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R. Capelletti, A. Gainotti. IONIC THERMOCONDUCTIVITY AS A METHOD TO STUDY NUCLEATION OF THE SUZUKI PHASE IN KCl: Pb AND IMPURITY CLUSTERS IN LiF: Be. Journal de Physique Colloques, 1976, 37 (C7), pp.C7-316-C7-321. 10.1051/jphyscol:1976774 . jpa-00216934

**HAL Id: jpa-00216934**

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Submitted on 4 Feb 2008

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## IONIC THERMOCONDUCTIVITY AS A METHOD TO STUDY NUCLEATION OF THE SUZUKI PHASE IN KCl : Pb AND IMPURITY CLUSTERS IN LiF : Be

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**Résumé.** — La versatilité de la technique ITC a été exploitée pour analyser :

- 1) les cinétiques de nucléation et de croissance d'occlusions d'une phase séparée aux dépens des dipôles lacune-impureté (L. I.) dans KCl : Pb, entre 420-500 K ;
- 2) la relaxation relative, du type Maxwell-Wagner, qui donne naissance à la grosse bande ITC-B ;
- 3) la structure des occlusions qui vient tentativement identifiée par la phase de Suzuki ;
- 4) la taille des occlusions qui paraît être celle d'une baguette ;
- 5) la grosse bande ITC qu'on observe du côté des hautes températures ( $T > 273$  K) dans la courbe ITC après trempe du LiF : Be dans l'intervalle de température  $100 \leq T_a \leq 700$  °C et qui peut être liée à des amas d'impuretés autour des dislocations.

**Abstract.** — The ITC technique versatility has been exploited to analyze :

- 1) the kinetics of the nucleation and growth of segregated phase occlusions at the expense of impurity-vacancy (I. V.) dipoles in KCl : Pb in the annealing temperature range 420-500 K ;
- 2) the related Maxwell-Wagner-like relaxation which originates the huge ITC-B band ;
- 3) the structure of the occlusions, which is tentatively identified as the Suzuki phase ;
- 4) the shape of the occlusions which turned out to be rod like.
- 5) the huge ITC band which appears in the high temperature ( $T > 273$  K) side of the ITC plot upon annealing LiF : Be in the temperature range  $100 \leq T_a \leq 700$  °C and which can be related to impurity clouds surrounding dislocations.

**1. Introduction.** — When divalent cation impurities are added to alkali halide crystals, solid solutions are obtained in which the thermodynamical equilibrium concentration of simple impurity defects is a function of the annealing temperature (see Fig. 1a). However, the equilibrium concentration  $n_{a,s}$  at a given annealing temperature  $T_a$  can be attained in the annealing time  $t_a$  in two different ways : through a precipitation process or through a dissolution process. In the former case (see the upper curve in Fig. 1b) the defects, introduced in excess by a quenching from a temperature  $T_q > T_a$ , leave the supersaturated solid solution by producing small clusters. In the latter the preexisting precipitates, formed at the temperature  $T_0 < T_a$ , are dissolved during the annealing at  $T_a$  of the unsaturated solid solution (see lower curve in figure 1b).

From the careful kinetics analysis of both processes one can learn informations about the nature of the precipitates. In the case of the former process, the kinetics analysis in early stage is expected to throw light on the first precipitation products. The meaning of the apparent third order kinetics observed by means of different techniques in most of the alkali halides doped with different divalent cations, has been discussed for

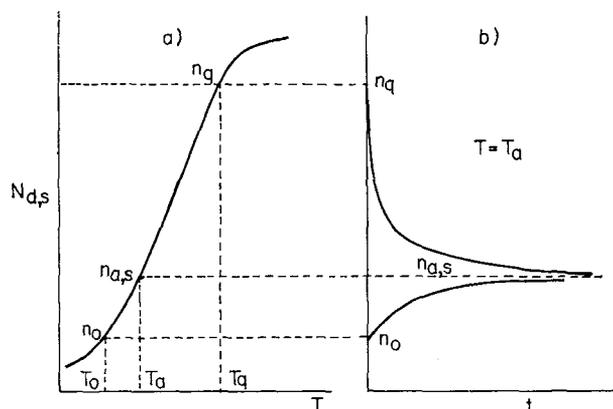


FIG. 1. — a) Solubility curve versus annealing temperature ; b) Precipitation vs annealing time (upper curve) and dissolution curve (lower curve).

