solid solutions of the type $Sr_{1-x}Dy_xF_{2+x}$ show a value of $T_{max} - 285$ K for $x \simeq 0.30$, whereas the corresponding value of T_{max} of the system $Sr_{1-x}Er_xF_{2+x}$ is equal to about 308 K. Another interesting observation one can make is that the slight fluctuations of the plot T_{max} vs $\log_{10}x$ occur just when the concentration of NNN dipoles reaches its maximum value. A similar observation can be made for the systems $Sr_{1-x}Er_xF_{2+x}$ (see Figs. 3 and 4) and $Sr_{1-x}Yb_xF_{2+x}$.[19]

The width of the HT band in $Sr_{1-x}Dy_xF_{2+x}$ behaves similarly to that of the system $Sr_{1-x}Er_xF_{2+x}$ (see Fig. 9). In the low-concentration range the width at half-height is approximately constant. For $x > 10^{-3}$ the width starts to rise with x until a maximum is reached for $x \simeq 3 \times 10^{-2}$; for $x > 3 \times 10^{-2}$ the width decreases with increasing values of x. Just as for $Sr_{1-x}Er_xF_{2+x}$ we observe for the system $Sr_{1-x}Dy_xF_{2+x}$ that for the highest concentrations the half-width has a value larger than the one for samples with small values of x. In Table III we have given the relevant parameters of the HT band in the solid solutions $Sr_{1-x}Dy_xF_{2+x}$.

For low concentrations we have carried out several dielectric loss experiments. A typical result for a crystal doped with 0.03 mol % DyF_3 has been presented in Fig. 10. We observe that for an excitation frequency of 1000
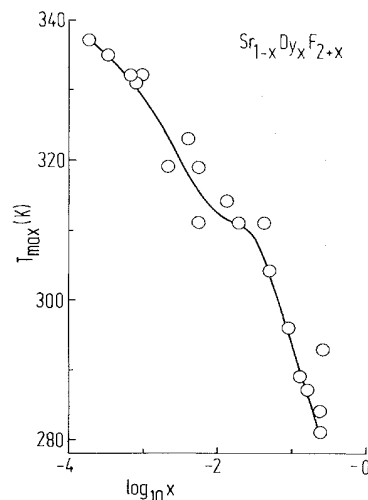

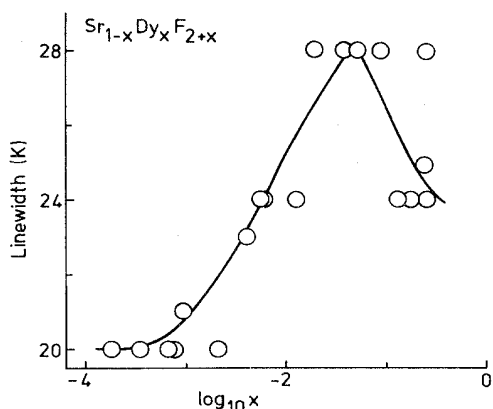FIG. 8. Behavior of the position of the space-charge-relaxation (HT) peak as a function of the DyF_3 concentration.

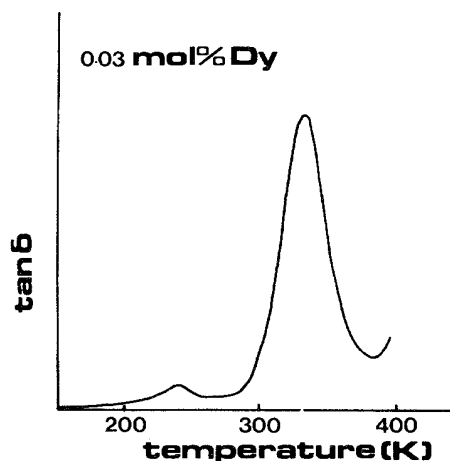FIG. 9. Behavior of the width of the space-charge-relaxation (HT) peak as a function of the DyF_3 concentration.

FIG. 10. Dielectric loss of an SrF_2 crystal doped with 0.03 mol % DyF_3 as a function of the measuring temperature. Excitation frequency in this experiment is 1000 Hz.

