Charge transport in Sr1-xLaxF2+x solid solutions : an ionic thermocurrent study

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Charge transport in $Sr_{1-x}La_xF_{2+x}$ solid solutions. An ionic thermocurrent study

J. Meuldijk and H. W. den Hartog

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

A comprehensive study of the relaxation of space charges in solid solutions of the type $Sr_{1-x}La_xF_{2+x}$ will be reported. In this investigation we have employed the ionic thermocurrent technique. LaF_3 concentrations between 0.01 and 42 mol % have been used. We have paid attention to the resemblance between space-charge relaxation and ionic conductivity in heavily rare-earth-doped fluorite-type solid solutions. We will show that the enhancement of the conductivity and the shift of the space-charge relaxation band to lower temperatures with increasing rare-earth concentration can be explained with the same mechanism. Charge transport is supported by two kinds of interstitial jumps: free interstitial jumps occurring relatively far from a rare-earth ion and energetically more favorable dipolelike jumps of interstitial fluoride ions in the neighborhood of a rare-earth ion. We will also discuss the influence of the defect concentration on the degree of dissociation of the dipoles present and the effect of the concentration on the defect structure of the $Sr_{1-x}La_xF_{2+x}$ solid solutions. It will be made clear that the charge transport in rare-earth-doped fluorite-type ionic crystals is supported by a percolation mechanism.

INTRODUCTION

In the last few decades a lot of experimental work has been performed on the elucidation of the charge transport in solid electrolytes.[1] Well-known solid electrolytes are alkaline-earth halides of the type MX_2 with the fluorite structure.[2] If these compounds are doped with metal-ion halides of the type RX_3, the trivalent ion R^{3+} will occupy an M^{2+} lattice site, whereas the excess positive charge is compensated by an interstitial X^- ion. Local charge compensation results in two kinds of electric dipoles: nearest-neighbor (NN) and next-nearest-neighbor (NNN) dipoles. NN and NNN dipoles have tetragonal (C_{4v}) and trigonal (C_{3v}) symmetry, respectively, as determined by electron-spin resonance (ESR).[3–5] If the charge-compensating interstitial ion has a larger distance from the R^{3+} ion than in NNN dipoles we have nonlocal charge compensation. In this case the R^{3+} ion has cubic (O_h) symmetry.[4] Also, defect clusters may appear in some cases; the symmetry of these centers is lower than trigonal. Static properties of dipole complexes have been studied with ESR, electron-nuclear double resonance (ENDOR), and the electric field effect in ESR (Refs. 6—9); dynamic properties have been studied with the ionic thermocurrent (ITC) and dielectric loss technique.[10–18] With ITC the reorientation of NN and NNN dipoles has been investigated extensively.[10–14] Also, the interactions with other defects in the neighborhood of the reorienting dipole have been taken into account.[13–15] The temperature at which the depolarization current reaches its maximum value is independent of the defect concentration. Besides the NN and NNN dipole relaxation peaks another, very intense, depolarization peak exists in the ITC spectra. The position of its maximum and the width at half-height are strongly concentration dependent. Contrary to Laredo et al.,[19] who have assigned this band to phenomena connected with dislocation lines, den Hartog and Langevoort[20] have given an explanation in terms of relaxation of space charges in solid solutions of LaF_3 and BaF_2. These space-charge clouds consist of either negatively charged interstitial fluoride ions or excess positive charges associated with the trivalent impurities, which are found opposite to the anode and cathode, respectively. The concentration dependence of the position of the space-charge relaxation band [which we will refer to as the high-temperature (HT) band] can be understood if we assume that the depolarization process is governed by a mechanism in which two types of jumps contribute: (a) jumps of free interstitial fluoride ions, and (b) jumps of interstitial fluoride ions associated with a dipolar complex. Both jumps have different activation energies and characteristic relaxation times τ_0. It is possible to describe the charge transport during the space-charge relaxation with a percolation mechanism as deduced by Kirkpatrick.[21] In $Ba_{1-x}La_xF_{2+x}$ the ratio C_{NNN}/C_{NN} is larger than one; therefore only NNN dipolelike jumps have to be taken into account. For NNN dipolelike jumps the calculated percolation threshold concentration has a value between 2 and 3 mol %.[20] Experimentally, the probability for an NNN dipolelike jump has been found to increase very quickly above 2–3 mol %.[20] Above these concentrations the contribution of the energetically more favorable dipolelike jumps to the charge transport process increases also very fast; for about 6 mol % LaF_3 only dipolelike jumps contribute to the charge transport. Wapenaar et al.[22] have studied the ionic conduction of the same solid solutions; LaF_3 concentrations were taken up to 45 mol %. In their explanation for the enhancement of the conductivity with increasing solute concentration they have proposed that the dissociation energy for the dipole present decreases and in addition the conductivity activation energy will be lowered because the point defects are screened by charge clouds consisting of oppositely charged point defects. The magnitude of these effects has been calculated by Lidiard,[23] who has applied Debye-Hückel

theory, developed for nonideal electrolyte solutions, to ionic solid solutions. The migration activation energy is broadened by defect-defect interactions as described by van Weperen et al.[13] This results in a decrease of the activation energy as deduced from conductivity experiments performed at different temperatures.[24] Also the role of defect clusters, which reduce the number of charge-carrying interstitial ions and influence their migration activation energy if they are in the neighborhood of such a cluster, has been taken into account. Recently, Meuldijk et al.[25] have performed an ionic thermocurrent study on $Sr_{1-x}Nd_xF_{2+x}$ solid solutions. In these materials local charge compensation of the excess positive charge on the Nd^{3+} ion occurs with interstitial fluoride ions in a NN position only. Samples with NdF_3 concentrations up to 45 mol % have been studied. For these materials shifts of the space-charge relaxation band (HT band) can also be explained with a percolation mechanism. Within this explanation the contribution of NN dipolelike jumps to the charge-transport process increases very fast above the percolation threshold concentration. For $Sr_{1-x}Nd_xF_{2+x}$ a value between 10 and 15 mol % has been observed for this concentration.

In this paper we present the ionic thermocurrent results of fluorite-type solid solutions of LaF_3 in SrF_2 with LaF_3 concentrations up to about 40 mol %. It appeared that the defect structure changes with increasing LaF_3 concentration. The HT band shifts downwards from about 370 K to about 190 K for the highest LaF_3 concentration which is between the position of the NN dipole relaxation band (about 155 K) and the position of the NN dipole relaxation band (about 219 K). The defect structure, the shift of the HT band as well as the position of the HT band at very high LaF_3 concentrations will be discussed. It appears that it is possible to describe the charge transport during the space-charge relaxation with a percolation mechanism. The space-charge relaxation phenomena will also be discussed in the light of ionic conduction experiments performed by other investigators.

EXPERIMENTAL PROCEDURE

The experimental setup and the procedure for the growth of single crystals has been described elsewhere.[20,25] The following chemicals have been used for the preparation of the crystals: SrF_2 (Merck, Suprapur 99.9% purity), LaF_3 (Ventron, 99.9% purity). $LuF_3 \cdot \frac{1}{2}H_2O$ has been prepared by dissolving Lu_2O_3 (Ventron, 99.999% purity) in a concentrated aqueous HCl solution (50 mol % excess HCl used). LuF_3 was precipitated by adding a concentrated HF solution (50 mol % excess HF). The precipitated LuF_3 has been separated from the remaining chemicals by means of a centrifuge and washed three times with distilled water. The precipitate has been dried in a furnace at 250 °C until a constant weight was reached. About 2 mol % PbF_2 (Koch-Light, 99.95% purity) was added in order to reduce the amount of O^{2-} or OH^- ions which are built in easily in the fluorite lattice.

Sample preparation, the ITC setup, and the measuring procedure has been described elsewhere.[20,25] The concentration of the La^{3+} ions in the samples have been determined with the x-ray fluorescence method as described in

a previous paper.[25] Below 1 mol % LaF_3 this method cannot be used because its sensitivity is too low. Below about 1 mol % weighted-in values have been taken to be the defect concentrations. Calculations were carried out with a Hewlett-Packard HP-9835B desktop computer.

