

# ITC measurements on sodium fluoride doped with Mg+2 D. Triantis

## ► To cite this version:

D. Triantis. ITC measurements on sodium fluoride doped with Mg+2. Journal de Physique, 1984, 45 (11), pp.1751-1753. <10.1051/jphys:0198400450110175100>. <jpa-00209916>

# HAL Id: jpa-00209916 https://hal.archives-ouvertes.fr/jpa-00209916

Submitted on 1 Jan 1984

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Classification Physics Abstracts 77.30

### ITC measurements on sodium fluoride doped with $Mg^{+2}(*)$

D. Triantis

Department of Physics, University of Athen, Solonos str. 104, Athen, Greece

(Reçu le 13 avril 1984, accepté le 24 juin 1984)

**Résumé.** — On a mesuré le courant thermoionique (ITC) d'un monocristal de NaF, dopé avec 50 ppm de  $Mg^{+2}$  et préchauffé. Le spectre ITC de ce cristal a été décomposé en deux bandes, avec les maximums à 236 K et 251 K ; elles correspondent à des enthalpies de migration  $h^m$  de 0,78 et 0,83 eV et à des entropies  $s^m$  de migration de 2,1 K et 2,6 K. Le rapport  $s^m/h^m$  est comparable à celui d'autres processus (de formation ou de migration de défauts) et à une estimation théorique.

Abstract. — Ionic thermocurrent measurements ITC were carried out on NaF doped with 50 ppm Mg<sup>+2</sup>. The ITC spectrum of a preheated crystal consists of two bands with maximum at 236 and 251 K. The analysis of these bands leads to a migration enthalpy  $h^m$  of 0.78 and 0.83 eV and to a migration entropy  $s^m$  of 2.1 and 2.6 K respectively. The value of the ratio  $s^m/h^m$  is comparable to the results of other processes (formation and migration) and is comparable to theoretical expectations.

#### 1. Introduction.

The migration parameters of the cations and anions in alkali fluorides avec known with less accuracy than those of the other alkali halides because of greater experimental difficulties. Furthermore, the parameters of the dipoles formed when aliovalent impurities are introduced into alkali fluorides are still unknown or at best uncertain for various combinations of the host crystal and impurities. Among other sodium halides, sodium fluoride exhibits a large interest because it has the highest melting point (1 265 K) and because the exact positions of the vacancies in respect to that of the aliovalent impurity have not yet been established with certainty.

The present paper studies the reorientation parameters of the dipoles formed in NaF doped with small amounts of  $Mg^{+2}$  (concentration 50 ppm). The parameters are derived from the thermally stimulated depolarization current (TSDC), alternately called the ionic thermocurrent (ITC) [1-3].

#### 2. Experimental.

The sample single crystal of NaF with 50 ppm  $Mg^{+2}$  was mounted in a cryostat between platinum elec-

trodes and the depolarization current was measured with a Carry 401 vibrating electrometer. The NaF crystal was kept under a vacuum of  $10^{-5}$  torr. An electric field of about 8.5 kV/cm was applied at a temperature  $T_p = 245$  K. After applying the field the crystal was cooled down to liquid nitrogen temperature; then the field was switched off and the sample was heated up to room temperature with a rate of 0.08 K/s.

The ITC spectrum of a sample that was preheated to 600 K for 6 h is shown in figure 1. It consists of two bands with maxima at 236 and 251 K. A computer fitting was made according to the relation :

$$J = \sum_{i=1}^{2} J_{i} = \sum_{i=1}^{2} \frac{P_{0i}}{\tau_{0i}} \exp\left[-\frac{h_{i}^{m}}{kT} - (b\tau_{0i})^{-1} \times \int_{T_{0}}^{T} \exp\left(-\frac{h_{i}^{m}}{kT'}\right) dT'\right]$$
(1)

where J is the depolarization current density,  $P_{0i}$  is the initial polarization, b is the heating rate and  $T_0$ denotes temperature from which the tail of the ITC spectrum starts.