long time. Infact the trimer which Cook and Dryden assumed as the simplest precipitation product, due to the observed third order kinetics, appeared less probable than the dimer [2, 3]. In several systems a more careful interpretation of the third order kinetics gave evidence for dimer formation during the early stage of precipitation. This happens when a diffusion controlled

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dimerization takes place [4] or the thermodynamical equilibrium concentration at  $T_a$  is no longer negligible with respect to the actual dipole concentration [1] or the back reaction, namely the solution of freshly formed dimers cannot be neglected as well [5, 6].

The dissolution process, which was studied at less extent, can be described by the superposition of monomolecular first order kinetics [7]: in the case of NaCl : Cd, for instance, two stages were found in which freshly formed aggregates are easily dissolved (fast stage) while the dissolution of large, hard aggregates require long annealing times (slow stage) [8].

The Ionic Thermoconductivity (ITC) [9], which was used extensively in other and in our laboratories, has given a substantial contribution to the understanding of the precipitation and dissolution processes [1]. Infact, thanks to its high sensitivity, the I. V. dipole concentration can be monitored with high accuracy and small amount of precipitates, which exhibit a dipole moment, can be detected as well. Moreover the measurements are performed at low temperatures, where the dissolution and precipitation processes are quenched. Recently the technique was applied to study the solution and precipitation phenomena in matrices other than alkali halides, as in CdF<sub>2</sub> doped with Eu<sup>3+</sup> [10].

In this work the versatility of the ITC technique has been exploited to study some different aspects of the solution-precipitation problem and to analyze the meaning of the huge ITC bands which cannot be ascribed to the relaxation of simple ionic dipoles. We are concerned with interfacial polarization phenomena which arise 1) from the nucleation of a segregated phase (possibly the Suzuki phase) in KCl : Pb and 2) from clouds of impurities possibly around dislocations.

**2. Experimental details.** — The KCl : Pb samples were obtained in the following ways. Some were grown in our laboratory by means of the Kyropoulos method in a controlled atmosphere in order to minimize the contamination by OH<sup>-</sup>, H<sub>2</sub>O and oxygen, which affect the precipitation and solution process [15]. Lead dichloride was added to the molten KCl in mole fraction ranging from 10<sup>-4</sup> to 10<sup>-3</sup>. Other samples were obtained by courtesy from Dr. Z. J. Damm (Institute of Low Temperature and Structure Research-Wroclaw-Poland). They were grown by means of the Bridgman method from the molten mixtures of KCl : PbCl<sub>2</sub> previously submitted to CCl<sub>4</sub> treatment in order to remove oxygen and OH<sup>-</sup> drastically [16].

The LiF : Be and pure LiF were obtained by courtesy from dr. K. Guckelsberger (Centre d'Etudes Nucléaires de Grenoble-France) and were purchased from Semielements Inc. (Saxonburg-U. S. A.).

The samples were cleaved in slices of area ranging from 1 to 3 cm<sup>2</sup> and thickness ranging from 0.2 to 1 mm. The ITC measurements were performed by the usual technique [8, 9, 12]. The annealing and quenching

were performed directly on the measuring cryostats [12], one of them was sketched in order to obtain very fast quenching of the samples (from 220 °C to 0 °C in 30").

**3. Results and discussion.** — **3.1 NUCLEATION OF HETEROGENEOUS PHASE OCCLUSIONS IN KCl : Pb.** — Some systems, such as KCl, NaCl and KBr doped with Sr, NaCl : Co and KCl : Pb, annealed at relatively high temperatures in order to dissolve I. V. dipoles from aggregates as described by figure 1b (lower curve) show a complex anomalous behaviour [11]. Infact a loss of dipoles is observed if the annealing time is very long.

The case of KCl : Pb is particularly lucky because the I. V. dipole loss is accompanied by the growth of a new ITC band (ITC-B band) on the high temperature side of the I. V. dipoles in the ITC plot, see figure 2.