Hz there are two dipole peaks which are located at 231 and 329 K. In Table IV we present the results obtained for the characteristic relaxation parameters of the two samples; the first one contains 0.03 mol % and the second one 0.55 mol % DyF_3.

IV. DISCUSSION

We have shown that the ITC results obtained for the solid solutions $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$ are in remarkable contrast with those found for the mixed crystals containing the first elements of the series of lanthanides (i.e., La, Ce, Pr, and Nd). In earlier papers on ITC experiments of slightly doped $Sr_{1-x}R_xF_{2+x}$ crystals we have found that the heavy R ions in the SrF_2 lattice give rise to NNN complexes, whereas the light ones produce predominantly NN dipoles. Obviously, the differ-

TABLE III. Experimental parameters of the HT band in $Sr_{1-x}Dy_xF_{2+x}$.

x (mol %)	T_{max} (K)	$\Delta T_{1/2}$ (K)
0.018	337	20
0.033	335	20
0.066	332	20
0.075	331	20
0.094	332	21
0.21	319	20
0.39	323	23
0.54	311	24
0.55	319	24
1.3	314	24
1.9	311	28
4.0	311	28
4.8	304	28
8.6	296	28
12.7	289	24
15.8	287	24
22.9	281	25
22.9	284	24
24.8	293	28

ence between the ionic radii of the host-lattice Sr^{2+} ion and the impurity ion (R^{3+}) is a very important parameter, one which determines the defect structure of the solid solutions.

We emphasize, however, that although the differences between the solid solutions seem to be quite significant, the differences between the energies of formation of NN and NNN dipoles are in some cases quite small. Aalbers and den Hartog[24] have found that the energy difference of NN and NNN dipoles in $Sr_{1-x}Gd_xF_{2+x}$ is only a few hundredths of an eV. From experiments on the other solid solutions of the type $Sr_{1-x}R_xF_{2+x}$ we have concluded that although there are differences between the various solid solutions, the energy gap between NN and NNN dipoles is of the same order of magnitude.[18]

The solid solutions containing Dy^{3+} ions show, as we have seen from our experimental results, both NN and NNN dipoles. This indicates that just as we have found for $Sr_{1-x}Gd_xF_{2+x}$ (see Ref. 24), the energy difference between these dipole configurations is quite small also. Although we have not investigated the ratios of NN and NNN dipole concentrations in great detail, we have observed clear variations of this ratio as a function of the concentration of Dy^{3+} ions. These variations have been discussed earlier by Aalbers and den Hartog.[24] They are due to dipole-dipole interactions; these interactions are found to modify the Boltzmann distribution even at moderate impurity concentrations.

The dielectric loss results for the system $Sr_{1-x}Dy_xF_{2+x}$ show a behavior which is in line with the ITC results. Here too, we find variations of the concentration ratios of the NN and NNN dipoles. In addition, we have observed variations of the concentration ratio as a function of the excitation frequency. We can understand these variations if we realize that with increasing frequency the loss peaks shift to higher temperatures. Therefore, the concentration ratios are determined at temperatures which increase with the excitation frequency.

TABLE IV. Relaxation parameters of some solid solutions of the type $Sr_{1-x}Dy_xF_{2+x}$.

x (mol%)	NN dipoles		NNN dipoles	
	E_a (eV)	τ_0 (10^{13} sec)	E_a (eV)	τ_0 (10^{-15} sec)
0.03	0.42 ±0.04	1.3	0.687±0.010	5.1
0.55	0.435±0.010	0.9	0.668±0.010	1.3

It appears that, with regard to clustering in $Sr_{1-x}R_xF_{2+x}$ solid solutions, slight differences in the R^{3+} radius are of decisive importance. In a recent paper we have concluded that even for very large values of the La concentrations in the system $Sr_{1-x}La_xF_{2+x}$, clustering is of minor importance.[18] On the other hand, we have found evidence for clustering in solid solutions $Sr_{1-x}Yb_xF_{2+x}$ (Ref. 22), i.e., in the final part of the series of lanthanides. This would suggest that also clustering depends upon the difference between the ionic radii of the host Sr^{2+} and the trivalent impurity ion R^{3+}.

