

INTERPRETATION OF HIGH-TEMPERATURE ITC BAND IN ALKALI HALIDES BY THE MODEL OF INTERFACIAL POLARIZATION

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The maximum on ITC curves observed at about 200 °C was interpreted by the model of interfacial polarization under the assumption of an insulating surface layer on the crystal. The experimentally found indirect proportionality of ITC to the thickness of the sample, a small shift of T_{max} with increasing thickness to higher temperatures and the linear voltage dependence of ITC are in qualitative agreement with the theoretically expected results. The discussed model makes it possible to determine the activation energy of the bulk conductivity and to evaluate the surface layer conductivity of the crystal. The found values are in accordance with the expected values.

INTRODUCTION

A new method for studying the polarization phenomena in ionic crystals has been developed by Fieschi and coworkers [1-3]. The principle of the method is based on measuring the discharging current of a condenser containing the investigated crystal (ionic thermocurrent - ITC) while the temperature is linearly increasing. ITC in alkali halides of NaCl type is characterized by several bands occurring at different temperatures. The bands, occurring below 0 °C have already been studied in detail both experimentally and theoretically [2, 3], and it is known that they are caused by the relaxation of dipoles formed by complexes of „divalent cation impurity-vacancy“. Two relatively intensive bands have been found in the temperature range between 0 °C and 300 °C. Bucci and Riva [4] concluded, that the first band at about 100 °C is due to dipoles of a structure unknown at present and it is consistent with the polarization phenomena which have been studied in detail by Sutter and Nowick [5] by the method of the time dependent dc conductivity. As for the second band the authors of the present paper are in agreement with Bucci and Riva as regards the space charge base of this effect. Moreover, they assume that it is caused by the same processes which lead to dielectric losses studied e.g. by Kessler and Mariani [6] and Wimmer and Tallan [7].

The extraordinarily heavy losses and also the magnitude of the second band of ITC give evidence of their non-dipolar nature.*) The nonlinear potential distribution in the sample, experimentally observed by Wimmer and Tallan and the successful explanation of the dielectric losses by means of the model, assuming a thin nonconductive layer at the surface of the crystal, directly support the hypothesis about the formation of the space charge at those temperatures. The aim of the present paper is to present some further experimental data on the high-temperature ITC maximum and their explanation based on the model of interfacial polarization.

EXPERIMENTAL PROCEDURE AND RESULTS

The ITC measurements were carried out on natural single crystals of high purity with respect to impurities. Crystals of high purity were chosen because of the requirement of a substantially higher impedance of the crystal at temperatures of up to 300 °C than the value of the measuring resistance $R = 10^9 \Omega$ connected in series with the sample. The surface of each sample 4.5×4.5 mm in size was coated with colloidal graphite in order to reach a reproducible contact between the sample and the electrodes. The samples were not subjected to any thermal treatment before the measurements. The apparatus for ITC measurement was similar to that described in [2]. Both plane electrodes were made of silver. The leads of the electrodes were made of very thin Ag-wire. The electrometer „VIBRON 30 C“ with an input resistance of $10^{16} \Omega$ and a capacitance of about 35 pF was used for the measurements of the current. Its input was connected parallel to the measuring resistance. The time constant of the measuring device was thus of the order of 10^{-2} sec and the current sensitivity of about 10-12 A. A Cu-Ko thermocouple located on one of the electrodes registered the temperature of the sample. The sample was warmed up in a furnace during the ITC measurement, under a dry nitrogen atmosphere of about 1 torr. The chosen warming rate 0.15 °K/sec was satisfactory with regard to temperature gradients in the sample (up to 5 °C at extremal thickness). The reproducibility of an individual measurement was about 2 % provided the measurements were carried out under the same thermal conditions. The ITC curves for five crystals of different thickness are in Fig. 1. All of the five samples were split off one piece of a single crystal. The polarizing voltage varied with the thickness of the crystal in order to keep the intensity of the electric field at the constant value $E_g = 1000$ V/cm. The plot of the magnitude

*) In spite of that, an explanation of analogous dielectric measurements on NaCl and KCl at temperatures near the melting point by vacancy pairs was attempted [8-10].