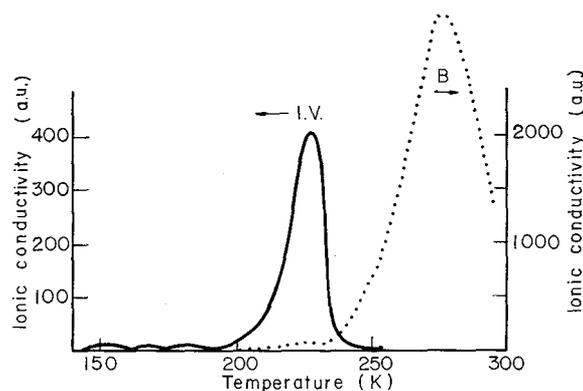


Fig. 2. — ITC plot of KCl : Pb ( $1.5 \times 10^{-4}$  m. f.): full line—sample quenched from 500 °C to RT; dotted line — sample annealed for 24 days at 200 °C.

Here the ITC plot of a sample in which I. V. dipoles are dissolved upon quenching from 500 °C (full line) is compared with that of the same sample annealed for 24 days at 200 °C (dotted line).

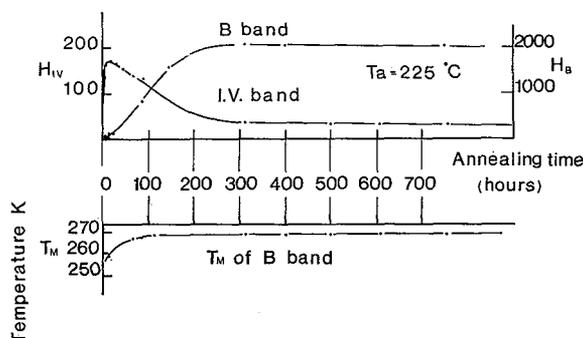


Fig. 3. — Aging of KCl : Pb ( $1.5 \times 10^{-4}$  m. f.) at 225 °C. *top*: height of I. V. dipole peak (scale on the left) and of B-band (scale on the right) versus annealing time; *bottom*: temperature of the B-band maximum  $T_M$  versus the annealing time.

Figure 3 shows the time evolution of the process : the I. V. dipoles are lost at increasing annealing times at  $T_a = 225$  °C while the ITC-B band continuously grows and levels up after long annealing times. On the bottom the temperature  $T_M$ , at which the maximum of ITC-B band occurs in the ITC plot, is drawn as well.  $T_M$  increases at the beginning and reaches a saturation value.

The principal features of the ITC-B band can be summarized as follows [12] :

1) It grows for long annealing times in the annealing temperature range  $150$  °C  $\lesssim T_a \lesssim 260$  °C at the expense of the I. V. dipole peak and for initial dipole concentration  $\geq 10^{17}$ /cc.

2) It can be suppressed by annealing for few hours at  $T_a > 400$  °C : in this case a complete recovery of I. V. dipole takes place.

3) The rate of growth is an increasing function of the  $T_a$  and of the starting concentration of I. V. dipoles (see Fig. 4).

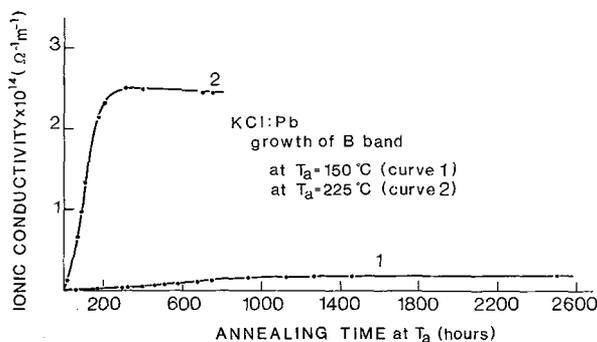


FIG. 4. — Growth of B band versus annealing time at different  $T_a$ 's and different available concentrations  $n_a$  of I. V. dipoles. Curve 1 :  $T_a = 150$  °C,  $n_a = 3.1 \times 10^{-5}$  m. f. Curve 2 :  $T_a = 225$  °C,  $n_a = 7 \times 10^{-5}$  m. f.

4) It is a complex band, i. e. it can be described as a distribution of relaxation times.

5) The *reorientation* activation energy determined for the *principal* peak is  $\sim 0.7$  eV (see Fig. 5).

6) The related polarization, as evaluated from the area under the peak, is a linear function of the electric applied field.