RESULTS

Moving from low to high LaF_3 concentrations, the ITC spectra change considerably. The intensity of the NN dipole relaxation band [low-temperature (LT) band] positioned at about 155 K increases with increasing LaF_3 concentrations up to 1.5 mol %. For concentrations greater than 1.5 mol % its intensity decreases again. At about 219 K a small band appears. This band will be assigned to NNN dipole relaxations in accordance with the experimental results presented by Aalbers and den Hartog,[9] den Hartog,[26] and Wapenaar.[27] An alternative interpretation of the band at 219 K has been given by Figueroa et al.[28] These authors conclude on the basis of the results of annealing experiments and the behavior of the intensities of the reorientation peaks as a function of the concentration that the band at 219 K cannot be due to NNN dipoles. Instead, Figueroa et al. have proposed that this band is associated with L-shaped or linear clusters containing one La^{3+} impurity and two nearby interstitial fluoride ions. This would mean that apart from these clusters there are also trivalent ions located at cubic states. Unfortunately, there is no spectroscopic information about La^{3+} impurities in SrF_2 available. For the system $SrF_2:Ce^{3+}$ Kiel and Mims[3] have given some information. In their discussion these authors do not mention the existence of an electron-paramagnetic-resonance (EPR) signal due to cubic Ce^{3+} ions. A particularly strong argument against eventual clustering in $Sr_{1-x}La_xF_{2+x}$ is the result obtained by Brown et al.[29] on $Sr_{1-x}Ce_xF_{2+x}$. These authors found from EPR experiments on these samples with $x \leq 0.02(!)$ that only tetragonal complexes are present. This result is in contrast with the observations made by the same authors on the systems $Sr_{1-x}Er_xF_{2+x}$, showing that with increasing Er concentrations more and more cubic Er^{3+} ions are present. The formation of these cubic ions can be connected with scavenging of interstitial F^- ions, resulting in the formation of, for example, linear or L-shaped clusters as proposed by Figueroa et al.[28] If a similar mechanism would be active in $Sr_{1-x}Ce_xF_{2+x}$ the cubic Ce^{3+} signal would be observable just as the cubic Er^{3+} ions in $Sr_{1-x}Er_xF_{2+x}$. Because of the absence of cubic Ce^{3+} ions in heavily doped materials we are inclined to reject the possibility of scavenging of F_i^- ions. In view of the very small concentrations of the (dipolar) defects associated with the peak at 219 K in the concentration range mentioned, we cannot exclude the possibility of the formation of NNN dipoles on the basis of the absence of the corresponding EPR signal. It is quite reasonable to assume that the EPR signal is too weak to be detected. In addition, we have studied in our laboratory the system $Sr_{1-x}Gd_xF_{2+x}$.[9] We have not been able to produce, with increasing Gd^{3+} concentrations, cubic Gd^{3+} ions in the SrF_2 lattice. Instead, we have observed very large variations of the ratio of the concentrations of NN and NNN dipoles. It appears that the number of NNN dipoles relative to the NN complexes increases with the Gd concen-

TABLE I. Ratio of charges displaced in the ITC band at 219 and 155 K and the ratio of the concentrations of NNN and NN dipoles as derived from the ratio of displaced charges for some $Sr_{1-x}La_xF_{2+x}$ solid solutions.

Concentration (mol %)	$Q(219\text{ K})/Q(155\text{ K})$	c_{NNN}/c_{NN}
0.40	0.08	0.016
0.65	0.10	0.020
1.9	0.15	0.028
4.0	0.36	0.070

tration. This turns out to be the case for the system $Sr_{1-x}La_xF_{2+x}$ also (see Table I). This means that in $Sr_{1-x}Gd_xF_{2+x}$ clustering, and more specifically the formation of L-shaped and linear clusters as proposed by Figueroa et al. does not occur at an extensive scale. The observation of the varying concentration ratio as a function of the La concentration and the behavior of the peak at 219 K after annealing needs some discussion in terms of our model. First, we have noted that the concentration ratio (c_{NN}/c_{NNN}) will decrease with increasing La concentration; this is in agreement with the observations of Figueroa et al. On the other hand, we have to explain the annealing behavior of the $Sr_{1-x}La_xF_{2+x}$ samples. From experiments carried out in our laboratory (see Table I) we found that the lattice parameter of $Sr_{1-x}La_xF_{2+x}$ changes considerably as a function of x. This indicates that the introduction of La^{3+} impurities causes a significant misfit in the crystal lattice. This misfit is considerably larger than in $Sr_{1-x}Nd_xF_{2+x}$.[30] As a result of this misfit the La^{3+} impurities will be accommodated more easily in the neighborhood of dislocations. Next to the possibility of clustering we should now consider seriously another mechanism of concentrating the La^{3+} ions in special regions of the sample. The concentration of La^{3+} impurities in the neighborhood of dislocation lines increases; consequently the interactions between the defects increases, which may result in a variation of the ratio c_{NN}/c_{NNN} as will be discussed later in this paper. This mechanism should be considered independently from the clustering mechanism. Whereas the concentrating mechanism mainly depends upon the misfit between the defects and the perfect lattice, clustering will depend upon a summation of many different interactions. In systems where clustering occurs large misfits between the lattice distances in the immediate surrounding of the cluster and the perfect crystal will probably lead to larger concentrations of clusters in the vicinity of dislocation lines. With regard to the question of eventual clustering of R^{3+}-F_i^- complexes we have studied solid solutions of the type $Sr_{1-x}R_xF_{2+x}$ ($R=$Dy, Er, and Yb), and we have observed that the dielectric relaxation results deviate completely from those presented in this investigation. The ratio c_{NN}/c_{NNN} is quite sensitive to small changes in the surrounding of the dipoles, because the energy difference between NN and NNN dipoles is quite small.

For concentrations higher than 5 mol % the ITC band at 219 K is overwhelmed by the LT tail of the space-charge relaxation band (HT band). The HT band shifts to lower temperature for increasing LaF_3 concentrations. Its
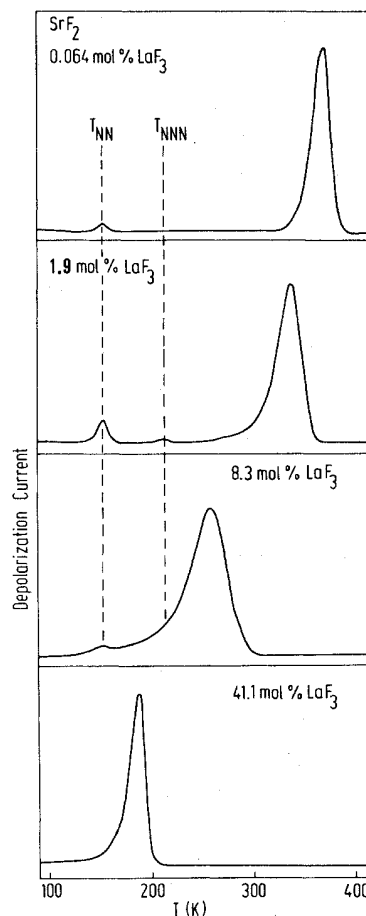

FIG. 1. Survey of the ITC results of solid solutions $Sr_{1-x}La_xF_{2+x}$ for $0<x<0.42$. The samples (1.75 mm thick) were polarized for 5 min at 4000 V. The sensitivity of the electrometer is the same for the different experiments.

intensity is about 1 order of magnitude larger than that of the LT band. The linewidth at half-height increases with increasing LaF_3 concentration, it reaches its maximum at about 6 mol % LaF_3 and decreases if the LaF_3 concentration is increased further. In Fig. 1 we show a survey of ITC results of SrF_2 crystals doped with different amounts of LaF_3. Graphic surveys of T_{max} and $\Delta T_{1/2}$ as a function of the LaF_3 concentration (x) have been given in the Figs. 2 and 3, respectively. The presence of the bands at 155 and 219 K at moderate (up to 5 mol %) LaF_3 concentrations proves that at these concentrations dipoles are still present. Because defect-defect interactions cause a broadening of the formation energies of different kinds of defects, the ratio of the concentration of the different defects changes with the total defect concentration. This has been observed earlier for $Sr_{1-x}Gd_xF_{2+x}$ (Ref. 9) and $Ba_{1-x}La_xF_{2+x}$ crystals.[20] These observations are also arguments against the assignment of the band at 219 K to relaxations of defect clusters.[31]