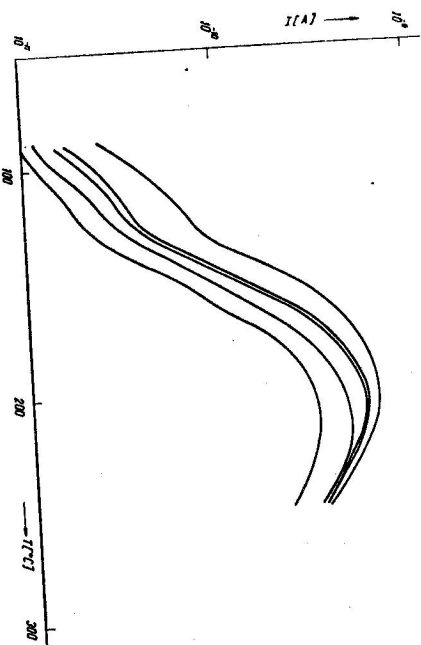


Fig. 1. Dependence of ITC of pure NaCl on the thickness of the sample. From above to down: a) $d = 1.05$ mm; b) $d = 1.60$ mm; c) $d = 2.30$ mm; d) $d = 4.02$ mm.

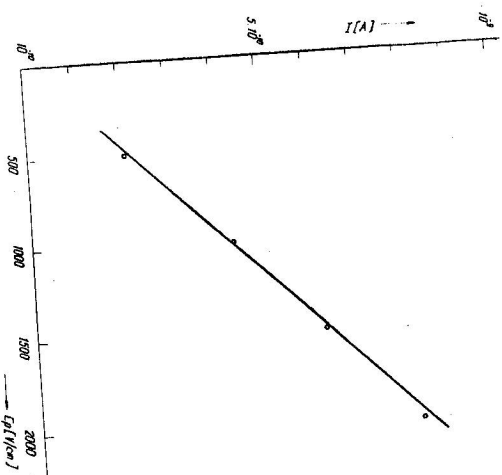


Fig. 2. Maximum of ITC as a function of the applied field.

ITC versus the polarizing field intensity is in Fig. 2. The deviations from linearity lie within the experimental errors.

THEORY AND DISCUSSION

If we consider models of space charge, problems concerning the physical principles of the process which causes the blockade of charge carriers arise. There are two possibilities of explanation in such a case:

1. To assume the blockade of charge carriers at the electrodes due to either imperfect contact between the crystal and the electrode (air gap), or due to slow rates of electrochemical reactions between the crystal and the electrode where the change from ionic conductivity to electronic conductivity [11—12] occurs.

2. To assume the existence of a thin layer on the surface of the crystal of a different conductivity from that of the bulk. The existence of such a layer has been already shown by Frenkel [13] and Lehovce [14] and later by Kliwer and Koehler [15]. Such a layer arises whenever the energies causing cation and anion vacancies differ from one another. So far the problem of the thickness of this layer has not been satisfactorily solved. Theoretical calculations [14, 15] have estimated the thickness to be of about 0.1μ at 400°C for a pure crystal, while Wimmer and Tallan have found experimentally by measuring the potential profile of the sample surface of NaCl the value to be 20μ . But the accuracy of such an experiment is affected by the point thickness of the probe used for taking the potential profile (8μ) and also by the fact that the potential profile on the sample surface differs from that within the crystal.

The good results reached by Wimmer and Tallan by means of the latter hypothesis for the explanation of dielectric losses inspired us to use the model of interfacial polarization also for the interpretation of the high-temperature ITC maximum.