The solid solutions studied in this paper are expected to behave rather similar to the system $Sr_{1-x}Yb_xF_{2+x}$ because the Er and Dy ions are both elements of the final part of the series of lanthanides. In addition, we note that a long time ago Brown et al.[17,25] found decisive evidence for the existence of four different Er^{3+} sites, which suggests that clustering in the system $Sr_{1-x}Er_xF_{2+x}$ occurs. From EPR experiments Brown et al. found that with increasing ErF_3 concentrations the relative concentration of cubic Er^{3+} increases. This is probably due to scavenging effects of clusters on the interstitial fluoride ions.

In more recent papers by Tallant and co-workers[7,8] and Moore and Wright[13] these authors have shown by means of extensive high-resolution optical spectroscopy on solid solutions of the type $Ca_{1-x}Er_xF_{2+x}$ that also in these materials clustering occurs already at relatively low concentrations. These authors were able to assign many lines of the complex emission spectra to particular Er^{3+} sites.

In the present work we have observed that the concentration of Er^{3+}-F_i^- dipoles (NNN dipoles) reach a maximum value for a total Er^{3+} concentration of 0.6 at%. In an earlier paper we have found the corresponding figure for $Sr_{1-x}Yb_xF_{2+x}$ to be approximately 0.4 at%. For $Sr_{1-x}Dy_xF_{2+x}$ crystals we find that the concentration of NNN dipoles has a maximum value for $x \sim 0.01$. It appears that the maximum dipole concentration is found at compositions which show a decreasing RF_3 concentration with increasing atomic weight of the lanthanide. This leads us to the tentative conclusion that the tendency to form clusters increases on going to rare-earth ions with increasing atomic weight (or decreasing R^{3+} radius).

The analysis of the dipole peaks in the ITC spectra and the dielectric loss results obtained for the different excitation frequencies are in reasonable agreement. The values for the activation energies E_a and the characteristic relaxation times τ_0 are found to be approximately constant in a wide range of concentrations (see also Tables II and IV). Although in the concentration range investigated the broadening of the ITC and loss peaks is found to modify

the relaxation parameters, and although we have taken this broadening into account in our analysis we do not present the broadening results here because they show (as can be expected in this case of clustering) a complicated behavior as a function of the concentration. In addition, the accuracy of the calculated broadening parameters is not sufficient to draw sound conclusions.

We shall now go into some detail describing the processes of polarization and ionic conductivity which must be employed to understand the ITC data presented in this paper. Especially, for large values of the R^{3+} concentration the types of defects present in the material determine to a very large extent the ionic conductivity processes. In recent investigations carried out in our laboratory we have found that in solid solutions containing trivalent ions of the first part of the series of lanthanides the conduction process is governed by dipolar defects, even for very large values of the R^{3+} concentration.[3,18,20] It is possible to describe this conduction process by means of the relatively simple model, which has been employed by den Hartog and Langevoort for the solid solutions $Ba_{1-x}La_xF_{2+x}$.[2] This model is based upon the idea of percolation conduction of a material consisting of two phases: (a) an insulating host, and (b) a phase which shows a high conductivity. The high-conductivity material is in fact a dipole system with a rapidly jumping F^- interstitial, which is connected with a substitutional trivalent impurity. The insulating material is the BaF_2 crystal containing free interstitial F^- ions.

In the materials under consideration, clustering, occurring at relatively low impurity concentrations, will modify the conduction properties considerably; in accordance with this it will also modify the ITC results. The number of dipoles, which control the percolation conduction, decreases. On the other hand, clusters are formed. These clusters may be of different types. Different authors have proposed models for the cluster centers.[10-15] An important one is the 2:2:2 cluster, which consists of two dipoles.[10] Another one is the 4:3:2 cluster. Both clusters have been investigated theoretically by Catlow.[10] A second class of centers, which are assumed to exist in concentrated solid solutions is that of the linear and L-shaped clusters, consisting of one R^{3+} impurity and two interstitial fluoride ions. We note that in the latter cases there should also be cubic trivalent impurities, because electroneutrality should be maintained. Brown et al.[17] have observed this phenomenon; with increasing ErF_3 concentration in SrF_2 crystals the number of cubic Er^{3+} ions increases, indicating that probably clusters, containing at least one extra interstitial fluoride ion, are found.