Andeen et al.[31] have made their assignment for the additional relaxation band (in our ITC experiment this band
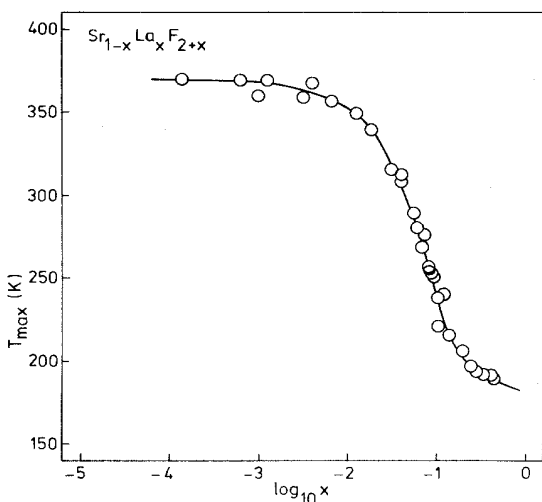
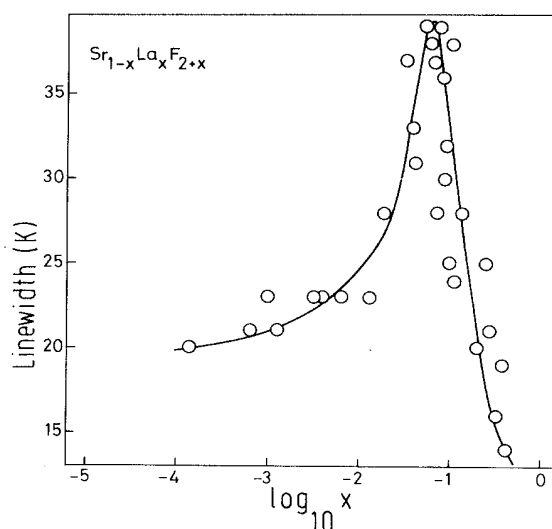FIG. 2. Experimentally observed HT-band position as a function of $\log_{10}x$ for solid solutions $Sr_{1-x}La_xF_{2+x}$.

FIG. 3. Experimentally observed linewidth at half-height on the HT band as a function of $\log_{10}x$ for solid solutions $Sr_1La_xF_{2+x}$.

is located at 219 K) on the basis of observations made on a number of solid solutions. Until now there is no spectroscopic evidence available supporting the model given by Andeen et al.[31] for this band in $Sr_{1-x}La_xF_{2+x}$. There is no other direct support for this model either. Andeen et al. have also noticed as discussed in their paper that there are differences between the results from laser work (which has been carried out in several rare-earth-doped CaF_2 crystals, $Sr_{1-x}Er_xF_{2+x}$ and $Ba_{1-x}Er_xF_{2+x}$) and the dielectric experiments on for example $Sr_{1-x}La_xF_{2+x}$ and $Ba_{1-x}La_xF_{2+x}$. Although the laser experiments suggest that the maximum dipole concentrations are found at about 0.05 mol % for CaF_2-based solid solutions (for $Sr_{1-x}R_xF_{2+x}$ this value is higher), the dielectric results indicate that maximum dipole concentrations are found at R^{3+} concentrations of about 1.0 mol %. We note that the deviations between the observations are probably largely due to the different properties of the impurities. In the system $Sr_{1-x}Yb_xF_{2+x}$ we have found that the maximum dipole concentration occurs for Yb concentrations of about 0.3 mol %. Another reason for the deviating results may be the different temperature treatment during and immediately after crystal growth. Anyhow, the experimental results obtained with various different techniques indicate that the solid solutions $Sr_{1-x}La_xF_{2+x}$ and $Sr_{1-x}Ce_xF_{2+x}$ behave differently from those containing ions of the second half of the series of lanthanides. From a direct comparison between the results of the dielectric experiments on the different SrF_2-based solid solutions we conclude that clustering is reduced if the atomic mass of the rare-earth element is reduced.

The assignment of Andeen et al.[31] suffers from the same problems as the model of Figueroa et al.[28] These models are not compatible with the observations made by Brown et al.[29] In addition we have made another observation with dielectric loss experiments which supports the assignment we have made for the 219-K ITC band in $Sr_{1-x}La_xF_{2+x}$. We have found that the intensity ratio of

the NN band and the extra band associated with the ITC band at 219 K depends upon the excitation frequency used in the dielectric loss experiment. We know that the relaxation peaks shift to higher temperatures when the frequency is increased; therefore, the ratio of the concentrations of the various defects is measured at different temperatures, if we vary the excitation frequency. From the behavior of the concentration ratio as a function of the temperature we conclude that the energy difference between the different defects (the NN dipole and the defect associated with the ITC band at 219 K) is of the order of a few hundredths of an eV. Another conclusion that can be drawn from the results is that there is an easy exchange between the NN dipole and the second defect. This behavior is not compatible with the model given by Andeen et al.[31] It is hard to see how an easy exchange can exist between gettered 2:2:2 clusters and NN dipoles. Our observations are more in line with the NNN dipole model for the 219-K band in the ITC spectrum.

In Table I we have compiled the ratio of the charge displaced in the band at 219 K and the band at 155 K for some different LaF_3 concentrations. We can explain the increase of the ratio of the charge displaced in the band at 219 K and the band at 155 K as an increase of the ratio of the concentrations of NNN and NN dipoles. The charge displaced during the dipole-reorientation process is proportional to the square of the dipole moment of the reorienting dipole. In our calculation of the ratio of the concentrations of NNN and NN dipoles we have used the dipole moments of the corresponding dipoles present in gadolinium-doped SrF_2.[9] These dipole moments have been determined from electric-field-effect measurements in ESR. The concentration ratio of the NNN and NN dipoles has also been given in Table I.

It could also be possible that other trivalent impurities in the dopant (LaF_3), giving rise to NNN dipoles, are responsible for the band at 219 K. We know from the work
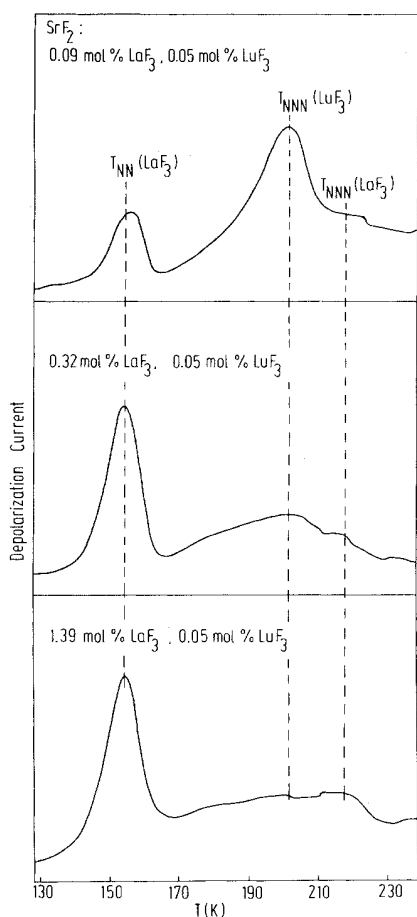
FIG. 4. Survey of the ITC results of solid solutions $Sr_{1-x-0.0005}La_xLu_{0.0005}F_{2+x+0.0005}$ for $0.0009 < x < 0.014$. The polarization conditions are the same as for the experiments presented in Fig. 1.

