

## ZDELENIA

CORRECTION OF THE FORMULA FOR THE ITC WITH  
RESPECT TO THE FINITE COOLING RATE OF THE SAMPLE

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A new method of investigation of dielectric relaxation, based on the measuring of the so-called ionic thermo-current (ITC) has been described in papers [1, 2]. The principle of the method is as follows:

1. The condenser containing the solid is charged (polarized) in a static electric field  $E_p$  at a temperature  $T_p$  for a time sufficient to saturate the polarization.

2. The sample is cooled down to such a low temperature that the relaxation time  $\tau$  is of the order of several hours.

3. The field  $E_p$  is taken off and the condenser containing the sample is connected to the current detector. After discharging the electronic and atomic polarization, the sample is warmed up at a constant rate  $b$  and the discharging current — ITC is registered.

The magnitude of ITC is directly proportional to the magnitude of the „frozen“ polarization  $P_0$  [1]:

$$i(T) = P_0 \frac{1}{\tau} \exp \left[ - \int_0^T (b\tau)^{-1} dT \right] \quad (1)$$

If we consider only dipolar polarization due to complexes (metallic divalent impurity — cation vacancy) then  $\tau = \tau_0 \exp(\varphi/kT)$ , where  $\tau_0$  is the frequency factor,  $\varphi$  the reorientational energy of the complex,  $k$  the Boltzman constant and  $P_0$ , under the assumption of instantaneous cooling ( $-dT/dt \rightarrow \infty$ ), is equal to a saturated polarization  $P_{sat}$  at a temperature  $T = T_p$ , which is given by

$$P_{sat}(T_p) = \frac{2N\mu^2 E_p}{3kT_p} \quad (2)$$

where  $N$  is the concentration of complexes in the crystal,  $\mu$  is their dipole moment and  $E_p$  is the applied external electric field.

Because of a finite cooling rate ( $W = -dT/dt$ ) in practice,  $P_0$  is not given by (2), but is larger, since the saturated polarization is increasing with decreasing temperature, until the relaxation time is not essentially larger regarding the time interval during which the sample is being cooled. Hence it follows that  $P_0$  is dependent on the cooling rate  $W$ , too. A quantitative estimation of this dependence is the aim of the present paper.

As it is well-known, the dipolar polarization in ionic crystals is of a relaxational type, i. e. it satisfies the relation:

$$\frac{dP(t)}{dt} = \frac{1}{\tau} (P_{sat} - P(t)) \quad (3)$$

By means of the substitution  $dt = -dT/W$ , we rewrite (3) in the form:

$$\frac{dP(T)}{dT} = \frac{1}{\tau(T)W} (P(T) - P_{sat}(T)) \quad (4)$$

The solution of (4) with respect to the condition  $P = \frac{2N\mu^2 E_p}{3kT_p}$  for  $T = T_p$ , is\*)

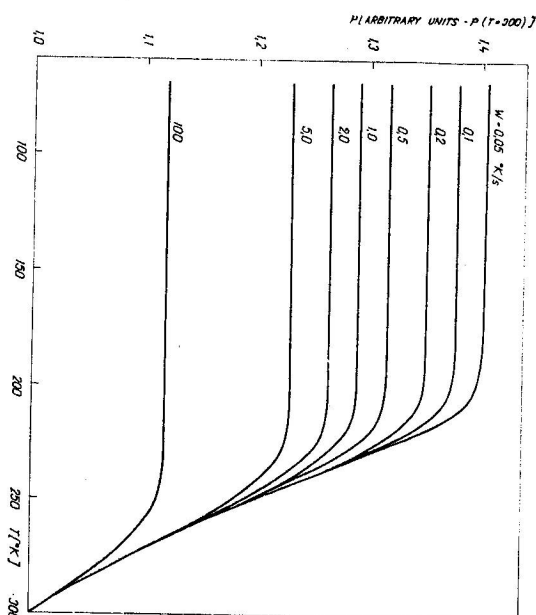


Fig. 1. Increase of polarization of the crystal in the constant field during cooling according to (5).  $\tau = 10^{-13} \exp(-0.67 \text{ eV}/kT)$ s;  $N = 10^{18}/\text{cm}^3$ ;  $E_p = 1000 \text{ V/cm}$ ;  $\mu = 14.4$  Debye.

