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Dielectric-relaxation experiments on cubic solid solutions of SrF_2 and CeF_3 or PrF_3

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In this paper we report results of ionic-thermocurrent (ITC) and dielectric-loss experiments on solid solutions of the types $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$. These solid solutions have the fluorite lattice structure and we have chosen $0 \leq x \leq 0.3$. We have investigated the behavior of the dipole reorientation and the space-charge relaxation bands in the "ITC spectra." During the dielectric-loss experiments we have concentrated our attention on the dipole peaks. The experimental methods employed in this paper enable us to draw conclusions about the defect structure of the solid solutions. It appears that up to relatively high concentrations the defects present are primarily charge compensation centers (nearest-neighbor or next-nearest-neighbor dipoles). Clustering is relatively unimportant, which is in contrast with our recent results obtained for solid solutions of the type $\text{Sr}_{1-x}\text{Yb}_x\text{F}_{2+x}$. This will be discussed in some detail. The space-charge relaxation peak, investigated in detail with the ITC method, shifts to lower temperatures with increasing concentrations of Ce^{3+} or Pr^{3+} . This phenomenon is discussed and explained in terms of a percolation-type conduction model. In this model, jumps of interstitial fluoride ions in the close vicinity of trivalent impurity ions, which have a relatively small activation energy, play an essential role.

I. INTRODUCTION

Charge transport in ionic crystals has been the subject of many investigations.¹⁻⁵ In most investigations ionic conduction experiments have been chosen to elucidate the charge-transport mechanism. The ionic-thermocurrent (ITC) technique has also been used to obtain information about the charge-transport mechanism.⁶⁻⁸ The attention has been focused on the relaxation of space charges building up during the polarization process. In $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ solid solutions with the fluorite structure, the trivalent rare-earth ion (R^{3+}) occupies an alkaline-earth (M^{2+}) position. The excess charge on the rare-earth ion is compensated by an interstitial fluoride ion. If the interstitial ion is in a nearest- or next-nearest-neighbor position with respect to the R^{3+} ion, there is local charge compensation. The geometry of the nearest-neighbor (NN) and the next-

nearest-neighbor (NNN) dipoles in the fluorite lattice has been shown in Fig. 1. If the distance between the R^{3+} ion and the interstitial fluoride ion is larger, there is nonlocal charge compensation. In ITC experiments NN and NNN dipoles give rise to dipole relaxation bands. NN dipole relaxation bands are found at lower temperatures than NNN dipole relaxation bands.⁹ Therefore these bands have often been called low-temperature (LT) and medium-temperature (MT) bands, respectively. The positions of the dipole relaxation bands are independent of the R^{3+} concentration. In $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$, LT and MT bands have been found at 151 and 206 K, respectively.⁹ Free interstitial ions, which provide the nonlocal charge compensation are responsible for the space charges, building up during the polarization stage of the ITC experiment. Opposite from the positive electrode excess interstitial fluoride ions are present, whereas opposite from the negative electrode there is an excess of noncompensated immobile (cubic) trivalent rare-earth ions. Relaxation of the space charges gives rise to a high-temperature (HT) band which shifts to lower temperatures if the R^{3+} concentration increases. The intensity of the space-charge relaxation band is about 2 orders of magnitude larger than the intensity of the dipole relaxation bands. den Hartog and Langevoort⁶ have proposed that the relaxation of space charges in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ occurs by means of two kinds of jumps of interstitial ions: free interstitial jumps and dipolelike jumps, which take place relatively far from a rare-earth ion or in the neighborhood of trivalent impurity centers, respectively. The relaxation time which determines the relaxation process obeys the following relation:

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

where α is the probability for a dipolelike jump to occur,

FIG. 1. Schematic representation of the SrF_2 lattice containing a trivalent rare-earth ion at a substitutional position. The local charge compensation is provided by a NN or NNN interstitial fluoride ion. These charge-compensation centers are referred to as NN or NNN dipoles, respectively.