of Lenting et al.[11] that the heavy lanthanide ions Ho-Lu form predominantly NNN dipoles in SrF_2. In order to simulate such a situation we have investigated some solid solutions of the type $Sr_{1-x-y}La_xLu_yF_{2+x+y}$. The excess positive charge on the Lu^{3+} ion is compensated locally only by an interstitial F^- ion in an NNN position.[14] It appears that the NNN dipole relaxation band decreases rapidly with increasing LaF_3 concentration. A survey of the ITC spectra of samples of the system $Sr_{1-x-y}La_xLu_yF_{2+x+y}$ has been shown in Fig. 4. If the band at 219 K originates from other rare-earth impurities than LaF_3 (which are present as impurities in the LaF_3), this band should also decrease with increasing LaF_3 concentration. Instead of a decrease of the band at 219 K, we have observed an increase with increasing LaF_3 concentration. The decrease of the LuF_3 NNN dipole relaxation band may be due to a shift of the dissociation equilibrium of the reaction

$$Lu^{3+}\text{-}F_i^-(\text{NNN dipoles}) \rightleftharpoons Lu^{3+}(\text{cubic}) + F_i^-(\text{free})$$
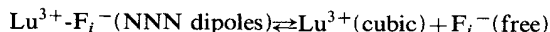
as a result of the presence of the partly dissociated La^{3+}-F_i^- dipoles. A second explanation may be a conversion of the Lu^{3+}-F_i^- NNN dipoles into cubic Lu^{3+} ions and free interstitial fluoride ions as a result of broadening of the formation energy of the defects concerned. Finally, the decrease of the Lu^{3+}-F_i^- NNN dipole relaxation band may be due to the possibility of the formation of clusters containing both Lu^{3+} and La^{3+} ions.

THEORY

In earlier investigations performed in our laboratory[20,25] attention has been focused on the behavior of the high-temperature space-charge relaxation ITC band in concentrated solid solutions $Ba_{1-x}La_xF_{2+x}$ (Ref. 20) and $Sr_{1-x}Nd_xF_{2+x}$.[25] It has been found that the behavior of this HT band is quite different from that of the dipole relaxation bands. At very low defect concentrations the activation energy $(E_{a,0})$ of dipole relaxations has a unique value, and also the characteristic relaxation time (τ_0) has a constant value. At higher defect concentrations, interactions between the defects make that the activation energy does not have a unique value; there is a distribution about the value for dipole relaxations at very low concentrations. The temperature at which the dipole relaxation band reaches its maximum does not vary as a function of the defect concentration. Only the bandwidth increases with increasing defect concentration. In earlier investigations van Weperen et al.[13] have approximated the distribution to be Gaussian. It can be described by

$$n(E_a) = \frac{N_d}{p\sqrt{\pi}}\exp\left[\frac{-(E_a - E_{a,0})^2}{p^2}\right],\qquad(1)$$

In Eq. (1), p is the broadening parameter and N_d is the number of dipoles of the type considered. The HT band, however, shifts to lower temperatures, if the defect concentration increases. This implies that the activation energy and the characteristic relaxation time (τ_0) vary with the defect concentration. We have attempted to explain the observed features of the HT band by means of a relaxation process with one (eventually varying) activation energy. This turned out to be impossible. Therefore, den Hartog and Langevoort[20] have explained the shifts of the HT band, which has been ascribed to the relaxation of space charges building up during the polarization process, with two jump processes proceeding simultaneously. At the anode an excess of interstitial fluoride ions is present, while at the cathode there is a deficiency of interstitial fluoride ions. Here not all the rare-earth ions present in the host lattice are compensated electrically by interstitial fluoride ions. The relaxation of this space charge has been assumed to occur by means of two different jumps of interstitial ions which have been referred to as free interstitial jumps and dipolelike jumps. If an interstitial ion moves relatively far from a trivalent ion it moves through the lattice by means of free jumps. An interstitial ion, which moves in the direct neighborhood of a rare-earth ion makes dipolelike jumps. These different types of jumps have different relaxation parameters. Because in a relaxation experiment these processes occur simultaneously, the relaxation time of the total process can be given by the following relation:

$$\frac{1}{\tau} = \frac{\alpha}{\tau_0^d} \exp\left[\frac{-E_{a,0}^d}{kT}\right] + \frac{(1-\alpha)}{\tau_0^f} \exp\left[\frac{-E_{a,0}^f}{kT}\right] . \qquad (2)$$

Here α is the probability for a dipolelike jump to occur; $E_{a,0}^d$ and $E_{a,0}^f$ are the activation energies for a dipolelike jump and a free interstitial jump, respectively, and τ_0^d and τ_0^f are the characteristic relaxation times for these processes. We note that in the extreme situations, where $\alpha = 0$ or 1, we are dealing with a simple relaxation process, which is governed by jump of free interstitials or dipolelike jumps, respectively. These situations occur for samples with either very low or very large LaF_3 concentrations. With the values of τ calculated with Eq. (2) we can calculate the depolarization current as a function of the temperature with

$$I(T) = \frac{dP}{dt} = B \exp\left[-\int_0^T \frac{dT'}{b\tau(T')}\right] \Big/ \tau(T) , \qquad (3)$$

where b is the heating rate during the ITC experiment and B is the charge displaced during the depolarization process.

We now discuss the processes which determine the values of the relaxation parameters in Eq. (2), and which are necessary to calculate the relaxation time of the overall space-charge relaxation process. In very diluted samples the jumps of free interstitial ions are preceded by dissociation of dipoles. For nearest-neighbor dipoles the following equation for the dissociation constant can be given:

$$K_{diss} = \frac{6c_{La^{3+}(cubic)}c_{F_i^-(free)}}{c_{La^{3+} - F_i^-(NN)}}$$

$$= \exp{-\frac{E_{diss}}{kT}} . \qquad (4)$$

As $c_{La^{3+}}(cubic) \simeq c_{F_i^-(free)}$, it can be seen that $c_{F_i^-(free)}$ is proportional to $e^{-E_{diss}/2kT}$.

The depolarization current introduced by free interstitial jumps is proportional to both the concentration of free interstitial ions and the hopping frequency of a real free interstitial ion. The activation energy for this hopping process is 0.94 eV for SrF_2 as derived from conduction experiments by Bollmann et al.[32] The charge-transport process governed by free interstitial jumps has the following overall activation energy $E_{a,0}^f$:

$$E_{a,0}^f = 0.94 + \tfrac{1}{2}E_{diss} . \qquad (5)$$

The best agreement between the experimentally observed values of T_{max} and $\Delta T_{1/2}$ for very low LaF_3 concentrations and the corresponding calculated values for $\alpha = 0$ have been obtained for $E_{a,0}^f = 1.205$ eV and $\tau_0 = 9.6 \times 10^{-15}$ sec. From (5) we derive a value of 0.53 eV for E_{diss}, which is a reasonable value for the dissociation energy of NN dipoles. The dissociation energies of various dipolar defects in $Sr_{1-x}R_xF_{2+x}$ crystals have been calculated by Wapenaar et al.[33] and Corish et al.[34] Wapenaar et al. have demonstrated that the theoretical value of E_{diss} depends upon the choice of the interionic potentials. These authors have employed potentials based upon the electron-gas (EG) method discussed by

Wedepohl[35] and Gordon and Kim[36]; in addition a set of semiempirical (SE) potentials have been employed. The dissociation energies for NN and NNN dipoles obtained with EG potentials are 0.71 and 0.54 eV, respectively. The corresponding values for the SE potentials are 0.75 and 0.41 eV. These results show that there is a deviation of about 0.20 eV in the dissociation energy (experiment and theory) of the NN dipoles. On the other hand, there is an appreciable difference between the formation energies of NN and NNN dipoles. On the basis of these results we expect that the ratio of the concentrations of NN and NNN dipoles is (at 220 K) about 5×10^5(!), implying that NNN dipoles are not observable. Recent theoretical results published by Corish et al.,[34] however, deviate appreciably from those obtained by Wapenaar et al.[33] The dissociation energies of the NN and NNN dipoles calculated by Corish et al. are for the system $Sr_{1-x}La_xF_{2+x}$ 0.592 and 0.515 eV, respectively. These results are clearly in far better agreement with our experimental data than the values calculated by Wapenaar et al.[33]