We know that in crystals of the type $Sr_{1-x}R_xF_{2+x}$, the interstitial fluoride ion is the mobile entity. Therefore, this point defect will also play an important role in the polarization associated with space-charge clouds. From the experimental results of Brown et al.[17] on $Sr_{1-x}Er_xF_{2+x}$ we can conclude that there are defects in the crystal which form stronger bonds with the interstitial fluoride ion than the "bare" R^{3+} ion at a substitutional lattice site. If the new defects are linear or L-shaped clusters we conclude that the simple dipole systems are effective traps for free interstitials. On the other hand, the NNN dipoles easily lose the interstitial fluoride ion. In this case the extra F^- ion present in the linear or L-shaped cluster causes relaxations of the ions in the immediate neighborhood of the defect, leading to a decrease in the energy. If the interstitials are bound more strongly to the linear and L-shaped clusters we expect the ITC peak associated with space-charge formation to shift to higher temperatures (as compared with a system containing NNN dipoles), because at moderate R^{3+} concentrations the position of this band is determined by the jump energy of free interstitials and the energy necessary to dissociate an interstitial fluoride ion from the complexes to which they are bound. In the case that NNN dipoles are the dominant defects the dissociation energy will be relatively low. If linear or L-shaped clusters are present with the properties mentioned above, the dissociation energy will be higher and consequently the space-charge-relaxation band will shift to higher temperatures. The presence of significant amounts of cubic R^{3+} ions cannot reverse this trend because the dissociation of the interstitials from the complexes determines the value of the conductivity.

A comparison of the results obtained for the different solid solutions $Sr_{1-x}R_xF_{2+x}$ shows that for the first part of the series of lanthanides the value of T_{max} (for small values of x) is approximately 360 K. In this paper we find for samples doped with DyF_3 and ErF_3 a corresponding value for the space-charge-relaxation peak, which is equal to about 330 K. A similar result has been found earlier[22] for solid solutions $Sr_{1-x}Yb_xF_{2+x}$. These results clearly show that in the temperature range in which the experiments are carried out the conductivity depends upon the type of dipole present. In samples where the NN dipoles are the dominant defect the HT band is found at 360 K, whereas in the materials which contain large numbers of NNN dipoles the space-charge-relaxation band is located at 330 K. In order to contribute to the ionic conductivity, the interstitial fluoride ions should dissociate from the dipolar defects. After dissociation these interstitial fluoride ions can jump from one interstitial position to another one. From this we conclude that the space-charge-relaxation process and the conductivity mechanism are governed by a dissociation energy E_{diss} and a jump energy E_a, which is equal to 0.94 eV.[26] The different values of T_{max} in the low-concentration range are due to the difference in E_{diss}; we conclude that the dissociation energy of NNN dipoles is smaller than the corresponding value for NN dipoles.

We note that experimentally we have indeed observed an increase in the value of T_{max} for ErF_3 concentrations higher than 1 mol %. T_{max} reaches a maximum value for approximately 7 mol % and decreases for concentrations higher than this value. If the interstitial fluoride ions in the clusters are mobile, i.e., if the external electric field induces them to move into a preferred direction, the clusters can contribute to the space-charge-relaxation process. The mechanism is quite similar to the percolation process proposed by den Hartog and Langevoort.[2] Because we are dealing with clusters the percolation concentration (expressed in mol % ErF_3) will be larger than for the system $Ba_{1-x}La_xF_{2+x}$, where simple NNN dipoles are involved. Thus also for the system $Sr_{1-x}Er_xF_{2+x}$ one expects that in the range of very high ErF_3 concentrations the value of T_{max} of the space-charge peak to decrease with increasing values of x. This decrease is due to the relatively easy jumps of the interstitial fluoride ions in the neighborhood of the clusters.