7) When ITC-B band is present, strong scattering of the light occurs and deep changes are induced in the optical absorption spectrum.

On the basis of the above results, we assume that the ITC-B band is due to the Maxwell-Wagner relaxation induced by the nucleation of heterogeneous occlusions, possibly of Suzuki phase, which takes place at moderately high  $T_a$ 's at the expenses of I. V. dipoles.

The Suzuki phase [13], which was found in a lot of alkali halides (AX) doped with different divalent impurities (Me), can be regarded as an ordered arran-

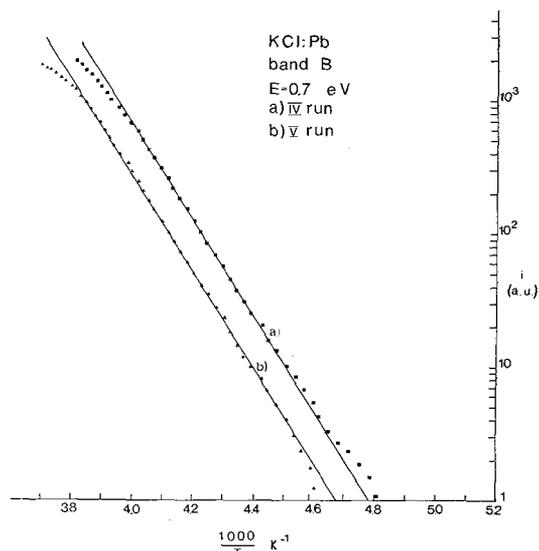


FIG. 5. — Semilog. plot of the initial rise current for B band vs  $1000/T$ . Different discharges of depolarization current are shown, upon using *cleaning* technique [9]

gement of I. V. dipoles in the n. n. n. coordination with the composition  $\text{MeX}_2 \cdot 6\text{AX}$  (see Fig. 6).

In the case of KCl : Pb the enhanced mobility of I. V. dipoles at  $\sim 200$  °C coupled with a still high association degree [14], close to unity can account for the migration of dipoles to form occlusions with a superlattice structure. Preliminary X-ray diffraction measurements support this hypothesis <sup>(1)</sup>. KCl with nucleating occlusions of the Suzuki phase can be regarded as an inhomogeneous dielectric whose dielectric behaviour can be described in term of Maxwell-Wagner-Sillars approach [17].

If the real part of the dielectric constant and the electrical conductivity of the medium are  $\epsilon_1$  and  $\sigma_1$  and those of the occlusions are  $\epsilon_2$  and  $\sigma_2$  and the occlusions are ellipsoid-shaped, it turns out that the relaxation process occurs with a pseudo-relaxation time  $\tau$  given by

$$\tau = [\epsilon_1(\lambda - 1) + \epsilon_2]/\sigma_2 \quad (1)$$

where  $\sigma_1 \ll \sigma_2$  and  $\lambda$  is an increasing function of the ratio  $a/b$  between the principal axes of the ellipsoid (two of them are assumed to be equal,  $b = c$ ), see figure 7.  $\sigma_2$  is actually an ionic conductivity related to the high vacancy concentration in the Suzuki phase ; as a consequence  $\tau$  decreases with the temperature with an exponential law as for the isolated ionic dipoles. On this way the ITC technique can detect the related polarization. Infact at temperatures at which the cation vacancies are still mobile the applied electric field induces a shift between the center of mass of the vacancies and that of the immobile divalent impurities. This configuration is frozen in when the temperature is

<sup>(1)</sup> Ghezzi, C., private communication.