$E_{a,0}^d$ and $E_{a,0}^f$ are the activation energies for a dipolelike and a free-interstitial jump, respectively, and τ_0^d and τ_0^f are the characteristic relaxation times for these processes. If only dipolelike jumps take place ($\alpha=1$) the kind of dipolelike jumps determines the position of the HT band. In solid solutions $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ there is, even at moderate LaF_3 concentration, a large majority of NN dipoles over NNN dipoles, but the HT band does not shift to temperatures below about 190 K.¹⁰ It has been proposed that the rate-determining step in the dipolelike jump mechanism is the formation of a NNN dipolelike situation followed by a rearrangement to a NN dipolelike situation, which is relatively fast compared to the jump creating the NNN dipolelike situation. The shift of the HT band below the temperature of the NNN dipole relaxation band (219 K) may be ascribed to a considerable increase of the lattice parameter on going to higher LaF_3 concentrations ($a=5.80$ Å for pure SrF_2 and 5.85 Å for $x=0.4$).

It is interesting to investigate solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$, where R^{3+} is between La and Nd in the Periodic Table. In this paper we present ITC and dielectric-loss results on solid solutions $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$. The dielectric-loss technique is a qualified tool for accurate determination of the activation parameters associated with the (dipole) relaxation processes observed. A combination of the ITC and dielectric-loss results has been used to test our assignment of the ITC bands with positions which are independent of the RF_3 concentration (relaxations of NN and NNN dipoles). Special attention will be given to the behavior of the space-charge relaxation ITC band as a function of the CeF_3 and PrF_3 concentration.

II. EXPERIMENTAL PART

Crystal growth and sample preparation have been described elsewhere.^{7,11} CeF_3 and PrF_3 have been obtained from Ventron (99.9% pure). The other chemicals used have the same origin as described by Meuldijk *et al.*⁷ Ce^{3+} and Pr^{3+} concentrations have been determined with the x-ray-fluorescence method. Below about 1 mol % the sensitivity of this method is too low to obtain reliable results. Below 1 mol % we have used the nominal values. ITC measurements have been performed as described in other papers presented by our group.^{7,9,11} We have chosen a heating rate of 0.05 K/sec. The heating rate was controlled by a Leeds and Northrup Electromax III temperature controller connected to a HP 9835B desktop computer (Hewlett-Packard Co.) via an interface which has been constructed in our own laboratory. The linearity of the temperature as a function of time was better than 1%. Dielectric-loss measurements were carried out using a cryostat in which the sample has been mounted, a General Radio model 1615A capacitance bridge and a Princeton Applied Research model 128TM lock-in amplifier operating at 100, 300, 1000, 3000, 10 000, and 30 000 Hz. Temperatures were measured with a copper-constantan thermocouple. Calculations have been carried out with a HP 9835B desktop computer and a Control Data Corp. Cyber 170/760 computer.

FIG. 2. ITC spectra of three different $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ crystals. The peak located at high temperatures in the sample containing 0.092 mol % CeF_3 shifts towards lower temperatures with increasing CeF_3 concentrations. For very large Ce concentrations this space-charge relaxation band approximately coincides with the NNN dipole peak which can be observed in the spectrum of the sample with 1.7 mol % CeF_3 . An interesting feature of the results is also that the NN dipole peak is located at a fixed position (~ 150 K).

III. RESULTS AND DISCUSSION

A. $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$

A survey of ITC results for $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ has been shown in Fig. 2. The band at about 150 K has been ascribed to the relaxation of NN dipoles. The intense band which shifts from about 370 to about 200 K on going from the lowest to the highest CeF_3 concentration originates from the relaxation of space charges building up during the polarization process. The very small band at about 193 K may be ascribed to the reorientation of NNN dipoles.

The relaxation responsible for the ITC bands at 150 and 193 K give also rise to bands in dielectric-loss measurements. The energy dissipation originating from mobile interstitial fluoride ions gives rise to a continuous increase of the dissipation factor with increasing temperature. In

FIG. 3. Results of dielectric-loss experiments of two SrF_2 samples doped with 0.27 or 1.7 mol % CeF_3 . The experiments have been carried out at an excitation frequency of 300 Hz.

