

Point defects in NaCl : NaF : Pb⁺⁺ single crystals (*)

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Résumé. — Les cristaux de chlorure de sodium, dopés avec des anions F⁻ et des cations divalents analysés par la technique de thermocourant ionique (I.T.C.) présentent trois nouveaux pics de relaxation indépendants et bien définis, B, C et D. La nature microscopique des défauts qui donnent lieu aux relaxations dipolaires observées n'est pas connue mais elle est due à l'interaction entre les ions F⁻ et Pb⁺⁺. La température des maxima des pics B, C et D est inférieure à celle des ions divalents isolés (pic A) tel que $T_D < T_C < T_B < T_A$. La cinétique d'aggrégation des ions Pb⁺⁺ et F⁻ a été mesurée à la température ambiante; elle est bien décrite par la réaction $Pb^{++} + F^- \rightarrow B + C$. Le pic D ne change pas d'intensité au cours de cette mesure.

Abstract. — Sodium chloride crystals doped with F⁻ anions and divalent cations as impurities show three new well defined independent relaxation peaks, B, C and D when analysed by ionic thermocurrent technique (I.T.C.). The microscopic nature of the defects that give rise to the observed dipolar relaxation is not known. Peaks B, C and D have their maxima in temperatures below that of the isolated divalent ion (peak A) such that $T_D < T_C < T_B < T_A$. The aggregation kinetics between Pb⁺⁺ and F⁻ ions was measured at R.T. and is well described by the reaction $Pb^{++} + F^- \rightarrow B + C$. Peak D does not change in intensity during this process.

Sodium chloride single crystals doped with fluoride anions and divalent ions such as Pb⁺⁺, Zn⁺⁺, Sn⁺⁺, Eu⁺⁺ and Mn⁺⁺ show new defect centers detected by the use of the ionic thermocurrent I.T.C. in a usual way [1]. In a recent paper several optical and electrical properties of these crystals doped with Pb⁺⁺ were described [2]. It is well known that in a quenched NaCl crystal doped only with one specie of divalent ion one prominent I.T.C. peak occurs in a temperature around 215 K due to the impurity vacancy dipole reorientation. If these quenched crystals are maintained at temperatures above R.T. the intensity of the I.T.C. peak decrease due to diffusion of I.V. dipole giving rise to aggregates whose electric dipole moment is zero (dimers, trimers, etc.).

However if NaCl single crystals are doped simultaneously with F⁻ anions (actual concentration in the crystal in the range of 10⁻³ molar fraction, as measured by chemical analysis) and divalent ions (concentration in the 10⁻⁴ molar fraction range, as measured by the integrated area of the I.T.C. spectrum) three new prominent I.T.C. peaks occur in the quenched crystals. The new peaks occur in temperatures below 215 K, therefore below that due to the unperturbed impurity vacancy dipole. The four well defined I.T.C. peaks found in these crystals we called A, B, C and D, their maxima occurring in the following temperatures 216 K, 155 K, 126 K and 104 K respectively. Figures 1 and 2 show the I.T.C.

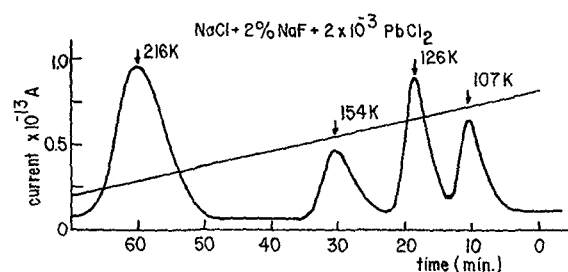


Fig. 1. — I.T.C. spectrum of a NaCl 1 % NaF doped with Pb⁺⁺ after fast quenching from 720 °C. The straight line is the sample temperature.

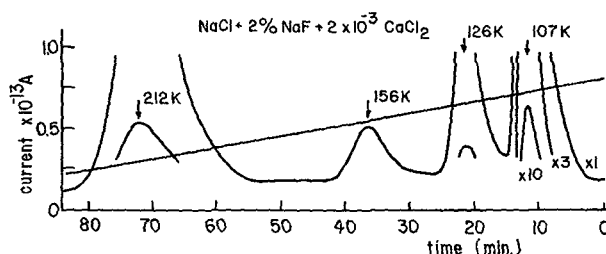


Fig. 2. — Same as figure 1 but for NaCl 0.1 + NaF doped with Ca⁺⁺.

spectrum for two different divalent ions, Ca⁺⁺ and Pb⁺⁺.