ITC of a two-layer condenser

We have in fact a capacitor with three layers, but if we assume the same electrical parameters of both side layers, then the three-layer capacitor is equivalent to a double-layer capacitor. Accordingly let us consider the two-layer condenser and denote by ϵ the permittivity, by σ the conductivity, by E the intensity of the electrical field, by d the thickness, by i the current density, and let the subscripts 1 and 2 refer to the surface layer and bulk, respectively. If a steady voltage V is applied to the condenser at the polarization temperature T_p , in a stationary state the ratio of the electrical field intensities of each of these layers equals the reciprocal ratio of their conductivities

$$\frac{E_1^{stac}}{E_2^{stac}} = \frac{\sigma_2(T_p)}{\sigma_1(T_p)}, \quad (1)$$

while the sum of voltage in both layers equals the total applied voltage V

$$E_1 d_1 + E_2 d_2 = E_p (d_1 + d_2) = V. \quad (2)$$

The charge q accumulated at the interface is given by

$$q = \frac{1}{4\pi} (\epsilon_2 E_2^{stac} - \epsilon_1 E_1^{stac}). \quad (3)$$

After a substitution from (1, 2) the expression for q takes the form

$$q = \frac{1}{4\pi} \frac{\epsilon_2 \sigma_1(T_p) - \epsilon_1 \sigma_2(T_p)}{d_2 \sigma_1(T_p) + d_1 \sigma_2(T_p)} \quad (4)$$

Let us now assume that the sample is cooled down sufficiently rapidly* to such a low temperature that the relaxation time of q on the interface is of the order of several hours. Then the condenser is connected to the current detector and warmed up at a constant rate b while the discharging ITC current is flowing through the circuit**)

$$i(T) = \sigma_1 E_1 + \frac{\epsilon_1}{4\pi} \frac{dE_1(T)}{dt} = \sigma_2 E_2 + \frac{\epsilon_2}{4\pi} \frac{dE_2(T)}{dt} \quad (5)$$

Since the voltage across the sample is now zero

$$E_1(T) d_1 + E_2(T) d_2 = 0, \quad (6)$$

using (6) we can eliminate e.g. E_1 from (5) and after substituting $dt = dT/b$, we obtain a differential equation for E_2

$$\frac{dE_2(T)}{dT} = - \frac{1}{b\tau} E_2(T), \quad (7)$$

where the relaxation time

$$\tau(T) = \frac{\epsilon_2 d_1 + \epsilon_1 d_2}{4\pi [d_1 \sigma_2(T) + d_2 \sigma_1(T)]} \quad (7')$$

The solution of (7) is

$$E_2 = E_{20} \exp \left(- \int_0^T \frac{dT}{b\tau} \right). \quad (8)$$

For the constant E_{20} from (3, 4, 6) it follows

$$E_{20} = \frac{[\epsilon_2 \sigma_1(T_p) - \epsilon_1 \sigma_2(T_p)] d_1 V}{[d_2 \sigma_1(T_p) + d_1 \sigma_2(T_p)] [\epsilon_2 d_1 + \epsilon_1 d_2]}. \quad (9)$$

By introducing (8) into (5) we obtain a relation for ITC in the form

* A little change of q in respect to the final cooling rate of the sample has no influence on our qualitative consideration.
** We have neglected eventual dependences of $\epsilon_{1,2}$ and d_1 on temperature.

$$i(T) = \frac{[\epsilon_1 \sigma_2(T) - \epsilon_2 \sigma_1(T)] [\epsilon_2 \sigma_1(T_p) - \epsilon_1 \sigma_2(T_p)] d_1 d_2}{(\epsilon_1 d_2 + \epsilon_2 d_1)^2 [\sigma_1(T_p) d_2 + \sigma_2(T_p) d_1]} V \exp \left(- \int_0^T \frac{dT}{b\tau} \right). \quad (10)$$

Discussion

The complicated formula (10) can be simplified assuming (improved experimentally [7]) that the surface layer has a much higher resistivity than the bulk of the crystal, but because of its thickness it has a lower resistance than the bulk, i.e.