Fig. 3 we have shown the dielectric-loss results for $x=0.0027$ and 0.017 at a frequency of 300 Hz. The bands at 226 and 287 K are due to the relaxation of NN and NNN dipoles, respectively. Andeen *et al.*¹² have ascribed the small ITC band at 193 K and the dielectric-loss peak at 287 K measured at a frequency of 300 Hz to the relaxation of clusters. We have observed, however, that for solid solutions with the same composition, the ratio of the displaced charges in the ITC bands at 193 and 150 K is considerably smaller than the ratio of the intensities of the bands in dielectric loss corresponding with the same relaxation processes. In Table I we have compiled the ratio of the displaced charge in the ITC bands at 193 and 150 K and the ratio of the intensities of the corresponding dielectric-loss bands measured at a frequency of 1 kHz for some $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ solid solutions. These observations show that the concentration of the defects responsible for the small ITC band at 193 K increases at the expense of the number of NN dipoles if the temperature increases. The clusters which have been proposed to be responsible for the ITC band at 193 K and the dielectric-loss peak at 287 K measured at 300 Hz contain two immobile rare-earth ions;¹² a shift of the equilibrium between those clus-

TABLE I. Ratio of charges displaced in the ITC bands at 193 and 150 K, ratio of the intensities of the corresponding dielectric-loss peaks at 287 and 226 K measured at a frequency of 300 Hz, and ratio of the concentrations of NNN and NN dipoles calculated from the ratio of the charges displaced in the ITC bands mentioned above for some $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ solid solutions.

Concentration (mol %)	$\frac{Q(193 \text{ K})}{Q(150 \text{ K})}$ (ITC)	$\frac{\tan\delta(287 \text{ K})}{\tan\delta(226 \text{ K})}$	
		(Dielectric loss, 300 Hz)	$\frac{c_{\text{NNN}}^a}{c_{\text{NN}}}$
0.42	0.037	0.046	0.0072
0.68		0.087	
0.70	0.065		0.013
1.3	0.093		0.018
1.7	0.087	0.17	0.017
2.4	0.19	0.32	0.037

^aWe have assumed that in our ITC experiments the equilibrium between NN and NNN dipoles is frozen in at about 193 K.

ters and the NN dipoles in the temperature region considered is very improbable. In an equilibrium between NN and NNN dipoles, however, only interstitial fluoride ions are involved. Shifts of the equilibrium between NN and NNN dipoles have been observed earlier in $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ solid solutions by Aalbers and den Hartog.¹³ The observations in $\text{Sr}_{1-x}\text{Gd}_x\text{F}_{2+x}$ combined with our observations for $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ provide evidence that the ITC band at 193 K and the corresponding dielectric-loss peak should be assigned to the relaxation of an NNN dipole.

For a concentration of 0.42 mol % CeF_3 we have measured the dissipation as a function of the temperature at 0.1, 0.3, 1.0, 3.0, 10, and 30 kHz. From the temperature where the dissipations belonging to the relaxation of NN and NNN dipoles have their maxima and the values of the relaxation times (τ) at these maxima, we have calculated values from the activation energies and the characteristic relaxation times (τ_0) for both relaxation processes using the relation

$$\ln\tau = \ln\tau_0 + \frac{E}{kT} \quad (2)$$

At the temperature where the dissipation factor has its maximum the following relation between τ and the angular frequency (ω) exists:

$$\omega\tau = (\epsilon_s/\epsilon_\infty)^{1/2} \quad (3)$$

For SrF_2 doped with 0.42 mol % CeF_3 we found the following values for the relaxation parameters of two types of dipoles present. For the NN dipoles, $E=(0.46\pm0.01)$ eV and $\tau_0=10^{-13.6\pm0.2}$ sec, and for the NNN dipoles, $E=(0.68\pm0.03)$ eV and $\tau_0=10^{-15.5\pm0.5}$ sec.