\*) Dependence of the dipole concentration  $N$  on temperature due to dissociation and creation was neglected.

$$P = \exp \left[ \int_{T_p}^T \frac{dT}{\tau W} \right] \left\{ - \int_{T_p}^T \frac{P_{sat}}{\tau W} \exp \left( - \int_{T_p}^T \frac{dT}{\tau W} \right) dT + \frac{2N\mu^2 E_p}{3kT_p} \right\} \quad (5)$$

As the solution of (4) given by (5) cannot be expressed in a closed form it was calculated numerically. Fig. 1 show the dependence of  $P$  on temperature for several different cooling rates  $W$ . As one can see, with decreasing temperature for  $P$  is increasing and at about 200 °K „freezes“ on the value representing the proper value of  $P_0$  in (2). The dependence of  $P_0$  on  $\log W$  (in the considered range of rates  $W$ ) is nearly linear [Fig. 2].

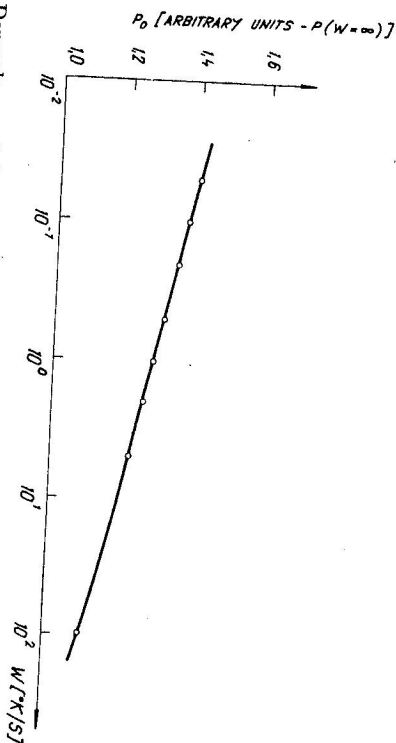


Fig. 2. Dependence of the frozen polarization on the cooling rate. The constants are the same as in Fig. 1.

For experimental verification an NaCl crystal doped with 3 mol %  $\text{CaCl}_2$  was chosen. The experimental arrangement was analogous to the one described in [2]. Four different cooling rates of the sample were realized in such a way that the system of electrodes with the sample was immersed into the liquid nitrogen and the thermal isolation of the system was being changed. The corresponding curves of ITC are in Fig. 3. We did not succeed in obtaining higher rates of cooling. As shown in Fig. 3, ITC increased about 40 % when the cooling rate decreased from 0.166 °K/s to 0.013 °K/s, while the theoretically expected increase was only about 8 %. The reason of this discrepancy is probably due to the fact that at 300 °K the association of the impurity ions of  $\text{Ca}^{++}$  with the cation vacancy has not been accomplished yet and during the cooling of the sample the number of complexes increases (c.f. Dreyfus and Nowick [4]). At present it is not possible to go into a more detailed analysis, because of the lack of experimental information about processes taking place at those tempe-

atures. The situation may be even more complicated by a possible formation of trimers of other aggregates and by precipitation [5].

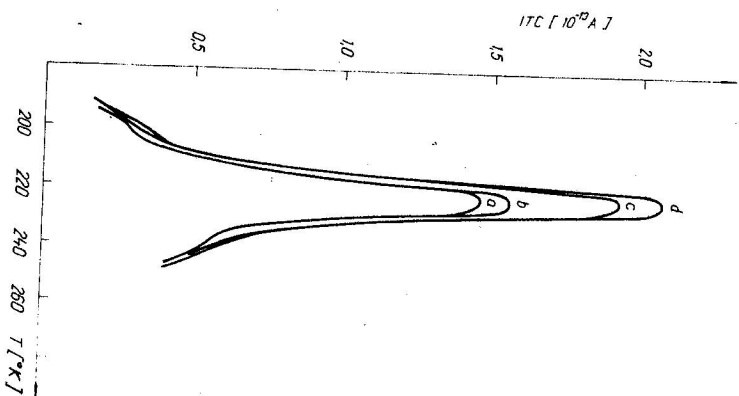


Fig. 3. ITC curves of a NaCl:  $3 \times 10^{-2}$  mol %  $\text{CaCl}_2$  crystal for different cooling rates.  $E_p = 1000$  V/cm;  $b = 0.1$  °K/s;  $T_p = 300$  °K. a)  $w = 0.166$  °K/s; b)  $w = 0.110$  °K/s; c)  $w = 0.018$  °K/s; d)  $w = 0.013$  °K/s.

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