ITC-EXPERIMENTS ON SrCl₂ : RE

E. J. BIJVANK and H. W. DEN HARTOG

Solid State Physics Laboratory, 1 Melkweg, Groningen, The Netherlands

Résumé. — Nous avons étudié par ITC des monocristaux de SrCl₂ contenant des pourcentages différents de terres rares. Nos mesures montrent que quand nous augmentons la concentration des terres rares les cations monovalents et les anions divalents sont compensés, puis, à concentration en ions trivalents de terres rares plus élevée, des paires de Cl⁻ en positions interstitielles et de terres rares substitutionnelles sont formées. Au moins trois types de dipôles Cl⁻ interstitiel + ion de terre rare substitutionnelle ont été observés. Nous avons indiqué ces dipôles par I, II et III.

Chaque dipôle donne une raie de ITC avec la forme :

$$\frac{d\sigma}{dt} = N_{dip} \cdot \frac{p^2 \, \alpha E_p}{k T_p} \cdot \frac{1}{\tau_0} \cdot \exp\left(-\frac{E}{kT}\right) \cdot \exp - \left[\int_0^T \frac{\exp\left(-\frac{E}{kT'}\right)}{b\tau_0} \, dT' \right] \tag{1}$$

comme il a été montré par Bucci *et al.* Les ions de terres rares étudiés sont La, Ce, Nd, Gd, Tb, Dy, Ho, Tm, Yb et Y. Les paramètres E et τ_0 pour les trois types de dipôles varient entre 0,90-0,77 eV et 3×10^{-14}-10^{-12} s, respectivement pour la raie I, entre 0,86-0,71 eV et 3×10^{-14}-10^{-11} s, respectivement pour la raie II, et entre 0,80-0,59 eV et 3×10^{-14}-10^{-9} s, respectivement pour la raie III. Si nous chauffons de 0,055 K/s, nous trouvons que les positions pour les raies I, II et III sont (288 ± 6) K, (276 ± 6) K et (262 ± 4) K respectivement.

Abstract. — ITC-signals of SrCl₂ single crystals with different levels of rare earth doping were studied. Our measurements show that with increasing RE-concentration first the monovalent cations and divalent anions which are present as impurities are compensated, whereas at higher concentrations of trivalent rare earth ions pairs of interstitial Cl⁻-ions and substitutional RE-ions are formed. At least three types of dipoles consisting of an interstitial Cl⁻ and a substitutional RE-ion are observed. They are referred to as dipoles I, II and III. Each of these dipoles gives rise to an ITC-peak of the form

$$\frac{d\sigma}{dt} = N_{dip} \cdot \frac{p^2 \, \alpha E_p}{k T_p} \cdot \frac{1}{\tau_0} \cdot \exp\left(-\frac{E}{kT}\right) \cdot \exp - \left[\int_0^T \frac{e^{-E/kT'}}{b\tau_0} \, dT' \right] \tag{1}$$

as described by Bucci *et al.* The RE-ions investigated are La, Ce, Nd, Gd, Tb, Dy, Ho, Tm, Yb and Y. The parameters E and τ_0 for the three kinds of dipoles are found to vary between 0.90-0.77 eV and 3×10^{-14}-10^{-12} s, respectively for peak I, between 0.86-0.71 eV and 3×10^{-14}-10^{-11} s, respectively for peak II and between 0.80-0.59 eV and 3×10^{-14}-10^{-9} s, respectively for peak III. For a heating rate of 0.055 K/s the ITC-peak positions for dipoles I, II and III were found to be (288 ± 6) K, (276 ± 6) K and (262 ± 4) K, respectively.

1. Introduction.

SrCl₂ crystallizes in the so-called fluorite (CaF₂) structure. The chlorine ions form a simple cubic sub-lattice. The centers of the cubes are alternatively occupied by Sr⁺⁺-ions. It can be seen very easily that the Sr⁺⁺-ions form an FCC sub-lattice (see Fig. 1).
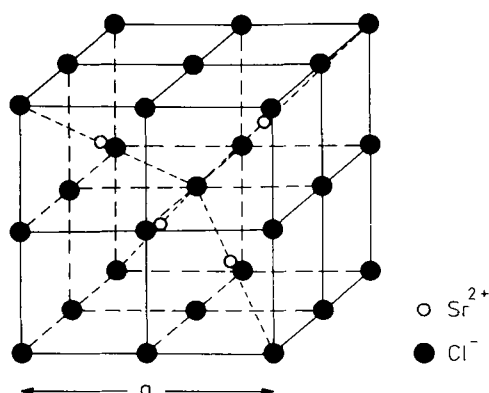

FIG. 1. — Schematic representation of the SrCl₂ lattice.