Another feature of our experimental results can also be explained by means of the theoretical values of the dissociation energy. As mentioned above we can estimate from the calculated values of the dissociation energies the ratio of the NN and NNN dipoles in $Sr_{1-x}La_xF_{2+x}$. According to the calculations of Corish et al.[34] the energy difference of NN and NNN dipoles is quite small (0.077 eV), the NN dipole being the most favorable configuration. At a temperature of 219 K (equal to the temperature of the NNN dipole peak) we expect that the ratio of the concentrations of NN and NNN dipoles (c_{NN}/c_{NNN}) is about 60, which is quite large as compared to the values found for the systems $Sr_{1-x}Gd_xF_{2+x}$, $Sr_{1-x}Tb_xF_{2+x}$, and $Sr_{1-x}Dy_xF_{2+x}$, published by Lenting et al.[11] As a consequence the NNN dipole peak cannot be observed in $Sr_{1-x}La_xF_{2+x}$. This line of reasoning holds for low impurity concentrations. For high concentrations, however, the Boltzmann distribution may be disturbed by defect-defect interactions. This mechanism has been described by Aalbers and den Hartog.[9] Instead of the usual Boltzmann factor one obtains for the ratio of the concentrations of NN and NNN dipoles a value of

$$c_{NN}/c_{NNN} = \exp\left[\frac{\Delta E}{kT} - \frac{(p_{NNN}^2 - p_{NN}^2)}{(2kT)^2}\right] , \qquad (6a)$$

where ΔE is the energy difference of NN and NNN dipoles and p_{NNN} and p_{NN} are the broadening parameters associated with NNN and NN dipoles as defined by Aalbers and den Hartog.[9] Aalbers and den Hartog have found that even for moderate concentrations (≤ 0.5 mol %) GdF_3 the value of p_{NNN} can be 0.05 eV. Assuming that p_{NN}, which is proportional with the strength of the NN dipole, is a factor of 2.3 smaller than p_{NNN}, we can calculate the concentration ratio c_{NN}/c_{NNN}. The ratio turns out to be 10; approximately a factor of 6 smaller than in the case without defect-defect interactions. We note that the theoretical concentration for high concentrations is in fair agreement with our experimental observations (see also Table I). We have to note, however, that for very low LaF_3 concentrations part of the charge transport may be provided by interstitial ions or vacancies, which are charge compensators for trivalent ions different from

La^{3+} or monovalent ions, respectively. These impurities are present in very small amounts in the samples.

Because NN dipoles are present in much larger concentrations than the NNN dipoles, it should be obvious that, just as in solid solutions $Sr_{1-x}Nd_xF_{2+x}$, the dipolelike jumps are of the NN type. We expect that the effect of the rare-earth concentrations on T_{max} of the HT band is about the same for $Sr_{1-x}La_xF_{2+x}$ and $Sr_{1-x}Nd_xF_{2+x}$. We have observed, however, that on going from $x = 10^{-4}$ to 10^{-2}, T_{max} decreases by 16 K for $Sr_{1-x}La_xF_{2+x}$ and by about 35 K for $Sr_{1-x}Nd_xF_{2+x}$. If both NN and NNN dipolelike jumps contribute to the relaxation process, we can write the following equation for the relaxation time associated with dipolelike jumps:

$$\frac{1}{\tau^d} = \frac{\beta}{\tau^d_{NNN}} + \frac{(1-\beta)}{\tau^d_{NN}} , \qquad (6b)$$

where β is the fraction of all dipolelike jumps which are of the NNN type and $(1-\beta)$ is the corresponding fraction associated with NN jumps. If we assume that β is equal to the ratio of the number of NNN dipoles and the total number of dipoles present, we estimate that $\beta \cong 0.03$. Inserting the mechanism as given in Eq. (6b) into Eq. (2), we find for these small values of β only minor variations of T_{max} as compared to the crude description ($\beta=0$). In order to find considerable changes of T_{max} (> 5 K) it is necessary to choose values of β larger than 0.50. From our results we tentatively conclude that the dominant contribution to the dipolelike jumps comes from the NNN dipoles.

We can describe the dipolelike jump part of the depolarization process alternatively, by means of the NNN dipolelike jumps, followed by a relatively fast rearrangement to an NN dipole. The rate of the formation of NN dipoles is now totally determined by the rate of the NNN dipole-forming jumps. We have to describe the dipolelike jump process with the relaxation parameters of NNN dipole reorientation now. Because the intensity of NNN dipole relaxation bands of the system $Sr_{1-x}La_xF_{2+x}$ is too low to calculate the relaxation parameters from them, we have chosen the τ_0 value of the NNN dipole relaxation band of system $Sr_{1-x}Ho_xF_{2+x}$.[14] Using the following relation for T_{max} of an ITC band,

$$\frac{E^d_{a,0}}{kT^2_{max}} = \frac{1}{b\tau_0}\exp\left[-\frac{E^d_{a,0}}{kT_{max}}\right] , \qquad (7)$$

we have calculated a value of 0.66 eV for $E^d_{a,0}$ with $b = 0.03$ K sec^{-1}, $T_{max} = 219$ K, and $\tau_0 = 10^{-13}$ sec. With the parameters $E^d_{a,0} = 0.66$ eV and $\tau^d_0 = 10^{-13}$ sec we have fixed the space-charge relaxation band at 219 K for $\alpha = 1$.

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

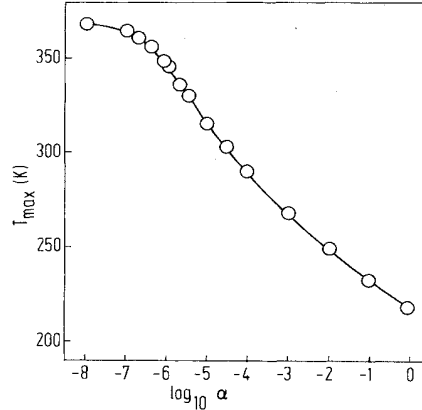| Concentration (mol %)	Lattice constant (Å)
pure	5.800
8.3	5.815
27.3	5.838
41.1	5.854

FIG. 5. Calculated HT-band position as a function of $\log_{10}\alpha$. The parameters used are $E^f_{a,0} = 1.205$ eV, $\tau^f_0 = 9.6 \times 10^{-15}$ sec, $E^d_{a,0} = 0.66$ eV, $\tau^d_0 = 1.0 \times 10^{-13}$ sec, and $b = 0.03$ K sec^{-1} (equal to the heating rate during the ITC experiment).

Experimentally, however, we have observed $T_{max} = 189$ K for $x = 0.41$. This deviation can possibly be ascribed to the increase of the lattice parameter with increasing LaF$_3$ concentration. We have compiled the experimental lattice parameters for some compositions of the solid solutions $Sr_{1-x}La_xF_{2+x}$ in Table II. From our observation that up to 10 mol % LaF$_3$ the values of T_{max} of the dipole relaxation bands remain the same within the experimental error, we conclude that the influence of the lattice constant on the values of the relaxation parameters can be neglected below 10 mol % LaF$_3$.

In Figs. 5 and 6 we show the relation between the probability for a dipolelike jump to occur (α) and the calculat-
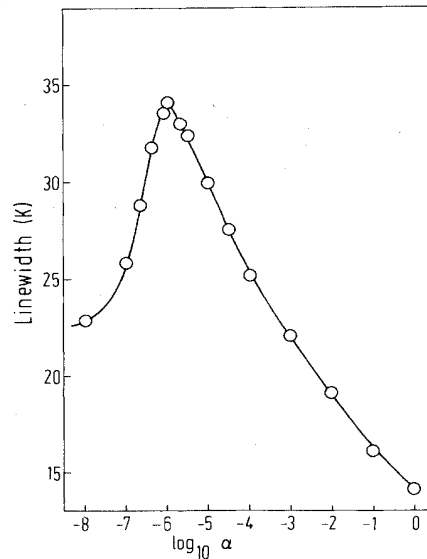

FIG. 6. Linewidth at half-height of the calculated HT bands as a function of $\log_{10}\alpha$. The same parameters as in Fig. 6 have been used.
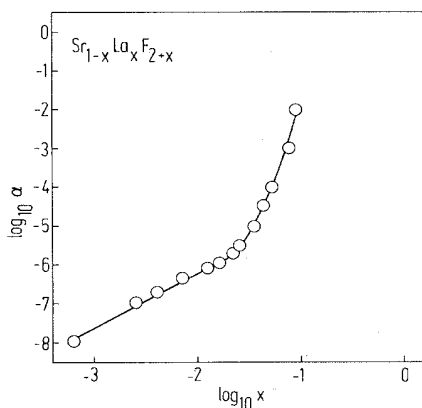
FIG. 7. Values of $\log_{10}\alpha$ plotted as a function of $\log_{10}x$ obtained by comparing the experimental Fig. 3 with the calculated Fig. 6.

ed values of T_{max} or the linewidth at half-height ($\Delta T_{1/2}$), respectively. We see that the calculated plots agree qualitatively with the corresponding ones determined experimentally. A striking feature is the maximum which appears in both the experimental and theoretical plots, showing the relation between the linewidth and x or α, respectively.