$$1 \ll \frac{\sigma_2}{\sigma_1} \ll \frac{d_2}{d_1} \quad (11)$$

In such a case, even if one takes in account that $\epsilon_1 = \epsilon_2 = \epsilon$ (ϵ is the permittivity of the crystal due to electronic and atomic polarization, it is of equal magnitude in both layers), the relation (10) may be simplified to

$$i = - \sigma_2(T) \frac{\sigma_2(T_p)}{\sigma_1(T_p)} \frac{d_1}{d_2} E_p \exp \left(- \frac{4\pi}{\epsilon b} \int_0^T \sigma_1 dT \right). \quad (12)$$

The function (12) has the following features:

1. It is indirectly proportional to the thickness of a crystal, which fact is in a qualitative agreement with the experimental statement (Fig. 1).
2. Since the conductivities of the individual layers can be written in the form

$$\sigma_\alpha = \sigma_{\alpha 0} \exp(-\varphi_\alpha/kT), \quad \alpha = 1, 2 \quad (13)$$

its maximum is at a temperature

$$T_{max} = \left(\frac{\epsilon b \varphi_2}{4\pi \sigma_1(T_{max}) k} \right)^{1/2} = \left(\frac{b \varphi_2 \tau(T_{max})}{k} \right)^{1/2}. \quad (14)$$

A small shift of T_{max} to higher temperatures, with increasing thickness of the crystal (Fig. 1) can be explained, provided the T_{max} is derived from the relation (10)

$$T_{max} = \left\{ \frac{b(\epsilon_1 d_2 + \epsilon_2 d_1) [\epsilon_1 \sigma_2(T_{max}) \varphi_2 - \epsilon_2 \sigma_1(T_{max}) \varphi_1]}{4\pi k [\sigma_1(T_{max}) d_2 + \sigma_2(T_{max}) d_1] [\epsilon_1 \sigma_2(T_{max}) - \epsilon_2 \sigma_1(T_{max})]} \right\}^{1/2}.$$

Under the assumption of (11) T_{max} increases with increasing d_2 .
3. Its low-temperature tail is such that

$$\ln i(T) = \text{const} - \frac{q_2}{kT} \quad (15)$$

$$\left(\text{At lower temperatures } \ln \exp \left(- \frac{4\pi}{eb} \int_0^T \sigma_1 dT' \right) \approx 0 \right).$$

The activation energy of the bulk conductivity can be obtained from (15) and the surface layer conductivity from expression (13). In case of natural NaCl we have found $q_2 = 0.83 \pm 0.05$ eV and $\sigma_1(200^\circ\text{C}) = 3.2 \times 10^{-15}(\Omega\text{cm})^{-1}$.

CONCLUSIONS

The maximum of the ITC curve observed at about 200°C was interpreted in terms of interfacial polarization associated with insulating surface layers. The applied model is in agreement with the experimental results of the present paper — a small shift of T_{max} to higher temperatures with increasing thickness of the crystal, the linear dependence of the ITC maximum on the applied polarizing voltage and also an increasing ITC with an increasing impurities content in the crystal [4]. The evaluated activation energy of the bulk conductivity of the crystal of 0.83 eV is in agreement with the energies published in papers [16–20], which appear to be between 0.72 and 0.85 eV. The calculated value of the surface layer conductivity at 200°C of $3.2 \times 10^{-15}(\Omega\text{cm})^{-1}$ is negligible compared with that of the bulk, at the same temperature, of $5 \times 10^{-2}(\Omega\text{cm})^{-1}$, obtained by means of conductivity measurements using Ohm's law. As to the second requirement $\sigma_2 d_2 \gg \sigma_1 d_1$, there follows from it as regards the thickness d_1 a value smaller than 1μ , which is in disagreement with the experimental results of Wimmer and Tallan.

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