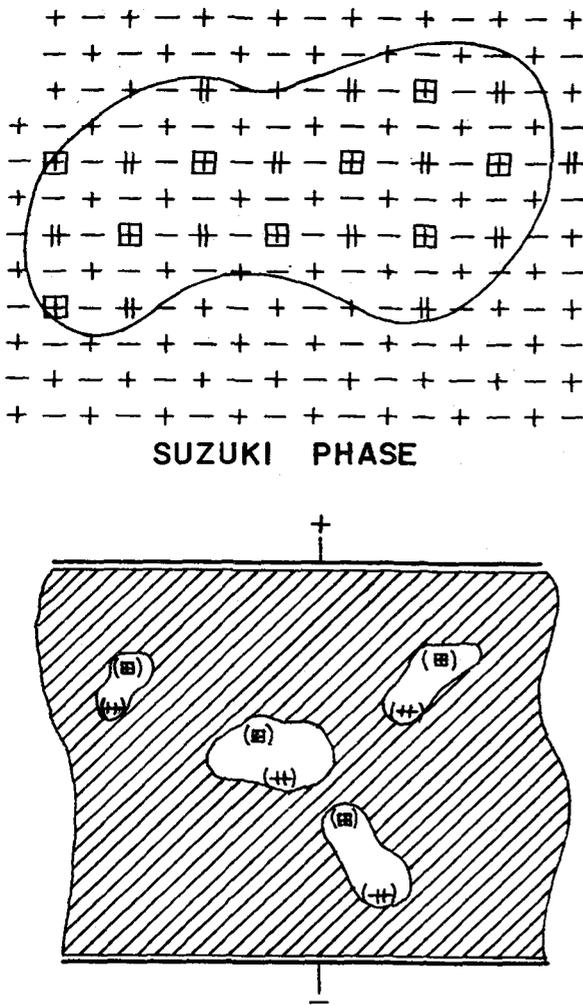


FIG. 6. — top : ordered arrangement in the Suzuki phase occlusion ; bottom : schematic distribution of cation vacancies and divalent impurities in sample within Suzuki phase and polarized with the electric field.

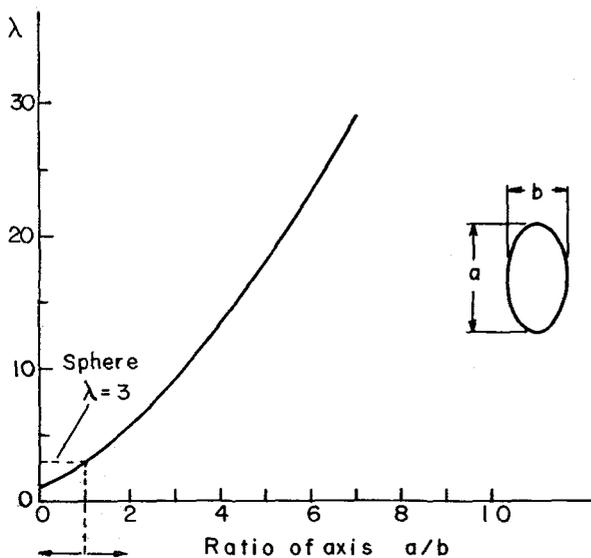


FIG. 7. — Shape factor  $\lambda$  vs the ratio  $a/b$  between the principal axes of the ellipsoids [17] ( $a$  is assumed parallel to the electric field).

lowered with the field on. A subsequent heating of the sample, with the field off, allows the vacancies to go back to recovery the initial situation, due to their increasing mobility. This means that a thermally stimulated displacement current can be detected by the electrometer. In this regard the activation energy, as determined, from the principal ITC peak,  $\sim 0.7$  eV (see 5) is in surprisingly good agreement with the activation energy for the motion of cation vacancy in KCl, 0.7 eV [14].

Moreover  $\tau$  must change (and consequently the  $T_M$  of the ITC peak) if the occlusion shape changes, as predicted by eq. (1), during the nucleation and growth processes up to reach an equilibrium value (see Fig. 3). The distribution of  $\tau$ 's, reported above for the ITC-B peak (see 4), can be accounted for as well ; infact it is expected that occlusions of different shapes and orientations can coexist.

The growth of particles of a second phase in a matrix of infinite extent can be reasonably described as a diffusion process. If this is the case, one can apply the Wert-Zener approach [18] to determine the shape of the precipitates. In the KCl : Pb system the analysis can be applied both to the ITC-B band, related to the occlusions, and to the I. V. band, related to the simple defects which contribute to the occlusions themselves.

The results, reported in detail elsewhere [12], support again that

- 1) the growth kinetics of the B band is tightly related to the I. V. dipole loss kinetics,
- 2) the same kinetics hold for different annealing temperatures and dipole concentrations (see Fig. 4) and
- 3) the occlusion shape is elongated, namely with high  $\lambda$  in eq. (1) (the simplified model suggests a cylindrical shape).

It must be stressed that both the analysis of the B band parameters and of the kinetics bring to the same consequences, namely elongated, rod-like, occlusions are formed upon long annealing at high  $T_a$ .