A microscopic model for the defects responsables for peaks B, C and D are not yet available partly because the I.T.C. technique does not provide information on the defect symmetry in a cubic crystal.

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However several properties of the defects are already known. The relaxation parameters are closely independent of the divalent ion nature. This means that the temperature where the I.T.C. maximum occurs is independent of divalent ion doping the NaClNaF crystal. Particularly the D peak has its maximum in the same temperature for all crystal we studied. If NaClNaFPb⁺⁺ crystals are heat treated at temperatures around R.T. peaks B and C grow, peak A decreases and peak D keeps constant. Peak D decays only if the crystal is treated at temperatures higher than 90 °C. The relative intensity of peaks A, B, C and D, in a crystal quenched from 720 °C, depends on the divalent ion nature and on the F⁻ and M⁺⁺ concentrations. The peak most sensitive to divalent ion nature is the peak B, being extremely small in Zn⁺⁺ doped crystal.

Table I shows the results obtained by annealing at R.T. a NaClNaF crystal doped with Pb⁺⁺ ions. It shows clearly that the primary products of the divalent ion aggregation with the F⁻ anions are peaks B and C. The same process can be followed optically because a new optical absorption band at 262 nm grows as a result of this aggregation. From table I it can be seen that the sum of integrated area below peaks A, B and C, (A + B + C) is a constant indicating that peaks B and C are due to defects with same electric dipole moment as the unperturbed impurity vacancy dipole. Table II shows results of similar experiments but with a crystal having much higher divalent ion concentration. In this experiment peak A decreases while peaks B and C grow but the sum A + B + C decreases. In this situation aggregation between divalent ions (not involving F⁻ ions) should be occurring. An intermediate situation was also observed. The sum A + B + C was constant only during the first 15 hrs in a crystal whose Pb⁺⁺ concentration was nearly 2.5 times that of the table I.

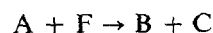
Table I. — *Aggregation Process in NaCl crystal doped with F⁻ and Pb⁺⁺ ions at 300 K. F⁻ concentration = 1.3×10^{-3} M.F. (measured by chemical analysis). Pb⁺⁺ concentration = 2.4×10^{-4} M.F. (measured by chemical analysis).*

Time hours	Polarization $\sigma = Np^2 E/3 kT_p$ in C/m ² $\times 10^7$						
	A	B	C	D	A + B + C	C/B	$\frac{A - 36}{A}$
0.0	75	40	85	74	200	2.12	0.52
1.5	62	42	88	72	192	2.09	0.42
3.0	58	49	96	76	203	1.96	0.38
5.0	54	50	100	77	204	2.00	0.33
8.0	46	51	101	78	198	1.98	0.22
12.0	42	54	104	77	200	1.92	0.14
16.0	40	55	108	77	203	1.96	0.10
26.0	36	56	109	77	201	1.95	
31.5	33	56	108	75	197	1.93	
45.5	33	55	108	76	196	1.96	

Table II. — *Aggregation Process in NaCl crystal doped with F⁻ and Pb⁺⁺ ion at R.T. F⁻ concentration = 1.6×10^{-3} M.F. Pb⁺⁺ concentration = 5.5×10^{-4} M.F.*

Time hours	Polarization = $\frac{Np^2 E}{3 kT}$ in C/m ² $\times 10^7$						
	A	B	C	D	A + B + C	C/B	
0.0	397	55	79	88	531	1.44	
2.0	345	68	102	88	515	1.50	
6.5	311	77	131	90	519	1.70	
14.5	294	85	137	86	516	1.61	
23	263	92	145	87	500	1.58	
37.5	225	100	158	88	483	1.58	
131.5	135	111	169	90	415	1.52	
169.0	135	103	166	88	404	1.61	