If trivalent rare earth ions (RE³⁺) are introduced substitutionally one obtains additional interstitial chlorine ions because of the electroneutrality condition. The formation of cation vacancies is energetically less favorable. If on the other hand monovalent cations like Na⁺ or K⁺ or divalent anions like O²⁻ are added for the same reasons anion vacancies are created. It will be shown in this paper that the trivalent rare earth impurities form dipoles together with the interstitial anions. Furthermore, the O²⁻ ions will attract anion vacancies which results in the formation of O²⁻-anion vacancy dipoles.

Dielectric relaxation of dipoles in ionic crystals is usually studied by means of dielectric loss experiments using a wide range of frequencies. The ITC-method developed by Bucci *et al.* [1], [2] proved to be an attractive alternative because of the relatively simple set-up. Basically this method is very similar to thermoluminescence.

A crystal containing dipoles comprised of RE³⁺ and an interstitial chlorine ion is polarized by means

of a static external electric field E_p at some polarization temperature T_p. The orientational polarization resulting from differences in the populations of the otherwise equivalent interstitial Cl^--positions can be frozen-in by cooling down to LN_2 temperature. During heating at an approximately constant rate each type of dipole present in the crystal gives rise to a well defined peak in the depolarization current. This current is due to reorientational jumps of the interstitial Cl^--ions. The shape and position of the peaks provide information about the activation energy for jumps of the dipoles. Furthermore, characteristic jump rates (τ_0) are obtained.

2. Experimental results and discussion. — Figure 2 shows the ITC-curve of a nominally pure $SrCl_2$ single

Fig. 3. — ITC-curve of $SrCl_2$: 0.1 % Ho polarized for 5 min at room temperature with an electric field of 10 000 V/cm.

characteristic jump rate τ_0 and the temperature at which the maximum current occurs (T_m). A typical result of the computer fitting together with the experimentally observed peak II in $SrCl_2$: Ho is shown in figure 4. The results of the calculations for peaks I, II

Fig. 4. — ITC-peak II of $SrCl_2$: 0.1 % H_0 obtained after peak-cleaning-procedures had been applied. A small residual contribution due to peak I at the high temperature side of peak II can be observed.
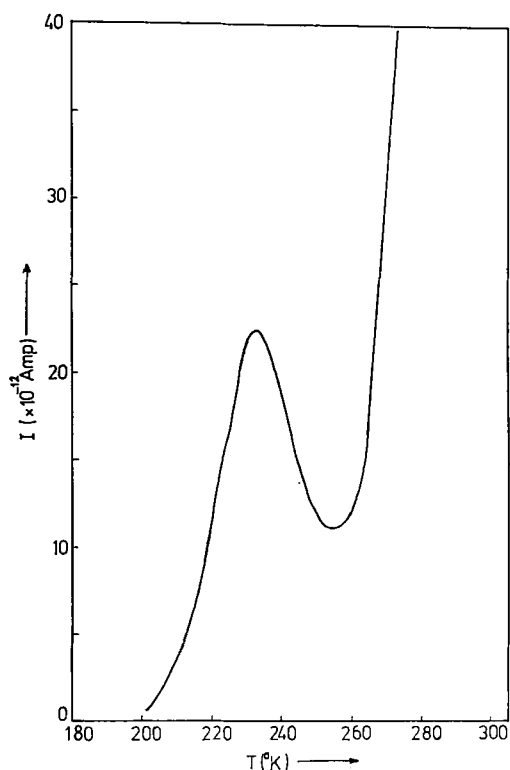

Fig. 2. — ITC-curve of a nominally pure $SrCl_2$ crystal polarized for 5 min at room temperature with an electric field of 10 000 V/cm.

crystal. The currents are probably due to the release of space charges. It was observed that in crystals doped very slightly with O^{2-}-ions the peaks are enhanced by several orders of magnitude. When on the other hand trivalent RE-ions are added the peak is reduced and a new ITC-peak is formed (see Fig. 3). Detailed investigations have shown that this new ITC-peak consists of four separate peaks which can be resolved by means of « peak-cleaning-procedures ». Three of them are related with RE-ions (peaks I, II and III) while peak IV may be related with O^{2-}-ions.