In order to obtain a relation between the defect concentration (x) and the probability for a dipolelike jump to occur (α), we have compared the experimental plot of T_{max} as a function of x with the calculated one of T_{max} as a function of α. We have used values of $T_{max} > 240$ K ($x < 0.1$ and $\alpha < 0.03$) because there is some uncertainty about the behavior of the relaxation parameters in the concentration region between 10 and 40 mol %. The resulting relation between α and x has been presented in Fig. 7. This figure shows a rapid increase of α vs x beyond 4 mol %. Above this concentration the dipoles are so close together that interstitial ions can jump from one dipole complex to another. A rapid increase of the contribution of dipolelike jumps to the charge-transport process with increasing LaF_3 concentration occurs. Now part of the charge transport through the sample may proceed without dissociation of the dipoles into cubic La^{3+} and free interstitial fluoride ions. If we mutually compare the plot of the experimental values of the linewidth as a function of the LaF_3 concentration (x) and the plot of the calculated linewidth as a function of the probability of a dipolelike jump to occur (α), we do not obtain the same relation between x and α as displayed in Fig. 7. This deviation may be explained by remarking that the activation energies do not have unique values but are distributed symmetrically about a mean value. This distribution is the result of defect-defect interaction as described by van Weperen and den Hartog.[14] The effect of this distribution on the calculated values of T_{max} is expected to be small, whereas the effect of the calculated values of $\Delta T_{1/2}$ may be considerable. We emphasize that it is very difficult to estimate the broadening of the activation energies as a function of the LaF_3 concentration. We should also take into account

that if the defects are not distributed homogeneously over the sample, the experimental value of $\Delta T_{1/2}$ will be larger than it should be in the case of a homogeneous distribution of the defects.

The very strong increase of α and consequently of the mobility of the interstitial ions above about 4 mol % LaF_3 is characteristic for a percolation mechanism. If a percolation mechanism governs the charge transport through the samples, we can write the following relation:

$$\alpha = B(x - x_c)^s , \qquad (8)$$

as derived by den Hartog and Langevoort[20] from the theoretical results of Kirkpatrick.[21] Here x_c is the concentration above which the charge transport due to dipolelike jumps increases very quickly, x_c is between 0.10 and 0.15 or between 0.02 and 0.03 for NN or NNN dipolelike jumps, respectively, while s is about 1.8. We can understand the values of x_c, remembering that the conductance of a material consisting of conducting spheres of equal size in a nonconducting medium can be described by

$$\sigma = A(x - x_c)^s , \qquad (9)$$

only if the volume fraction of the conducting material exceeds values between 0.25 and 0.3.[21] In the case of fluorite-type materials the host is considered to be nonconducting, whereas the NN and NNN dipoles consisting of a trivalent rare-earth ion and an interstitial halide ion are considered to be the conducting domains. As the NN and NNN dipole spheres are 2 and 11 times as large as an alkaline-earth molecule, respectively, a volume fraction between 0.25 and 0.30 occupied by conducting materials is reached for NN dipole concentrations between 10 and 15 mol % and for NN dipole concentrations between 2 and 3 mol %. In the case of $Sr_{1-x}La_xF_{2+x}$ a difficulty arises: We have predominantly NN dipoles but the rate determining step in the dipole formation from a free interstitial ion and a cubic La^{3+} ion is the formation of an NNN dipole, which rearranges very quickly to the thermodynamically more stable NN dipole. Consequently, is it not correct to use the percolation threshold between 2 and 3 mol % for NNN dipolelike jumps. The percolation threshold is expected to be achieved for LaF_3 concentrations higher than 3 mol %. We have tried to calculate a value of x_c by means of a least-squares fit of the values of α, obtained by comparing the experimental Fig. 2 and the calculated Fig. 5 to Eq. (8). Unfortunately, we have obtained values for x_c (< 0.01) and s (> 5), which do not have any physical meaning. The failure of this very simple model may be associated to a (rapidly) changing defect structure between 1 and 10 mol % LaF_3. The ratio of the concentration of NNN and NN dipoles increases with increasing LaF_3 concentration as described by Aalbers and den Hartog.[9] This states that the mean dipole size increases with increasing LaF_3 concentration; above a certain LaF_3 concentration dissociation and association of NNN dipoles also contribute considerably to the charge transport. So Eq. (8) gives a too simple description of the real percolation process. An attempt to develop a more advanced model will be ineffective without a detailed knowledge of the structural and thermodynamic properties of the solid solutions between 1 and 10 mol %.

DISCUSSION

For our interpretation of the results we assume that clustering of the defects is relatively unimportant. For example, the predominant defects present in the $Sr_{1-x}La_xF_{2+x}$ samples are assumed to be NN and NNN dipoles, which consist of a trivalent impurity and a nearby interstitial fluoride ion. This is in contrast with the results of laser spectroscopy for $Ca_{1-x}Er_xF_{2+x}$.[37,38] In general one can probably say that in the CaF_2 hosts there is extensive clustering; also in the system $Ca_{1-x}Pr_xF_{2+x}$ clustering has been observed for relatively small values of x.[39] From the results obtained in our laboratory[25,40] and spectroscopic information [Brown et al. (Ref. 29)] on the system $Sr_{1-x}Ce_xF_{2+x}$ we conclude that at least the systems $Sr_{1-x}La_xF_{2+x}$, $Sr_{1-x}Ce_xF_{2+x}$, $Sr_{1-x}Pr_xF_{2+x}$, and $Sr_{1-x}Nd_xF_{2+x}$ behave differently from the solid solutions $Ca_{1-x}R_xF_{2+x}$.

The most important reasons why we assume that in $Sr_{1-x}La_xF_{2+x}$ NN and NNN dipoles are the dominant defects are the following.

(i) In the ITC experiments there are only two dipole reorientation bands, which are located at approximately the same temperatures as the NN and NNN dipole peaks in $Sr_{1-x}Gd_xF_{2+x}$; the latter peaks have been assigned to the corresponding dipoles by means of combined ITC and EPR experiments by Aalbers and den Hartog.[9]

(ii) The ratio of the intensities of the dipole peaks at 219 and 155 K increases with increasing La concentration; this behavior is the same as that observed by Aalbers and den Hartog[9] for $Sr_{1-x}Gd_xF_{2+x}$. We should note, however, that a similar behavior is expected for a defect structure containing clusters. Recent experimental results on $Sr_{1-x}Ce_xF_{2+x}$ show that there is an easy exchange between the defects associated with the two relaxation peaks. From the behavior of the intensity ratio of the relaxation peaks as a function of the temperature we estimate that the energy difference between the NN and NNN dipole configuration is a few hundredths of an eV, which agrees quite well with the theoretical values calculated by Corish, Catlow, Jacobs, and Ong.[34]

(iii) The theoretical calculations carried out by Corish et al.[34] have shown that the NN and NNN dipoles are energetically appreciably more favorable than the most simple clusters in $Sr_{1-x}La_xF_{2+x}$.

(iv) In crystals $Sr_{1-x}La_xF_{2+x}$:Gd^{3+} we have not found significant concentrations of centers containing both an La and a Gd ion (see Ref. 41) even if we introduce 6 mol % LaF_3 into a crystal; a similar observation has been made in our laboratory for the system $Ba_{1-x}La_xF_{2+x}$.