In Fig. 4 we have presented two plots; in Fig. 4(a) we have plotted the position of the HT band as observed with ITC as a function of $\log_{10}x$ and in Fig. 4(b) the behavior

FIG. 4. (a) Survey of the results obtained for the position of the space-charge relaxation peak in $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ crystals as a function of $\log_{10} x$. (b) Survey of the results obtained for the width at half-height of the space-charge peak in $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ crystals as a function of $\log_{10} x$.

of the width at half-height of the HT band as a function of $\log_{10} x$ has been given. The shape of these figures shows a strong resemblance with the corresponding ones for the solid solutions $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$.¹⁰ It is striking, however, that for the highest CeF_3 concentration ($x=0.323$) T_{max} of the HT band is 196 K. This temperature is rather close to 193 K, the value of T_{max} of the NNN dipole relaxation band. For $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ the difference between T_{max} of the HT band for the highest LaF_3 concentration ($x=0.411$, $T_{\text{max}}=189$ K) and the position of the NNN dipole relaxation band ($T_{\text{max}}=219$ K) is much larger.¹⁰ An explanation for this difference between the solid solutions $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ may be that the influence of LaF_3 on the lattice parameter of SrF_2 is larger than that of CeF_3 . In

Fig. 5 we have depicted the lattice parameters for solid solutions $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$ ($\text{R}^{3+}=\text{La}^{3+}$, Ce^{3+} , Pr^{3+} , and Nd^{3+}) as a function of the RF_3 concentration. The influence of the lattice parameter on the position of the HT band at very high RF_3 concentrations as well as other characteristic features of the HT band as a function of the RF_3 concentration are now elucidated using the two-jump model for the relaxation of space charges developed by den Hartog and Langevoort for $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ (Ref. 6) and applied successfully in a slightly modified form to the relaxation of space charges in solid solutions $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$ (Ref. 7) and $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$.¹⁰ In this model the charge transport during the relaxation of space charges formed during the polarization process is assumed to be governed by two kinds of jumps of interstitial fluoride ions: (a) free jumps occurring relatively far from a rare-earth ion, and (b) dipolelike jumps occurring in the direct neighborhood of a trivalent rare-earth ion. We note that *not all* jumps of interstitial fluoride ions occurring in the neighborhood of a trivalent impurity contribute to the conduction process. This is most clearly illustrated by the fact that for samples containing 5 mol % Ce or Pr we observe an NN and an NNN dipole peak, indicating that the corresponding jumps do not contribute to the conductivity process. In general one can say that in order to contribute to the conduction process a dipolelike jump should meet some extra requirements, which are taken care of by the percolation model. It may be obvious that the probability of a dipolelike jump, α , increases with increasing RF_3 concentration. Although in some cases α is rather small, the dipolelike jumps govern completely the conduction process because the relaxation time associated with dipolelike jumps is much smaller than the relaxation time of free interstitial F^- jumps. At very high RF_3 concentrations ($x>0.3$) only dipolelike jumps occur ($\alpha=1$). For $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ we have explained that, although there are

FIG. 5. Results of x-ray determinations of the lattice parameter as a function of the R^{3+} concentration for various solid solutions of the type $\text{Sr}_{1-x}\text{R}_x\text{F}_{2+x}$ ($\text{R}=\text{La}$, Ce , Pr , or Nd).

far more NN than NNN dipoles, the rate-determining step for a dipolelike jump is the formation of an NNN dipolelike situation, which rearranges very quickly to a more stable NN dipolelike situation. Using this model one should expect that at very high LaF_3 concentrations ($x > 0.3$, $\alpha = 1$), $T_{\max}$ of the HT band and $T_{\max}$ of the NNN dipole relaxation band should be the same within a few K. Experimentally a difference of about 30 K between both values of $T_{\max}$ has been observed [$T_{\max}(\text{HT}) = 189$ instead of 219 K]. This deviation has been explained by reasoning that for concentrations higher than about 10 mol % changes of the relaxation parameters due to an increased lattice constant are responsible for the relatively large difference between $T_{\max}$ of the NNN dipole relaxation band, observed at low and moderate LaF_3 concentrations, and the value of $T_{\max}$ of the HT band at the highest LaF_3 concentration investigated. For $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ this difference is much smaller and also the influence of the lattice parameter of the SrF_2 lattice is

smaller. These observations for $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ support our explanation of the experimentally observed difference between $T_{\max}$ of the HT band for $x > 0.3$ and $T_{\max}$ of the HT band in solid solutions $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$.

