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Electric dipole-dipole interaction in $\text{CaF}_2 : \text{R}^{3+}$ and $\text{SrF}_2 : \text{R}^{3+}$: Results of ITC and EPR experiments

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Résumé. — Le travail concerne des concentrations totales de R^{3+} entre 0,02 et 6 % mol. ! Les centres de compensation de charge localisée ont été étudiés au moyen de la RPE, de l'influence d'un champ électrique sur RPE et TCI. On trouve que :

- i) des échanges dipôle-dipôle modifient de façon significative la forme des courbes TCI même à des concentrations modérées de R^{3+} ;
- ii) à des concentrations plus élevées ($> 0,1$ % mol.), des échanges dipôle-dipôle modifient la structure des défauts, par exemple le $\text{SrF}_2 : \text{Gd}^{3+}$. Des grandes variations du quotient des concentrations des centres de compensation de charge tétraonaux et trigonaux (= premiers voisins et seconds voisins, respectivement) ont été observées comme fonction de la concentration totale des Gd^{3+} ;
- iii) les dipôles permanents associés aux centres de compensation de charge exercent une influence sur les paramètres du champ cristallin de l'ion Gd^{3+} dans les cristaux du type fluorite.

Abstract. — The present study deals with total R^{3+} concentrations ranging from about 0.02 to 6 Mol. % ! The different types of local charge compensation centers have been investigated by means of EPR, electric field effect in EPR and ITC and it was found that :

- i) dipole-dipole interactions significantly modify the shape of the ITC-curves even at moderate R^{3+} concentrations ;
- ii) at higher concentrations (> 0.1 Mol. %) dipole-dipole interaction changes the defect structure of for example $\text{SrF}_2 : \text{Gd}^{3+}$. Large variations of the ratio of the concentrations of tetragonal and trigonal (= n.n. and n.n.n., respectively) charge compensators have been observed as a function of the total Gd^{3+} concentration ;
- iii) the permanent electric dipoles associated with the charge compensation centers influence the crystal field parameters of the Gd^{3+} -ion in fluorite type crystals.

The alkaline earth fluorides CaF_2 , SrF_2 and BaF_2 are known to show interesting ionic conduction phenomena in the temperature range ($T_m - 100$ to 200 °C) — T_m (where T_m is the melting temperature). For pure samples in this temperature region the ionic conductivity is comparable to that of liquids. The behaviour of the conductivity as a function of temperature is described theoretically by classical models; i.e. $\sigma/T = \alpha \cdot \exp(E/kT)$. As for most ionic materials the activation energy measured for CaF_2 , SrF_2 and BaF_2 in the intrinsic region is of the order of 1 eV. In the temperature region of interest the behaviour of the ionic conductivity is quite different from that in the intrinsic region. Like for liquid electrolytes the variations of the conductivity with temperature are much smaller; if we associate an activation energy with the behaviour of the conductivity as a function of temperature we would find values of the order of 0.1 eV.

Croatto and Bruno [1], using the X-ray diffraction technique, obtained evidence that at temperatures

close to the melting point SrCl_2 shows a high degree of disorder. Later many authors have investigated this phenomenon. The experimental techniques employed for these investigations are : ionic conductivity, specific heat, NMR, neutron diffraction and Raman spectroscopy [2]. Particularly, the experiments carried out by Dworkin and Bredig [3] show that some of the fluorite type materials go through an order-disorder transition well below T_m .

In order to obtain more information about super-ionic alkaline earth halides it is important to study concentration effects caused by defect-defect interactions. We have shown that even at moderate concentrations of about 0.1 Mol. % appreciable changes of the depolarization dynamics may be observed resulting in a broadening of the ITC peaks associated with dipoles [4, 5]. This broadening can be described assuming that the activation energy connected with the reorientation jumps form a Gaussian distribution. The width of the distribution function is determined by the interaction between the dipoles. Van Weperen

et al. [4] have found for the dipole system $\text{SrF}_2 : \text{Ce}$ that at a concentration of 5×10^{18} dipoles/cc the width of the distribution is about 6×10^{-3} eV; i.e. about one half of kT at T_{max} (= the temperature at which the maximum depolarization current occurs)!

At higher concentrations (> 0.5 Mol. %) clustering may become more and more important and some evidence for the existence of different types of clusters has been obtained in the literature [3, 6, 7]. With ITC and EPR we have observed changes in the defect structure at R^{3+} -concentrations higher than 0.1 Mol. %, but we did not find any support for the proposals dealing with clustering of dipoles.