As outlined above we assume that in our $Sr_{1-x}La_xF_{2+x}$ crystals clustering is relatively unimportant; evidence supporting this assumption can be obtained from a comparison of the results presented in this paper and the ITC data obtained for the systems $Sr_{1-x}Dy_xF_{2+x}$ and $Sr_{1-x}Er_xF_{2+x}$.[42] The latter solid solutions have been investigated in detail in Kurz and Wright[43] by means of the selective laser excitation method for Er concentrations up to 0.2 mol %. From both the ITC results and the results of selective laser excitation experiments one concludes that there is significant clustering even for relatively low Er concentrations. We have found for solid solutions $Sr_{1-x}Yb_xF_{2+x}$ a stronger tendency towards clustering.[44]

This indicates that the results of selective laser excitation experiments, obtained by Kurz and Wright,[43] the EPR results obtained by Brown et al.,[29] which give spectroscopic information about the defects present are in agreement with our ITC results. In the solid solutions studied in this paper none of the features characteristic for dominant clustering have been observed with ITC. It is therefore suggested that in $Sr_{1-x}La_xF_{2+x}$ clusters, if present, are minority defects, which do not modify the conductivity results significantly.

If there is significant clustering, this can be observed readily with the ITC technique, because this phenomenon affects the position of the HT band drastically.[42,44] These observations agree with the spectroscopic data of Brown et al.[29]; these authors also mention the clear difference of the behavior of the rare-earth ions from the opposite ends of the lanthanide series. In $Sr_{1-x}Er_xF_{2+x}$ Brown et al. have found apart from the trigonal dipole cubic Er^{3+} ions. This may be due to the presence of L-shaped or linear clusters as suggested by Figueroa et al. for $Sr_{1-x}La_xF_{2+x}$.[28] These clusters consist of one trivalent impurity ion and two interstitial fluoride ions. Because for each trivalent impurity only one interstitial fluoride ion is introduced into the crystal some of the impurity ions are located at cubic sites.

It appears that eventual clustering depends strongly upon the differences between the ionic radius of the host lattice ions (M^{2+}) and the trivalent impurity; in addition the lattice parameter is important. From the experimental results which are available up to now we are inclined to conclude that the systems $Ca_{1-x}R_xF_{2+x}$ show clustering for all different R^{3+} ions of the series of lanthanides. For the series of solid solutions $Sr_{1-x}R_xF_{2+x}$ the situation is more complicated. The heavy impurities show clustering; for the light ones the clustering is probably weak. We emphasize, however, that the discussion given above does not imply that clustering is totally absent.

The second basic assumption used in this paper concerns the nature of the HT band. We assume that this band is associated with space charges, i.e., this depolarization phenomenon is connected with the bulk ionic conductivity of the samples. Among the many indications to support this assumption are the following.

(i) Space-charge relaxation peaks in ionic materials usually have very large intensities as compared with dipole relaxation bands; the HT bands in our samples also have large intensities, which are comparable with the intensity of the space-charge band observed for KCl:Sr^{2+}.[45]

(ii) From a comparison of the ITC and the ionic conductivity results Wapenaar et al.[22] have found that there is close agreement between the behavior of the HT band and the bulk ionic conductivity data for the solid solutions $Ba_{1-x}La_xF_{2+x}$; in addition we have found in this laboratory that in solid solutions of the type $Sr_{1-x}Yb_xF_{2+x}$, where clustering plays an important role, the anomalous behavior of the HT band can be explained in detail by using the results obtained for the ionic conductivity in these samples.[44]

(iii) The positions of space-charge relaxation peaks vary as a function of the concentration of the dopant.

(iv) In order to exclude the possibility of interface problems we note that the HT band intensity varies approximately linearly with the sample thickness. Another obser-

vation we can mention in this regard is the effect of the electrodes. We have found that the position of the HT peak does not change as a result of the introduction of the Teflon foils; only the intensity of the peak is influenced. This behavior can be understood if we assume that the HT band is associated with space charges. The most import-nat effect of the Teflon foils is that the distance between the space charges and the neighboring electrodes is increased, which leads to smaller values of the total polarization charge. If interface problems or injection of charge carriers are important the application of Teflon foils is expected to lead to significant changes of the ITC results.

Apart from the indications given above Vanderschueren and Gasiot[46] have presented some other possible methods for differentiating between the various polarization processes. First there is the decrease of T_{max} with increasing polarizing fields observed by Hickmott.[47] We have not observed any shift of the HT band as a function of the electric field strength for values of E_p in the range 100–3000 V/mm. Another test that has been carried out shows that with the configuration using insulated electrodes (Teflon foils), employed in the present investigation, we did not observe deviations from the linear relationship between the total polarization charge associated with the HT band and the polarizing field E_p. This behavior deviates from that observed by Bucci et al.[45] for $KCl:Sr^{2+}$; these authors observed a saturation behavior of the HT band for values of E_p larger than 500 V/mm. Bucci et al., however, employed graphite electrodes, which had been applied directly to the crystals without any insulator. Referring to the discussion about the E_p dependence given above we note that Bucci et al.[45] did not find an E_p dependence for the value of T_{max} of the HT band in $KCl:Sr^{2+}$ either. It has been noticed by Vanderschueren and Gasiot[46] that the field-dependence argument should be viewed with caution, reason why we think that this dependence is not a critical test for the assignment of depolarization peaks to space-charge phenomena.

In the preceding section we have given a two-jump model for the charge transport in $Sr_{1-x}La_xF_{2+x}$. There is a qualitative agreement between the experimental and the calculated results. For a more quantitative description a much more detailed insight in the thermodynamic and structural properties of the materials between 1 and 10 mol% is necessary. A very striking argument for the two-jump process against the one-jump mechanism used to explain the conductivity experiments on $Ba_{1-x}La_xF_{2+x}$ (Ref. 24) is the maximum in the linewidth at half-height $(\Delta T_{1/2})$ found in both experimental and calculated plots of $\Delta T_{1/2}$ as a function of x (Fig. 3) and α (Fig. 6), respectively. If a one-jump process is used to explain the results, a continuous decrease of the linewidth has been found for increasing LaF_3 concentrations. To obtain this result we have performed calculations as described below. The activation energy and the characteristic jump time τ_0 for the HT band at the lowest LaF_3 concentration have been calculated in the preceding section: $E_a = 1.205$ eV and $\tau_0 = 9.6 \times 10^{-15}$ sec. Using the same characteristic jump time for the HT band at the highest LaF_3 concentration $(x = 0.4111$ and $T_{max} = 189$ K) we have calculated a value of 0.61 eV for the activation energy with Eq. (7) (heating rate $b = 0.03$ K sec^{-1}). Beginning at 0.61 eV we have in-
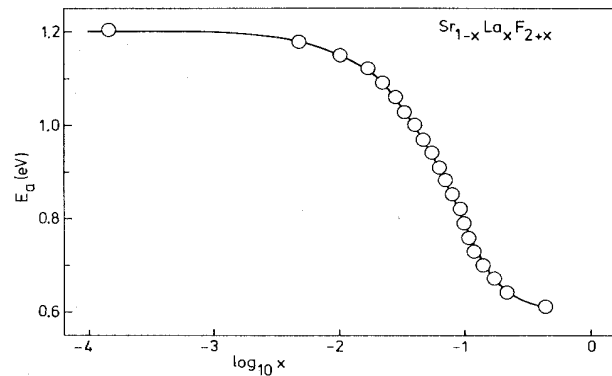

FIG. 8. Activation energy of the HT band, as calculated for a one-jump space-charge relaxation mechanism, as a function of $\log_{10}x$. A constant value for $\tau_0 = 9.6 \times 10^{-15}$ sec and a heating rate of 0.03 K sec^{-1} have been used.

creased the activation energy with steps of 0.03 eV until a value of 1.2 eV has been reached. For each value of the activation energy, a fixed value of 9.6×10^{-15} sec for τ_0 and a heating rate of 0.03 K sec^{-1} we have calculated T_{max} using Eq. (3). Comparing the values of T_{max} (associated with the different activation energies) with the experimental results presented in Fig. 2, we obtain a relationship between the activation energy and the LaF_3 concentration (Fig. 8). With the values of E_a and τ_0 we have also calculated the linewidths at half-height $(\Delta T_{1/2})$ of the ITC bands. From these calculations and Fig. 8 we obtain a relationship between $\Delta T_{1/2}$ and the LaF_3 concentration. This relationship has been displayed in Fig. 9. In this figure we do not observe a maximum in the linewidth on going from low to high LaF_3 concentrations. Our conclusion is that it is highly impropable that a one-jump mechanism governs the charge transport during the space-charge relaxation process.