For all the observed ITC-curves computer fits of the form given in eq. (1) were obtained. These fits provided the parameters E (activation energy), the
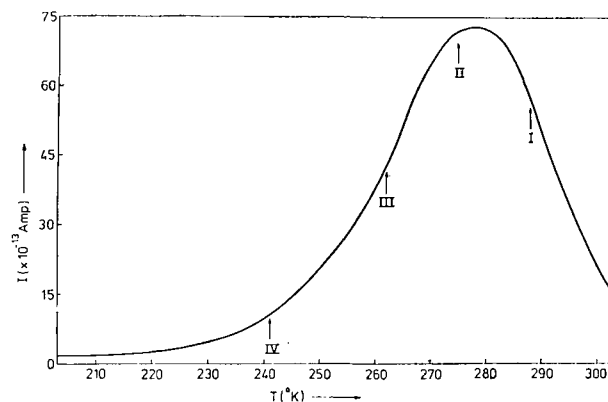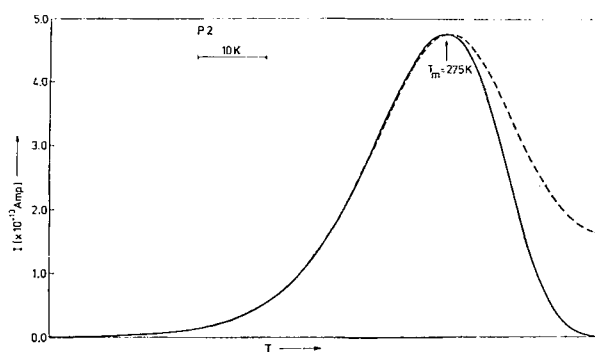
and III corresponding with the various RE-ions are shown in tables I, II and III, respectively. The activation energies given in the tables correspond to jumps of the interstitial chlorine ions to equivalent positions.

TABLE I

Experimental parameters for peak I *in* $SrCl_2$: RE^{3+}

Dopant	$\hat{\varepsilon}$ (eV) (*)	τ_0 (s)	T_m (K)
Y^{3+}	0.85	3×10^{-13}	289
La^{3+}	0.90	3×10^{-14}	289
Nd^{3+}	0.86	8×10^{-14}	282
Gd^{3+}	0.89	6×10^{-14}	289
Ho^{3+}	0.77	6×10^{-14}	288
Tm^{3+}	0.80	2×10^{-12}	289
Yb^{3+}	0.78	7×10^{-12}	290

(*) The experimental accuracy of $\hat{\varepsilon}$ is 0.02 eV.

TABLE II

Experimental parameters for peak II *in* $SrCl_2$: RE^{3+}

Dopant	$\hat{\varepsilon}$ (eV) (*)	τ_0 (s)	T_m (K)
Y^{3+}	0,71	2×10^{-11}	277
La^{3+}	0.86	3×10^{-14}	277
Ce^{3+}	0,75	7×10^{-12}	281
Nd^{3+}	0.81	2×10^{-13}	272
Gd^{3+}	0.75	4×10^{-12}	277
Tb^{3+}	0,75	6×10^{-12}	280
Dy^{3+}	0.79	3×10^{-13}	270
Ho^{3+}	0,71	2×10^{-11}	275
Tm^{3+}	0.74	6×10^{-12}	277
Yb^{3+}	0.76	2×10^{-12}	273

(*) The maximum error of $\hat{\varepsilon}$ is 0.02 eV.

TABLE III

Experimental parameters for peak III *in* $SrCl_2$: RE^{3+}

Dopant	$\hat{\varepsilon}$ (eV) (*)	τ_0 (s)	T_m (K)
Y^{3+}	0,67	3×10^{-11}	262
La^{3+}	0.61	4×10^{-10}	264
Ce^{3+}	0.72	3×10^{-12}	264
Nd^{3+}	0.59	1×10^{-9}	265
Gd^{3+}	0.81	3×10^{-14}	260
Tb^{3+}	0.70	5×10^{-12}	260
Dy^{3+}	0.75	5×10^{-13}	259
Ho^{3+}	0.70	7×10^{-12}	262
Tm^{3+}	0.77	2×10^{-13}	261
Yb^{3+}	0.68	7×10^{-12}	258

(*) The maximum error in $\hat{\varepsilon}$ is 0.02 eV.