For a calculation of the HT-band positions ($T_{\max}$) and the linewidths at half-height ($\Delta T_{1/2}$) as a function of α we have substituted Eq. (1) in the following expression for the depolarization current as measured with the ITC method:

$$I(T) = \frac{dP}{dt} = B \left[\exp \left[- \int_0^T \frac{dT'}{b\tau(T')} \right] \right] / \tau(T), \quad (4)$$

where b is the heating rate during the ITC experiment and B is the charge displaced during the depolarization process. Taking the first derivative of the resulting equation with respect to the temperature (T) equal to zero we obtain the following expression for the temperature at which the depolarization current has its maximum:

$$(T_{\max})^2 = \frac{b \left[\frac{(1-\alpha)E_{a,0}^f}{\tau_0^f} \exp \left[- \frac{E_{a,0}^f}{kT_{\max}} \right] + \frac{\alpha E_{a,0}^d}{\tau_0^d} \exp \left[- \frac{E_{a,0}^d}{kT_{\max}} \right] \right]}{\left[\frac{1-\alpha}{\tau_0^f} \exp \left[- \frac{E_{a,0}^f}{kT_{\max}} \right] + \frac{\alpha}{\tau_0^d} \exp \left[- \frac{E_{a,0}^d}{kT_{\max}} \right] \right]^2}. \quad (5)$$

[The square in the denominator of Eq. (5) has been omitted in our previous paper on $\text{Sr}_{1-x}\text{Nd}_x\text{F}_{2+x}$ (Ref. 7) as a result of a typing error.]

For $\alpha = 0$ and $b = 0.05$ K/sec with $E_{a,0}^f = 1.22$ eV and $\tau_0 = 7.0 \times 10^{-15}$ sec, we have calculated $T_{\max} = 375$ K and $\Delta T_{1/2} = 23$ K, which values are in very good agreement with the experimentally observed values for very low CeF_3 concentrations. Because the NN dipoles, which are the dominant defects in the samples with low and moderate CeF_3 concentrations, are only partly dissociated at the temperatures at which the depolarizations take place; the following equation holds for $E_{a,0}^f$, as discussed in our paper on $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ solid solutions:¹⁰

$$E_{a,0}^f = \frac{1}{2} E_{\text{diss}} + 0.94. \quad (6)$$

Here E_{diss} is the dissociation energy of the NN dipoles. The value 0.94 eV has been substituted for the activation energy of the hopping process of completely dissociated interstitial fluoride ions as determined by Bollmann *et al.*² We derive a value of 0.56 eV for the dissociation energy of NN dipoles, which is a reasonable value for the dissociation energy of NN dipoles. As discussed earlier¹⁰ E_{diss} decreases to some extent with increasing CeF_3 concentrations as a result of the interaction of the free defects with their surrounding charge clouds as described by Lidiard who applied Deybe-Hückel theory to nonideal solid solutions.¹⁴ In our calculations we have neglected this decrease of E_{diss} , because it is very difficult to estimate this decrease as a function of α .

Because at the highest CeF_3 concentration investigated $T_{\max}$ of the HT band (equal to 196 K) is only a few degrees higher than the value of $T_{\max}$ of the MT band (equal

to 193 K) which has been observed at rather low and moderate CeF_3 concentrations, it seems to be reasonable that the rate determining step of a dipolelike jump is the formation of a NNN dipolelike situation, which may eventually rearrange relatively fast to a NN dipolelike situation. The ratio of the numbers of these two configurations is determined by the equilibrium between NN and NNN dipoles which exists in the samples investigated. In our calculations we have used values for the relaxation parameters $E_{a,0}^d$ and τ_0^d which are, within experimental error, identical to the relaxation parameters of the NNN dipole relaxation in the sample containing 0.42 mol % CeF_3 as determined from the dielectric-loss measurements at different frequencies (see Table II), and which result in $T_{\max} = 193$ K for $\alpha = 1$: $E_{a,0}^d = 0.66$ eV and $\tau_0^d = 4.0 \times 10^{-16}$ sec.