If we assume that aggregation between Pb⁺⁺ and F⁻ ions is described by the reaction



where we described the trapping of the Pb⁺⁺ ion by F⁻ anions without back reaction, the following equation can be written

$$\frac{dn}{dt} = -\beta n f. \quad (1)$$

In this equation n and f are the concentration of the unperturbed Pb⁺⁺ \boxplus dipole and isolated F⁻ anions respectively and β a constant depending on the annealing temperature. The solution of this simple equation is

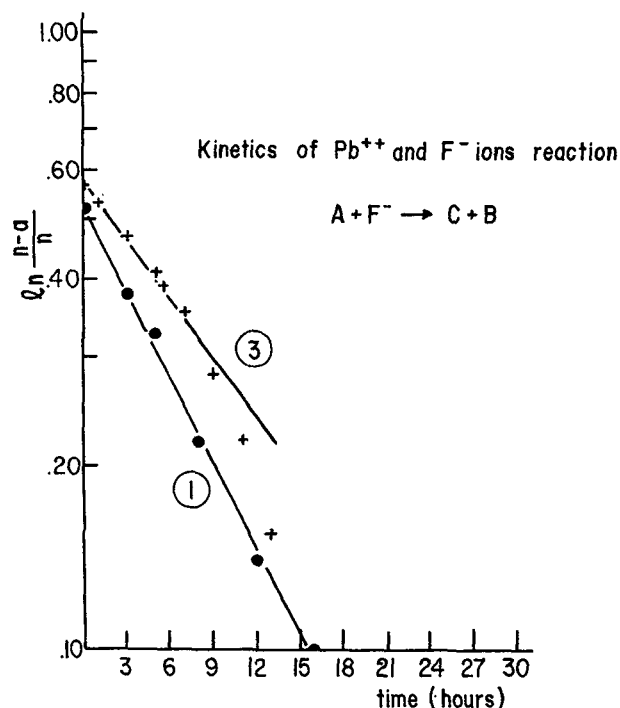
$$+ \ln \frac{f_0}{n_0} - \ln \frac{n - a}{n} = a\beta t \quad (2)$$

where n_0 and f_0 are the initial values of n and f respectively and $a = n_0 - f_0$. Figure 3 show how the data on table I is described by the above equation.

Tables I and II show that the ratio between peaks C and B are different being smaller for higher divalent ion concentration.

The following conclusions can be taken from the above results. Peak B, C and D are caused by three independent microscopic defects. Defects B and C have the same dipole moment as the Pb⁺⁺ \boxplus dipole. As peak C appears in all the studied systems we tentatively identify it as one Pb⁺⁺ \boxplus dipole having one fluorine anion as a close neighbour. This defect configuration satisfy the condition that the aggregation between Pb⁺⁺ \boxplus dipole and the F⁻ anion keeps constant the electric dipole moment of the defect.

The possibility that peaks B and C are due to different relaxations of a same defect or defects in equilibrium, is discarded because the ratio between the intensity of peaks B and C is not constant.



At this stage of the knowledge of this problem a speculative discussion for the model of the microscopic defects would involve defect aggregates, trapping of defects at dislocations, vacancy pairs $\oplus\ominus$, and the formation of $(MF)^+$ molecular ion. An interesting difference between these defects is that peak D is generated only if crystals are quenched from high temperatures while peaks B and C can be generated at R.T.

The anelastic properties of these crystals and the electro induced optical dichroism of the Pb⁺⁺ and Sm⁺⁺ doped samples are under study.

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Fig. 3. — Kinetics of Pb⁺⁺ and F⁻ reaction. Curve 1 is the plot of data of table I according with the equation (2) with $n_0 = 75$; $f_0 = 39$; $a = 36$. Curve 3 is a plot of data obtained from experiments where the sum $A + B + C$ was not constant.

References

- [1] CAPELLETTI, R. and DE BENEDETTI, E., *Phys. Rev.* **165** (1968) 981.
- [2] PINATTI, D. M. G., ZILIO, S. C. and DE SOUZA, M., Point Defects in NaCl doped with divalent ions. Accepted to be published *Phys. Status Solidi* (b) **94** (1979).