Our experimental results obtained by EPR and ITC of $\text{SrF}_2 : \text{Gd}$ suggest that the energy levels of the dipoles are broadened more and more resulting in a change of the ratio of the concentration of n.n. and n.n.n. dipoles (tetragonal and trigonal dipoles, respectively); at about 200 K the concentration ratio is about 20 and it decreases for concentrations of 3.5×10^{19} Gd cm^{-3} to 2.2 [8]!

It is the purpose of the present paper to present results covering the concentration range between about 0.01-6 Mol. % R^{3+} impurities in CaF_2 or SrF_2 . The consequences for the interpretation of the phenomenon fast-ion-conduction will be discussed.

In CaF_2 , SrF_2 and BaF_2 doped with R^{3+} -ions one observed two different kinds of these charge compensators : n.n. and n.n.n. dipoles. An other possible type of charge compensation is the so-called non-local charge compensation. In the latter case one deals with free F^- -interstitials and unperturbed cubic R^{3+} impurities. It has been established that the interstitials are the mobile entities, that provide for the ionic conductivity. The trivalent impurities are more or less immobile up to rather high temperatures and consequently they do not contribute significantly to the ionic conductivity of these materials. It appears that both types of charge compensation : i.e. local and non-local charge compensation are of importance for the interpretation of the ITC results.

Let us confine ourselves for a moment to the system $\text{SrF}_2 : \text{La}^{3+}$. At low concentrations one observes one reorientation peak which is located at approximately 150 K. It has been established that this peak is due to n.n. dipoles. The ITC peak can usually be fitted with the Bucci formula [9].

The modified ITC peak formula, to be employed for higher concentrations, has been given for the first time by van Weperen *et al.* [4]. The broadening parameter obtained from these ITC experiments appears to be linear with the concentration (see Fig. 1). At increased La^{3+} concentrations ($c > 0.1$ Mol. %) an additional ITC peak develops at about 205 K; i.e. the same position as the peak associated with n.n.n. dipoles in SrF_2 . This result is in contrast with those reported by Lenting *et al.* [10] and van Weperen *et al.* [4] who found that no n.n.n. dipoles could be

Fig. 1. — Plot of the experimental width of the dipole-dipole interaction energy distribution as a function of the dipole concentration.

detected in SrF_2 crystals doped with the trivalent rare earth impurities La, Ce, Pr, Nd and Sm. From the experimental results it becomes clear that we may be dealing with a concentration effect. A similar concentration effect has been observed by Aalbers and den Hartog [8].

An additional concentration effect occurs when the amount of La^{3+} is increased to more than 1.5 %. This effect has been illustrated in figure 2 and it can be seen that at concentrations higher than 1.5 Mol. % a new intense ITC peak develops at temperatures between 200 and 300 K. An interesting feature of the new peak is that the position depends strongly upon the La-concentration. The peak position shifts continuously to lower temperatures with increasing concentration. The n.n. and n.n.n. dipole peaks on the contrary have fixed positions.

The changes of the high temperature peak cannot be described by the modified ITC formula because the broadening parameter p does not lead to a change in the ITC peak position (see also van Weperen *et al.* [4]). The variations in the peak position of the high temperature peak are probably due to gradual changes in the jump mechanism associated with the depolarization effect.

A second feature of the high temperature peak, and which is shown clearly by figure 2 is the very large intensity of this depolarization phenomenon. This large intensity may be due to very large dipole concentrations or to large dipole moments. Comparing the high temperature peak with those due to n.n. and n.n.n. dipoles we calculate that : or the concentration should be about $5 \times 10^{22} \text{ cm}^{-3}$ or the dipole length should be 65 Å !

It is possible to introduce cubic Gd^{3+} -ions into SrF_2 if simultaneously LaF_3 is added. When sufficient amounts of LaF_3 are added the local charge compensation centers with Gd^{3+} of both types (n.n. and n.n.n.) are suppressed completely. Probably, the La^{3+} impurities are efficient F_i^- -traps, which are capable to attract in some cases more than

Fig. 2. — ITC spectra of various $\text{SrF}_2 : \text{La}^{3+}$ crystals showing the shift of the high temperature (h.t.) peak. Note that the dipole peaks n.n. and n.n.n. are located at a fixed position.

one interstitial fluoride ion. This property can be used to investigate the effect of the $\text{La}^{3+}-\text{F}_i^-$ dipolar complexes on the EPR spectrum of cubic Gd^{3+} probes which had been added to the sample.