There is qualitative agreement between the experimentally observed behavior of $T_{\max}$ and $\Delta T_{1/2}$ as a function of the CeF_3 concentration and the behavior of the calculated values of $T_{\max}$ and $\Delta T_{1/2}$ as a function of α . The relaxation mechanism given in Eq. (1) leads to a very characteristic maximum for the linewidth of the HT relaxation peak. This maximum becomes more pronounced for increasing differences between the activation energies $E_{a,0}^d$ and $E_{a,0}^f$. It is not possible to explain the observed behavior of the linewidth with a simple relaxation mechanism of the form

$$\tau = \tau_0 e^{E/kT}, \quad (7)$$

where the value of E decreases gradually with increasing Ce concentrations.

In our calculations we have neglected the broadening of

TABLE II. Ratio of charges displaced in the ITC bands at 180 and 151 K and the ratio of the concentrations of NNN and NN dipoles derived from the ratio of the charges displaced in the ITC bands mentioned above for some $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ solid solutions.

Concentration (mol %)	$\frac{Q(180 \text{ K})}{Q(151 \text{ K})}$	$\frac{c_{\text{NNN}}^a}{c_{\text{NN}}}$
	(ITC)	
0.063	0.040	0.0077
0.14	0.045	0.0087
0.32	0.10	0.019
0.78	0.096	0.019
1.4	0.084	0.016
1.7	0.13	0.025
2.6	0.17	0.033

^aWe have assumed that in our ITC experiments the equilibrium between NN and NNN dipoles is frozen in at about 180 K.

activation energies due to defect-defect interactions as described by van Weperen and den Hartog.⁹ This may be the reason for the difference between the observed maximum of $\Delta T_{1/2}$ (equal to 42 K) for 4.7 mol % CeF_3 and the calculated maximum of $\Delta T_{1/2}$ (equal to 35 K) for $\alpha = 6 \times 10^{-9}$. Also an inhomogeneous distribution of the Ce^{3+} ions in the samples may be the reason for this difference. An inhomogeneous distribution of R^{3+} ions in the samples should have a much smaller influence on the values of T_{max} .

We have obtained a relation between the probability of a dipolelike jump to occur and the CeF_3 concentration by comparing the experimentally observed relation between the CeF_3 concentration and T_{max} of the HT band and the calculated behavior of T_{max} as a function of α . From Fig. 6, where we have shown the relation between the CeF_3 concentration (x) and the probability for a dipolelike jump to occur (α) we derive that α increases very quickly above 1–2 mol % CeF_3 . These observations indicate that the charge transport in these solid solutions is supported by a percolation mechanism. A quantitative description of this percolation mechanism is hampered strongly because NN

FIG. 6. Relation between the concentration of the Ce^{3+} ions and the value of α .

dipoles dissociate, whereas NNN dipoles are formed in the rate-determining step of the dipole formation. Secondly, the decrease of E_{diss} with increasing CeF_3 concentration plays a role. These considerations have been discussed thoroughly for $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$.¹⁰

B. $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$

The results obtained for $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ are similar to those found for the system $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$. Here too we have observed one dipole relaxation peak (NN) and one space-charge band in samples with low concentrations of Pr^{3+} impurities. If the impurity content is increased we observe a second dipole relaxation peak (the NNN band). The two dipole peaks, which are located at fixed positions, are found in $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ at 151 and 180 K. The difference between $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ is that the NNN dipole band in the latter system is observable at relatively low Pr^{3+} concentrations; this has been demonstrated by the results compiled in Table II, which is readily comparable with Table I.

The space-charge peak in $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ is located at about the same temperature as in $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ for low R^{3+} concentrations, indicating that the dissociation energy of the dipolar complexes in the two systems is approximately the same. For very large Pr^{3+} concentrations (~ 0.3) the space-charge peak in $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ is located at 183 K, which is again very close to the position of the NNN dipole relaxation band in dilute materials.

By means of dielectric-loss measurements we have determined the relaxation parameters of the two different dipolar complexes in $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$. This has been done by measuring the relaxation spectra for six different excitation frequencies: 100, 300, 1000, 3000, 10000, and 30000 Hz. For the NN dipole we find $E = (0.46 \pm 0.01)$ eV and $\tau_0 = 10^{-13.5 \pm 0.2}$ sec. For the NNN dipole the corresponding values are (0.58 ± 0.01) eV and $10^{-14.2 \pm 0.1}$ sec.