Until now we did not consider the possibility of the existence of the so-called 2:2:2 or the 4:3:2 clusters as suggested by Catlow.[10] The formation of these clusters will increase the average distance between the defects. As a result the percolation threshold is situated at a higher concentration. In addition, it should be noted that in the literature various models have been suggested of clusters with excess interstitial fluoride ions. This means that defects consisting of two or more dipolar complexes may trap an additional interstitial fluoride ion. It is clear that these models lead to a description of the conductivity and ITC results, which resembles very much the one given above using linear and L-shaped clusters. In particular, these clusters could also lead to the presence of cubic R^{3+} ions. This shows that we are not able on the basis of the present knowledge of these solid solutions to choose a specific model of clustering. From the observed differences between the solid solutions containing ions of the first or the final part of the series of lanthanides we may conclude however that in the materials under investigation in this paper clustering plays a decisive role for moderate R^{3+} concentrations.

From Figs. 4 and 8 we see that the behavior of T_{max} as a function of x is a peculiar one, especially if we compare our observations with those of the solid solutions $Ba_{1-x}La_xF_{2+x}$ and $Sr_{1-x}La_xF_{2+x}$ (Refs. 2 and 18). Also the behavior of the linewidth of the HT peak can be used to obtain additional information concerning the depolarization processes. There is a difference between the present results and those obtained for the solid solutions $Sr_{1-x}La_xF_{2+x}$ and $Sr_{1-x}Nd_xF_{2+x}$ (see Refs. 3 and 18). The minimum value of $\Delta T_{1/2}$ obtained for large values of x is still relatively large as compared with the corresponding $\Delta T_{1/2}$ values for the solid solutions $Sr_{1-x}La_xF_{2+x}$ and $Sr_{1-x}Nd_xF_{2+z}$ (see Refs. 3 and 18). In the latter cases the width of the HT band at very high concentrations is approximately equal to the values of the dipole peak, which is located at about the same position. As discussed in earlier papers (see Refs. 2, 3, and 18) this result suggests that the conduction mechanism for large values of x is governed by dipolar jumps. The results obtained for the solid solutions studied in this paper show that for the systems $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$ the situation is completely different, especially for large values of x. First, the value of T_{max} of the HT band does not tend

to the one of the NNN dipole peak. This strongly suggests that the conduction mechanism in the materials under consideration is more complicated than in the materials investigated earlier (see Refs. 2, 3, and 18); from the discussion given in the preceding part of this section we conclude that this more complicated behavior is related with the clustering processes.

We have already noted that for the polarization properties of the space-charge clouds the jumps of interstitial fluoride ions are very important. The nature of these jumps has been found to vary as a function of the concentration of trivalent ions. If there is one dominant cluster configuration present in heavily doped materials we can employ a model like the percolation model used for $Ba_{1-x}La_xF_{2+x}$. Consequently, the position of the HT band is determined by the jumps of the interstitial fluoride ions in the cluster. The important parameters are the jump activation energy E_c and the characteristic relaxation time τ_0^c of the cluster. From the position of the HT band at very high Dy or Er concentrations we conclude that the jump activation energy is significantly larger than the corresponding values for NN or NNN dipoles. Also the halfwidth of the HT band can be explained with a relatively large value of the jump energy.

On the other hand, we note that it is possible that more than one type of cluster exists in the heavily doped materials. If these clusters contribute to the relaxation processes as described above, it is rather difficult to interpret the ITC results. The relaxation time associated with space-charge formation consists of different contributions showing different temperature dependences. Assuming that here too a percolation-type conduction process is operative and that the different clusters contribute to the ionic conductivity, the behavior of T_{max} and $\Delta T_{1/2}$ as a function of x may be quite complicated because the ratio of the concentration of the different clusters will probably vary as a function of the R^{3+} concentration. If more than one cluster contributes to the space-charge-relaxation process the ITC peak will be broadened as compared with a simple percolation mechanism. The peak position as observed in our samples provides us with information about the activation energy of the jumps in the clusters. If these activation energies have relatively large values, the temperature T_{max} is also expected to have a large value. From the detailed shape of the HT band at high DyF_3 and ErF_3 concentrations we prefer the model with only one type of cluster contributing to the conductivity process.

ACKNOWLEDGMENTS

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