It appears that the $-5/2 \leftrightarrow -7/2$, $-3/2 \leftrightarrow -5/2$, $-1/2 \leftrightarrow -3/2$, $3/2 \leftrightarrow 1/2$, $5/2 \leftrightarrow 3/2$ and the $7/2 \leftrightarrow 5/2$ transitions show a broadening effect that depends linearly upon the concentration. In figure 3 we have plotted the behaviour of the $3/2 \leftrightarrow 1/2$, $5/2 \leftrightarrow 3/2$ and the $7/2 \leftrightarrow 5/2$ transition as a function of the concentration and it is obvious that the slopes of the three lines are different. The slopes of the straight lines indicated by 1/2, 3/2 and 5/2, which are associated with the $3/2 \leftrightarrow 1/2$, $5/2 \leftrightarrow 3/2$ and the $7/2 \leftrightarrow 5/2$ transition, respectively, give the following ratio 1 : 1.8 : 3.0 which is close to 1 : 2 : 3. The latter ratio is expected if the broadening is due to

Fig. 3. — The linear relationships between the linewidths of three EPR lines of cubic Gd impurities in $\text{SrF}_2 : \text{La}$ and the concentration of LaF_3 . The transitions $5/2 \leftrightarrow 7/2$, $3/2 \leftrightarrow 5/2$ and $1/2 \leftrightarrow 3/2$ are denoted by 5/2, 3/2 and 1/2, resp.

second degree crystal field perturbations of statistical nature.

Our experimental results allow us to draw the following conclusions :

i) At high concentrations the dissociation of the defects takes place at lower temperatures. In this way the interstitial fluoride ions may form space charges even at rather low temperatures.

ii) The defect structure (i.e. the ratio of n.n. and n.n.n. dipoles) is affected significantly by dipole-dipole interactions. This conclusion agrees with the one drawn from the experimental results obtained by Aalbers and den Hartog [8].

iii) The space charge ITC peak can not be described in a way similar to that of the usual dipole-peaks.

iv) The conductivity of the samples doped with large concentrations of R^{3+} impurities is of significance for the intensity of both the dipole and the h.t. peaks.

v) The broadening of the EPR lines with increasing R^{3+} concentrations can be explained by a dominant statistically varying second degree crystal field. This extra crystal field may be due to electrostatic interaction between the $4f^7$ electron configuration with distant defects as discussed by Bijvank *et al.* [11] and Lefferts *et al.* [12].

DISCUSSION

Question. — J. J. FONTANELLA.

Is it possible that the appearance of a nnn dipolar relaxation at high dopant concentrations could be due to the presence of a small rare earth impurity in the dopant material ?

Reply. — H. W. DEN HARTOG.

It is possible that the rare earth impurities are contaminated with other trivalent impurities. We used 99.9 % pure materials. The reason why we associate the peak at T_{nnn} with nnn La³⁺-F_i⁻ dipoles is that we have also observed a similar dramatic increase of (with EPR observable) Gd³⁺-F_i⁻ dipoles of the nnn-type in SrF₂ for increased Gd³⁺ concentrations.

Question. — P. W. LEVY.

What do you believe to be the physical arrangement in the crystal that produces the distribution of activation energies ?

Reply. — H. W. DEN HARTOG.

The distribution of activation energies is, as I have said, due to interactions with distant dipoles. Consider the reorienting dipole to be located at the centre of a sphere in which we have somewhere another dipole. This additional dipole can have different orientations. Using this formation one can construct a histogram of the resulting activation energies (= difference between the energies associated with the equilibrium position and the saddle point). See also :

VAN WEPEREN, W. *et al.*, *Phys. Rev.* **B 16** (1977) 2953.

Question. — M. BÖHM.

In your opinion the broadening of ionic thermal current (ITC) peaks is caused by the dipole-dipole interaction — the energy contribution is only about one magnitude smaller than the activation energy even at high dipole densities. What do you think about the idea that the broadening is due to a temperature dependent frequency factor which involves both an entropy term and a contribution of lattice frequencies ?

Reply. — H. W. DEN HARTOG.

The broadening model as proposed here for the ITC activation energy has also been employed for the association energy of dipoles in SrF₂ (I have mentioned this in my talk), but they have also been used to describe results of ionic conductivity experiments (paper p. C6-220 of this meeting) in a wide range of temperatures. In all these cases the broadening model works quite well. Therefore I am confident that this model is all right.

Question. — W. A. EDGAR.

We have observed (*) dielectric relaxation in SrF₂ : Gd³⁺ and observe a relaxation peak wider than a Debye curve. However the width of the peak is temperature independent, which is incompatible with a distribution of activation energies. Do you have any comment on this ?

Reply. — H. W. DEN HARTOG.

We are fairly confident about this broadening model. Without any more specific details I cannot answer this question.

(*) *J. Phys. C*, 1979, February.

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