In conclusion we can say that the solid solutions $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ behave very similarly. For small values of x the position and width of the space-charge relaxation band are determined by the jump energy of free interstitial fluoride ions and the dissociation energy of NN-type dipoles. With increasing values of x the value of T_{max} decreases, because "dipolelike" jumps contribute more and more to the ionic conductivity process. For very large concentrations of Ce or Pr dipolelike jumps govern the conductivity process. It is important to note that instead of the NN dipoles the NNN complexes are very important in this concentration range; firstly because, as mentioned above, as a result of dipole-dipole interactions the concentration ratio $c_{\text{NNN}}/c_{\text{NN}}$ increases with increasing R^{3+} concentrations, and secondly, because NNN dipoles are larger and consequently the percolation threshold is lower than for NN complexes.

A slight difference between the results obtained for $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ and $\text{Sr}_{1-x}\text{Pr}_x\text{F}_{2+x}$ is that for very large R^{3+} concentrations the space-charge peak in the former solid solutions is located at higher temperatures. This can be explained by two reasons: First, the NNN dipole peak in Pr-doped materials is located at 181 K, while the corresponding band in $\text{Sr}_{1-x}\text{Ce}_x\text{F}_{2+x}$ is situated at 193 K; the

second reason may be that with increasing concentrations of RF_3 the lattice is perturbed significantly more strongly in the case of $Sr_{1-x}Ce_xF_{2+x}$ than for the system $Sr_{1-x}Pr_xF_{2+x}$. This can be deduced from the behavior of the lattice parameter as a function of the R^{3+} concentration (see also Fig. 5). In both cases, $Sr_{1-x}Ce_xF_{2+x}$ and $Sr_{1-x}Pr_xF_{2+x}$, the space-charge relaxation peak approximately coincides with the NNN dipole peak, if x is large ($x \approx 0.3$). This is strong evidence for the correctness of the model proposed for the ionic conductivity in solid solutions of the type $M_{1-x}R_xF_{2+x}$.

IV. SUMMARY

The solid solutions $Sr_{1-x}Ce_xF_{2+x}$ and $Sr_{1-x}Pr_xF_{2+x}$ studied in this paper are comparable with the system $Sr_{1-x}La_xF_{2+x}$ studied earlier.¹⁰ Clustering is relatively unimportant and R^{3+} - F_i^- dipoles exist up to relatively high R^{3+} concentrations. As a consequence dipolar jumps are very important for the description of the conductivity process at these concentrations. This description is in contrast with that of solid solutions of the type $Sr_{1-x}Yb_xF_{2+x}$, which have been investigated quite recently by Meuldijk and den Hartog.⁸ It was shown by these authors that clustering in $Sr_{1-x}Yb_xF_{2+x}$ is of major importance for Yb concentrations higher than about 0.1 mol %.

It appears that the ionic conductivity of $Sr_{1-x}La_xF_{2+x}$, $Sr_{1-x}Ce_xF_{2+x}$, and $Sr_{1-x}Pr_xF_{2+x}$ can be described by a percolation model, which has been proposed by den Hartog and Langevoort.⁶ In this model the crystals are subdivided into two materials: (a) the insulating "perfect fluorite crystal," and (b) highly conducting spheres each con-

taining a rapidly reorienting dipole. With increasing R^{3+} concentrations the total volume of the "conducting" material increases and this leads, especially for R^{3+} concentrations higher than a few mol %, to a rapid increase of the ionic conductivity as a function of x .

The detailed defect structure varies as a function of the concentration of R^{3+} ions. In the materials investigated in the present paper we have found evidence supporting the ideas proposed by Aalbers and den Hartog.¹³ In both $Sr_{1-x}Ce_xF_{2+x}$ and $Sr_{1-x}Pr_xF_{2+x}$ the ratio of the concentrations of NN and NNN dipoles varies significantly as a function of the concentration of R^{3+} ions. The relative concentration of the NNN dipoles increases with increasing values of x . This behavior can be understood by assuming that the energy of the above-mentioned dipole systems does not have unique value; there appears to be a distribution of energies because of the defect-defect interactions.

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