In deriving equation (1) the following Arrhenius relation was assumed :

$$\tau = \tau_0 \exp\left(\frac{h^{\rm m}}{kT}\right) \tag{2}$$

<sup>(\*)</sup> This is a partial fulfillment of Ph. D. thesis of the author to the University of Athen.



Fig. 1. — ITC-spectrum of NaF :  $Mg^{+2}$ . The open circles denote experimental values. The squares (**n**) and solid circles (**o**) depict the contribution of the two mechanisms as they result from a computer fitting. The solid curve is the sum of the values (**n**) and (**o**) calculated for the two mechanisms.

where  $\tau$  denotes the relaxation time for the dipole reorientation process,  $h^{\rm m}$  the migration enthalpy for the bound cation vacancy motion and  $\tau_0$  the usual pre-exponential factor.

#### 3. Discussion.

In table I we give the values of  $h^{\rm m}$  and  $\tau_0^{-1}$  for two bands along with the values determined by previous workers. We attribute the two bands to jumps of a bound cation vacancy around the divalent impurity from nearest neighbour positions (nn) to nn or next nearest positions (nnn) [7]. In the same table we include the migration entropies  $s^{\rm m}$  [6] according to the formula [8, 9] :

$$s^{\rm m} = -k \ln\left(\lambda . \tilde{v} . \tau_0\right) \tag{3}$$

where  $\tau_0$  is the experimentally determined value,  $\lambda$  indicates the number of orientations of the dipole in the space and  $\tilde{v}$  is the frequency [6, 10] of the moves in the direction of the potential well. The latter is usually taken equal to  $v_{TO}$ , i.e. to the transverse optical mode frequency.

In the present case  $\lambda$  has been taken equal to 4 corresponding to a nn or nnn position of the vacancy in respect to the divalent cation.

By comparing the migration enthalpy values for the two mechanisms we see that their difference lies anyhow beyond experimental error; the corresponding  $\tau_0^{-1}$ -values follow the same sequence i.e. the higher  $\tau_0^{-1}$ -factor corresponds to the mechanism having the higher migration enthalpy.

We feel that the present experimental results are not fortuitous as they agree with the following theoretical expectations : according to a recent suggestion of Varotsos and Alexopoulos [6, 8, 9] the values of  $s^{\rm m}$  and  $h_{\rm exp}^{\rm m}$  for a certain mechanism cannot be independent; their ratio is pre-determined from the anharmonic properties of the host lattice according to :

$$\frac{s^{\mathrm{m}}}{h_{\mathrm{exp}}^{\mathrm{m}}} = -\frac{1}{B_{0}^{\mathrm{SL}}} \cdot \left(\beta B + \frac{\partial B}{\partial T}\Big|_{p}\right) \cdot \exp \int_{0}^{T} \beta \, \mathrm{d}T \qquad (4)$$

where  $\beta$  is the volume thermal expansion coefficient, *B* the isothermal bulk modulus and  $B_0^{SL}$  the bulk modulus of the harmonic crystal. According to their suggestion, equation (4) should hold not only for the free cation and anion motion but also for bound vacancy motion irrespective of the kind of the impurity added to the host crystal.

They also suggest that the parameters for the formation of a Schottky defect should have the same ratio as the migration parameters.

In order to examine the validity of equation (3) we give in table I the values of  $s^m$  and  $h^m$  for the motion

Process	<i>h</i> (eV)	$\tau_{0}(s)$	s (k-units)	Ref.
Schottky	2.56		9.86	[a]
formation	2.42		7.54	[b]
Anion vacancy migration	1.54		6.5	[a]
Cation vacancy dipole orientation with ITC-technique				
Ca <sup>+2</sup>	$0.86~\pm~0.02$	$10^{-15}$	3.7 ± 1	[c]
Ca <sup>+2</sup>	$0.86 \pm 0.02$	$10^{-15}$	$4.25 \pm 1$	[d]
Mg <sup>+2</sup> nn	0.78 ± 0.01	$(4.0 \pm 2.0) \times 10^{-15}$	$2.1 \pm 0.6$	present
Mg <sup>+2</sup> nnn	$0.83 \pm 0.01$	$(2.7 \pm 1.3) \times 10^{-15}$	$2.6 \pm 0.6$	work

Table I. — Defect entropies and enthalpies in NaF; (see the text).