Attempts to compare the results of the ionic conductivity experiments with the results derived from the space-
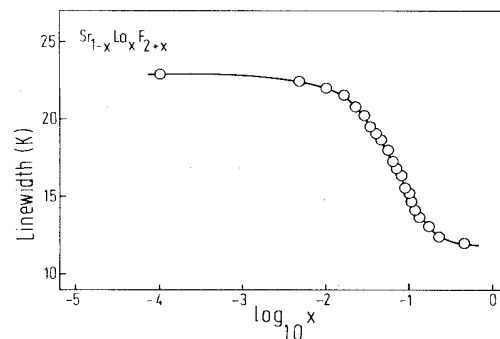

FIG. 9. Linewidth at half-height of HT band, calculated with the activation energies presented in Fig. 9, a constant value of 9.6×10^{-15} sec for τ_0 and a heating rate of 0.03 K sec^{-1}, as a function of $\log_{10}x$.

charge relaxation band in our ITC spectra are hampered by the large difference between the temperatures at which ionic conductivity experiments are performed and the temperature at which the space-charge relaxation occurs. This difficulty appears particularly if the dissociation of the dipoles in free defects is taken into account. We have calculated, using the dissociation energy of about 0.53 eV for NN dipoles, that the dissociation constant is about 10^{-7} at 370 K. At 570 K this dissociation constant is about 10^{-5}. For samples with low rare-earth fluoride concentrations the number of free charged defects increases with about one power of ten on going from 370 to 570 K. For increasing LaF_3 concentrations the dissociation energy decreases, as a result of the interaction between the free charged defect and its surrounding charge cloud. The amount of this decrease has been described theoretically by means of the Debye-Hückel theory, modified by Lidiard for solid electrolyte solutions.[23]

The following equation for the dissociation energy resulted from this theory:

$$E_{diss} = E^0_{diss} - \frac{q^2\kappa}{4\pi\epsilon\epsilon_0(1+\kappa R)} , \tag{10}$$

in which R is the La^{3+}-F_i^- distance in an NN dipole. The Debye-Hückel screening constant κ has been equated as follows:

$$\kappa = \left[\frac{2q^2 x_f}{v\epsilon\epsilon_0 kT} \right]^{1/2} , \tag{11}$$

where x_f is the free-defect concentration and v is the volume of a SrF_2 molecule. For $x_f = 10^{-3}$ the dissociation energy is lowered by 0.22 and 0.19 eV at 370 and 570 K, respectively. At 370 K the LaF_3 concentration associated with this *free*-defect concentration is about 10 mol %. At 570 K this LaF_3 concentration is about 0.6 mol %. The screening of the defects by charge clouds results in an enhancement of the degree of dissociation. For $Ba_{1-x}La_xF_{2+x}$ (Ref. 22) one should be able to explain the conductivity enhancement up to a few mol % LaF_3 with Debye-Hückel theory. A decrease of 0.22 eV of E_{diss} results in a value of 339 K for T_{max}, as calculated using Eqs. (5) and (7) and assuming that only free interstitial jumps occur and that the value of τ_0 remains the same. We have neglected the decrease of the Debye-Hückel screening constant κ on going from 370 to 339 K at a constant amount of free charged defects $(x_f = 10^{-3})$. From the dissociation constant at 339 K we have calculated that a total LaF_3 concentration of about 24% is needed to obtain a free charged defect concentration of 10^{-3}. From our experimental observations (Fig. 2) we can derive that a LaF_3 concentration of 1.9 mol % results in a value of 339 K for T_{max}. From this disagreement we conclude that the decrease of T_{max}, which we have observed on going from an almost pure SrF_2 crystal to samples containing a few mol % LaF_3 cannot be explained by means of the Debye-Hückel-Lidiard theory of nonideal solid electrolyte solutions[23] alone. From these considerations, however, it becomes clear that the overall activation energy of free interstitial jumps decreases with increasing LaF_3 concentration. The gradually decreasing activation energy of free interstitial jumps combined with the arguments used in the

preceding section hamper a quantitative description of the charge-transport mechanism during the space-charge relaxation process.

With the use of our two-jump model for the charge transport and assuming that the activation entropy of both dipolelike jumps and free interstitial jumps have about the same values we can equate the ionic conductivity (σ) as follows:

$$\sigma T = A \left[\frac{\alpha}{\tau_0^d} \exp - \left[\frac{E^d_{a,0}}{kT} - \frac{p_d^2}{4k^2T^2} \right] \right.$$

$$\left. + \frac{(1-\alpha)}{\tau_0^f} \exp - \left[\frac{E^f_{a,0}}{kT} - \frac{p_f^2}{4k^2T^2} \right] \right] . \tag{12}$$

in which A is a proportionality factor, being a function of the charge on, and the concentration of the mobile defects and the activation entropy of motion; p_d and p_f are the broadening parameters of the activation energy of dipolelike and free interstitial jumps, respectively; the other parameters have their usual meaning. For moderate and high LaF_3 concentrations and a temperature of about 600 K the activation energy of a free interstitial jump has probably a value of 0.94 eV (Bollmann[32]), because for these concentrations and at this temperature the dissociation energy of dipoles has diminished as a result of the interaction between free charged defects and their surrounding charge clouds as discussed earlier in this section. The parameters τ_0^d and τ_0^f will have the same values as used before in our calculations of T_{max} and $\Delta T_{1/2}$ as a function of α. A reasonable value for both the broadening parameters p_d and p_f at moderate and high LaF_3 concentration will be about 0.1 eV.[24]

Using Eq. (12) with the values assigned to $E^f_{a,0}$, $E^d_{a,0}$, p_d, p_f, τ_0^d, and τ_0^f as described above and the qualitative relationship between x and α as displayed in Fig. 7, we have calculated the contribution of dipolelike jumps to the charge-transport process at 570 K. Between 9 and 10 mol % the contribution of dipolelike jumps to the overall conduction process increases from 7% to 77%. Above 10 mol % LaF_3 the charge transport is governed by dipolelike jumps. In the system $Ba_{1-x}La_xF_{2+x}$ in which there is a large majority of NNN dipoles, den Hartog and Langevoort[20] have derived that above 6 mol % LaF_3 the charge transport is governed by dipolelike jumps. In both $Sr_{1-x}La_xF_{2+x}$ and $Ba_{1-x}La_xF_{2+x}$ the concentration, above which only dipolelike jumps govern the charge transport, is about twice as large as the percolation threshold concentration. Unfortunately there are no conductivity data available between 5 and 6 mol % LaF_3 in $Ba_{1-x}La_xF_{2+x}$ and between 9 and 10 mol % LaF_3 in $Sr_{1-x}La_xF_{2+x}$. In these concentration regions both dipolelike and free interstitial jumps contribute significantly to the charge-transport process. This may imply that if the charge transport is governed by dipolelike and free interstitial jumps one should not obtain a linear relationship between $\log_{10}\sigma T$ and $1/T$ in the LaF_3 concentration re-

gions given above. In these concentration regions a simple calculation of activation parameters from conductivity data will probably not be possible.

As a conclusion we can say, although we cannot fit our ionic thermocurrent data to a percolation model, the charge transport in solid solutions of the type $Sr_{1-x}La_xF_{2+x}$ is governed by a percolation mechanism. In addition we can say that the ionic ITC technique is a very useful tool to investigate charge transport mechanisms in ionic superconducting materials complementary to the ionic conductivity technique.

ACKNOWLEDGMENTS

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