From the tables it follows that the values for T_m of the three peaks is fairly constant for all rare earth ions investigated :

$$T_m (I) = (288 \pm 6) \text{ K} ,$$

$$T_m (II) = (276 \pm 6) \text{ K} \quad \text{and} \quad T_m (III) = (262 \pm 4) \text{ K}.$$

The values for E however turn out to vary considerably while τ_0 changes over several orders of magnitude.

Although we tried to relate the variations in E and τ_0 with the ionic properties of the lanthanide ions we did not find any correlation between these two parameters and the ionic radius, mass and ionization energy of the RE-ions. There is however an exponen-

tial relationship between E and τ_0 which has the form

$$\tau_0 = \tau_0' \, e^{\alpha E} . \tag{2}$$

The relationship between the various ITC-peaks was studied by means of quenching experiments. It was observed that for most of the rare earth ions quenching from temperatures higher than 250 °C produces changes in the relative intensities of the peaks. In general peak I is reduced while peaks II and III increase. Moreover it was found that there is no appreciable increase of the integrated current indicating that the effect of coagulations of RE-ions if there is any can be neglected. From the above results we tentatively propose the following models for the dipoles I, II and III.

Dipole I consists of a rare earth ion at a Sr^{++}-site and a nearest neighbour interstitial site the distance between the RE-ion and the interstitial chlorine is $\frac{1}{2} a$ (where a is the lattice parameter). Dipoles II and III also contain a RE-ion and an interstitial Cl^--ion but the distance between the two ions is $\frac{1}{2} a \sqrt{3}$ and $\frac{1}{2} a \sqrt{5}$, respectively. It is interesting to note that the RE-ions corresponding with dipoles I, II and III have C_{4v}, C_{3v} and orthorhombic symmetry, respectively.

In general the jump energies for $SrCl_2$ are twice as high as compared with the corresponding values obtained for CaF_2 [3], [4]. Unfortunately, no ionic conductivity results of $SrCl_2$: RE^{3+} from which conclusions about the activation energy of motion of free anion interstitials can be drawn are available yet. There are however indications that anion vacancies in $SrCl_2$ are far more mobile than the Cl^- interstitials.

No ITC-peaks similar to the other RE-doped crystals could be observed in samples with Fe, Er, Eu and Sc. It is highly probable that the majority of these ions is present in $SrCl_2$ in the divalent state. This is supported by EPR results for Eu obtained in our laboratory which show very intense signals due to Eu^{2+} having cubic symmetry. Furthermore, Fe^{3+} would give EPR signals at room temperature because it is an S-state ion with usually long enough relaxation times. No EPR-signals were observed indicating that the Fe-ions are present in the divalent state which is a non S-state. Finally, it was observed that the trivalent RE-ions can be reduced to the divalent state by additive coloration. After this treatment no ITC-peaks due to RE-ions and interstitial anions (peaks I, II and III) are present. Instead the ITC-signals observed are very similar to the one characteristic for pure $SrCl_2$.

References

[1] Bucci, C. and Fieschi, R., *Phys. Rev.* **148** (1966) 816.
[2] Bucci, C. and Fieschi, R., *Phys. Rev. Lett.* **12** (1964) 16.
[3] Stott, J. P. and Crawford, J. H., *Phys. Rev. Lett.* **26** (1971) 384.
[4] Royce, B. S. H. and Mascarenhas, S., *Phys. Rev. Lett.* **24** (1970) 98.

DISCUSSION

K. ZIEROLD. — Is it possible, that one of the measured ITC-peaks is not due to a dipole but due to point charge defects (like vacancies), which have been press to one electrode ? The peak then should come from the depolarisation of this local vacancy concentration by heating.

H. W. DEN HARTOG. — We don't think so because the RE ions will suppress the concentration of anion vacancies. Moreover the ITC-curves induced by space charges cannot be described by the ordinary dipole mechanism. Our results indicate that the peaks are due to proper dipoles.

A. D. FRANKLIN. — With respect to the trigonal center you have reported in ITC and preliminary EPR measurements, other trigonal centers have been observed in both CdF_2 and CaF_2 doped with rare earth ions. For instance, oxygen in both crystals forms a complex center containing anion vacancies as well. This center has been studied using EPR in both CdF_2 and CaF_2 and very recently Kitt and Crawford reported on some ITC studies. It is very necessary to apply other techniques as well to confirm that the observed peak really does arise from the rare earth ions with associated fluorine interstitial ions in next-nearest neighbour sites.

H. W. DEN HARTOG. — I agree with you that the assignation of the trigonal center is not unambiguous. More experiments (especially ENDOR) are needed to confirm our interpretation.