3.2 AGGREGATION PHENOMENA IN LiF : Be. — The solution and precipitation of I. V. dipoles in LiF doped with Be has been scarcely investigated. Recently *dips* in the thermal conductivity plot of LiF : Be, Ni, Mg annealed at  $100 \leq T_a \leq 250$  °C have been reported and attributed to aggregates ranging from 10 to 40 Å [19]. Moreover rod-like Suzuki phase occlusions were detected in LiF : Mg.

As a consequence we were interested to study by means of ITC if large aggregates are formed at the expense of I. V. dipoles upon annealing at moderately high  $T_a$ 's as in the case of KCl : Pb.

The figure 8 gives the ITC plot for LiF : Be submitted to different annealings. For the sake of clarity the plot can be divided into region I (I. V. dipole peak region) and region II (for  $T > 273$  K. Curve a) is related to the sample as received : a huge band is present in the region II ; curves b) and c) are related to the same

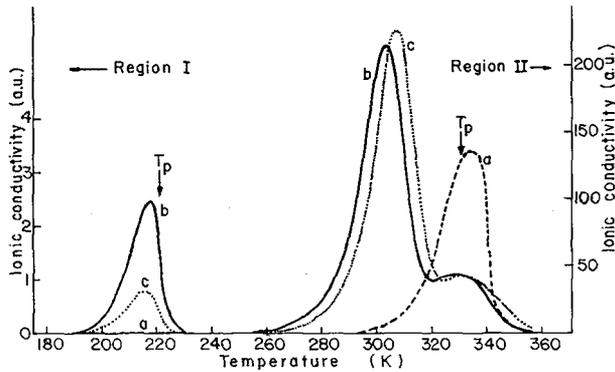


FIG. 8. — ITC plot of LiF : Be (nominal concentration 500 ppm) : a) sample as received ; b) sample annealed 1 h at 220° and quenched to LNT (30" from 220° to 0 °C) ; c) sample annealed at 220 °C 1 h and slowly cooled to RT (3 h).

sample annealed at 220 °C for 1 h and quenched very quickly (curve b) and slowly cooled (curve c). In both cases the annealing induces the growth of I. V. dipole peak ( $T_M \sim 217$  K), as expected if a dissolution process takes place, even if the higher concentration ( $1.9 \times 10^{18}/\text{cc}$ ) is preserved in the quenched sample. In the region II the band at 334 K decreases and a new huge band appears between 300 and 310 K ; the position of the peak  $T_{M,II}$  is affected by the rate of cooling (see curves b and c).  $T_{M,II}$  is affected as well by the annealing temperature  $T_a$  (see Fig. 9) : namely  $T_{M,II}$  shifts to lower temperatures the higher is the annealing temperature  $T_a$ .

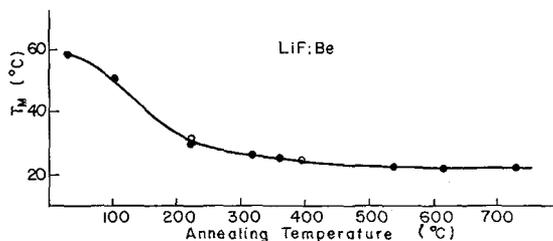


FIG. 9. — Temperature  $T_M$  at which the ITC band appears in region II, vs the annealing temperature  $T_a$ .

The ITC parameters of the observed bands can be summarized as follows. The activation energy for reorientation of I. V. dipoles is  $\sim 0.66$  eV. The peaks in the region II fit nicely a first order kinetics [9] with a single relaxation time, in contrast with the results for ITC-B band in KCl : Pb. The activation energy found are  $\sim 0.99$  eV for the peak at 304 K and 1.08 eV for the peak at 334 K respectively.

The ITC plots of annealed LiF : Be in region II show

some similarities with those of KCl : Pb, in which ITC-B band is present : in both cases 1) huge ITC peaks appear on the high temperature side of the I. V. peak and can be accounted for by a Maxwell-Wagner relaxation and 2) the peak position is affected by the annealing.

The comparison between curves b) and c) in figure 8 shows that the loss of I. V. dipoles, due to the slow cooling, is accompanied by a small increase and shift of the region II band : this means that both the growth and the shift towards high  $T$  is connected to some precipitation phenomena in which  $\text{Be}^{++}$  is involved.