[a]: Ref. [4]; from the fitting of the ionic conductivity curve without considering long range electrostatic interactions.

[b] : Values given in Ref. [4] when electrostatic interactions are included.

[c] : Ref. [5]; the entropy value has been extracted by setting  $\tilde{v}$  equal to the Debye frequency.

[d] : Ref. [5]; assuming  $\tilde{v} = v_{TO}$ .

of the host cation and anion along with that of the dipoles formed in NaF with other impurities studied previously. Instead of calculating the ratio  $s^m/h^m$  individually for each mechanism we plot in figure 2 for various cases  $s^m$  versus  $h^m$  and find the corresponding slope by making a least square fitting to a straight line. This procedure is an unbiased check of equation (3) as we solely use experimental data from various sources extracted from different experimental techniques. The calculation gives the straight line drawn in figure 2 i.e. a slope value equal to  $2.94 \times 10^{-4} \text{ K}^{-1}$  with a correlation coefficient 0.95. The intercept is



Fig. 2. — Defect entropies *versus* defect enthalpies for various processes in NaF :  $\Box$  Schottky formation process; × anion vacancy migration;  $\circ$  ITC spectrum of NaF + Ca<sup>+2</sup>;  $\blacktriangle$  present work.

quite small i.e.  $3.36 \times 10^{-5}$  eV/K which practically is around zero if one recalls that its exact value depends on the value of the  $\tilde{v}$  that was arbitrarily selected equal to  $v_{TO}$ .

By using the elastic and expansivity data [11] we find that the second member of equation (4) has a value equal to  $2.7 \times 10^{-4} \text{ K}^{-1}$  which is practically constant in the temperature range at which the present experiment was carried out.

This value can be favourably compared to the slopevalue of figure 2.

This shows that not only  $s^m$  scales with  $h^m$  for a given material but also that their ratio is actually governed by properties of the host crystal.

To summarize, the ITC spectrum of NaF :  $Mg^{+2}$  consists of two superimposed single bands. The resulting migration enthalpies are (0.78  $\pm$  0.01) eV and (0.83  $\pm$  0.01) eV.

Furthermore by assuming  $\tilde{v} = v_{TO}$  the migration entropies are (2.1 ± 0.6) k and (2.6 ± 0.6) k respectively.

For the two mechanisms the ratios  $s^{m}/h^{m}$  agree within 15%; these values are comparable to the ratio for other processes (formation and migration) in agreement to a recent thermodynamical model.

#### Acknowledgments.

The author would like to express his indebtedness to Prof. P. Varotsos and K. Alexopoulos for their very useful discussions.

#### References

- [1] BUCCI, C., FIESHI, R. and GUIDI, G., Phys. Rev. 148 (1966) 816.
- [2] BUCCI, C., Phys. Rev. 164 (1967) 1200.
- [3] RADHAKRISHNA, S. and HARIDOSS, S., in Crystal Lattice Defects 7 (1978) 191-207.
- [4] BAUER, C. F. and WHITMORE, D. H., Phys. Status Solidi 37 (1970) 585.
- [5] VAROTSOS, P., KOSTOPOULOS, D. and MOURIKIS, S., Phys. Status Solidi (a) 57 (1980) 331.
- [6] VAROTSOS, P. and ALEXOPOULOS, K., Phys. Status Solidi (b) 110 (1982), Review article p. (9-31).

- [7] DREYFUS, R. W., Phys. Rev. 121 (1961) 1675.
- [8] VAROTSOS, P. and ALEXOPOULOS, K., J. Phys. Chem. Solids 41 (1980) 443.
- [9] VAROTSOS, P. and ALEXOPOULOS, K., J. Phys. Chem. Solids 42 (1981) 409.
- [10] VAROTSOS, P. and ALEXOPOULOS, K., in Thermodynamics of Point Defects and their Connection to Bulk Properties (North Holland) 1984 (in press).
- [11] VALLIN, J., MARKLUND, K., SIKSTRÖM, J. O. and BECKMAN, O., Ark. Fys. 32 (1966) 515.