The presence of the peak after quenching from 220 °C (curve b) rules out that the precipitates of few tens of Å diameter, observed by Guckelsberger [19], are responsible for our peak : in fact the number of these aggregates is strongly decreased upon quenching from  $T > 200$  °C. Moreover it is difficult to interpret the region II bands in a straightforward way, as arising from the slow nucleation of a segregated phase as in KCl : Pb. In that case ITC-B band is absent in quenched specimens and grows slowly with the annealing time. Conversely in LiF : Be, up to now, we never succeeded in eliminating the region II bands, notwithstanding severe quenchings from high  $T$ . Moreover the shift and the growth of region II band takes place after rather short annealing times (1 h, see Fig. 8) at 220 °C. This can be related to a high mobility of defects in which  $\text{Be}^{++}$  ion is involved, due to its small ion size. Tentatively one can suppose that the impurity defects, for instance I. V. dipoles, are easily captured by the electric and elastic fields around dislocations. The annealing at high temperatures allows the *evaporation* of such a defects from the dislocations, but the quenching is never fast enough to prevent a partial decoration of the dislocations themselves.

The medium with the decorated dislocations can be regarded again as inhomogeneous and the Maxwell-Wagner approach can be applied to describe its dielectric behaviour. Within the cloud of defects surrounding the dislocations the cation vacancies can move under the electric field and give rise to ITC peak in a way similar to that described previously for the Suzuki phase rod in KCl : Pb. An analogous hypothesis was put forward to explain the *dielectric chaos* (d. c.) ITC band [9] by Bucci *et al.* in KCl [21].

However the above interpretation remains a preliminary tentative approach which requires further measurements to be either confirmed or ruled out.

4. **Conclusions.** — As a concluding remark it must be stressed that the ITC technique, which was successfully employed to study [22] 1) simple dipolar defects (as I. V. dipoles and off center ions in alkali halides or R. E.-F. I. dipoles in divalent metal fluorides) and 2) space charge phenomena both in alkali halides and in  $\text{CaF}_2$ , can be exploited to study different kind of relaxations which arise from extended defects.

Moreover, as in the case of KCl : Pb, it must be emphasized that the nucleation process can be studied easily yet in the early stages and watched along its whole time evolution by monitoring both the simplest defects (I. V. dipoles) and the signals arising from the nucleating aggregates.

In this way it is possible to study extended defects, which, due to their size and their low concentration, escape the detection by means of the electron micro-

scopy and X-ray diffraction, employed traditionally for analyzing the segregated phases.

**Acknowledgments.** — The authors wish to thank Prof. Roberto Fieschi for the continuous encouragement and helpful discussions, Dr. Luigi Pareti for performing some of the ITC measurements and for the discussions and Dr. Vincenzo Fano for the determination of the lead contents in KCl samples.

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### DISCUSSION

F. BÉNIÈRE. — A peak in the ITC of Mn<sup>++</sup> in KCl was already clearly shown and clearly identified to be due to precipitates by Brun, Dansas and Bénière (*J. Phys. & Chem. Solids*, **35** (1974) 249). This conclusion was well supported by simultaneous EPR spectra.

R. CAPELLETTI. — I agree that the peak you have mentioned is due to precipitates. However I think that it resembles closely other peaks assigned to small precipitates, for instance the peaks detected in KCl : Pb at low temperatures (CAPELLETTI R., FIESCHI R., *Cryst. Latt. Def.* **1** (1969) 69). In fact, as for these latter peaks, it is rather small, comparable or

weaker, than the I. V. peak, while the present B-band related to Suzuki phase nucleation, is a very huge band, as expected from Maxwell Wagner relaxation, and grows at moderately high temperatures.

P. W. M. JACOBS. — What was the pre-exponential factor for the B-band relaxation ? Was it of the order of the normal value  $\sim 10^{-13}$  s.

R. CAPELLETTI. — Due to the fact that the B-band is complex, with a distribution of relaxation times, it is difficult to determine a precise value of  $\tau_0$  ; however by using the cleaning technique to isolate the main peak, the  $\tau_0$  can be evaluated roughly as  $10^{-12}$  s, which can be considered normal.