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Polarization and depolarization currents resulting from the temperature or pressure induced volume changes in polarized dielectrics

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Abstract. We investigate the emission of electric current from a polarized dielectric whenever the matrix dilates. The thermal volume expansivity, the isothermal bulk modulus, its temperature and pressure derivatives and the rate of temperature or pressure variation would determine the shape and the magnitude of the electric signal. We emphasize the permanent dipole polarization and the ionic (induced) polarization. Numerical estimates of the current density, which would be recorded in polarization or depolarization experiments in a model system with cubic symmetry, such as sodium chloride doped with a small amount of divalent cation impurities, are obtained.

1. Introduction

Two categories of dielectric relaxation experiments are employed so as to study the dipole dynamics and space charge relaxation in insulators. In the first type of experiment, such as the impedance spectroscopy and charging or discharging techniques, the system is maintained at equilibrium during the measuring procedure (isothermal or isobaric experiments). Another category involves the polarization or depolarization of the sample by continuous variation of temperature or pressure and therefore are regarded as quasistatic techniques. The latter experimental schemes are known as the thermal stimulated polarization (TSPC) or depolarization (TSDC) current [1, 2] and the pressure stimulated polarization (PSPC) or depolarization (PSDC) current [3, 4]. In the TSDC scheme, which is the most popular dielectric relaxation technique, a dielectric is polarized at room temperature by applying an external electric field. Afterwards, the temperature is reduced drastically to liquid nitrogen temperature (LNT), whereas the polarizing electric field is switched off. The removal of the field results in the rapid annihilation of the induced (electronic and ionic) polarization; however, the permanent dipoles remain polarized, since their relaxation time at LNT is practically infinite. Afterwards, the specimen is heated at constant pressure in the absence of an external electric field. A transient depolarization current is released at the temperature range where dipoles are mobile enough to reach a random orientation state. The PSDC scheme resembles the TSDC, but pressure is the thermodynamic parameter that is modified. The polarization state becomes ‘frozen’ by subjecting the sample to high compression. In the PSDC, the dipolar depolarization signal is produced as pressure is reduced from its initial high value to the ambient pressure. In the polarization experiments (TSPC and PSPC), the current is

recorded in the presence of an external electric field. In this case, both dipolar and induced (ionic) polarizations are excited on a temperature or pressure variation.

However, the temperature or pressure variation yield volume expansion or contraction. As a consequence, the density of dipole centres and their length are modified. Moreover, the induced polarization is sensitive to temperature or pressure variation. The modification of the sample's volume leads also to the modification of the induced dipole density and the polarizability. In the present study, emphasizing dipolar and ionic *polarization*, we develop expressions for the (polarization or depolarization) current, which is produced from a polarized cubic ionic crystal, when the temperature or pressure change. The electric current emission results neither from dipole relaxation nor by the transfer of (space) charge, but is merely governed by the expansivity and the elastic properties of the material. The phenomenon is entirely different from the pyroelectric and the piezoelectric effects [5] in the sense that the latter are associated with the *spontaneous* polarization of the crystal on temperature or stress variation. The dilatancy currents are actually controlled by the anharmonicity and the elasticity of the crystal, which modify the (volume) concentration of polarizable entities. To the best of our knowledge, a discussion on the dilatancy currents has not yet appeared in the literature.

2. Permanent dipole polarization

2.1. Current emitted on temperature variation

Consider a population of oriented (polarized) dipoles, which are embedded into a cubic lattice, with lattice constant a . The system under consideration might be sodium chloride doped with a low concentration of divalent cation impurities; divalent cations substitute for sodium and form impurity–cation vacancy pairs. The latter electric dipoles are called defect dipoles. The polarization Π is

$$\Pi(T, P) = N(T, P)p(T, P) \quad (1)$$

where N and p denote the density of dipoles which are aligned to an external electric field and the dipole moment, respectively. By definition, the dipole moment is $p = qr$, where q and r denote the absolute charge value of one of the charges constituting the dipole and the dipole length, respectively. In the present section, the system undergoes isobaric changes; thus, temperature is the independent variable. We assume that the dipoles' charges are either located at lattice or interstitial sites; thus, $r \propto a$. The dipole length variation follows the sample's volume variation upon temperature:

$$3 \left. \frac{\partial \ln a}{\partial T} \right|_P = \left. \frac{\partial \ln V}{\partial T} \right|_P \equiv \beta(T) \quad (2)$$

where β is the thermal volume expansion coefficient. The reduced dipole moment variation is

$$\left. \frac{\partial \ln p(T)}{\partial T} \right|_P = \frac{1}{3} \beta(T). \quad (3)$$

The density of dipoles changes on volume modification:

$$\left. \frac{\partial \ln N}{\partial T} \right|_P = - \left. \frac{\partial \ln V}{\partial T} \right|_P \equiv -\beta(T). \quad (4)$$

By differentiating the logarithm of (1), with the aid of equations (3) and (4), we obtain

$$\left(\left. \frac{\partial \ln \Pi(T)}{\partial T} \right)_P \right) = -\frac{2}{3} \beta(T). \quad (5)$$

Equation (3) indicates that the dipole moment augments with temperature, due to the elongation of dipoles resulting from the lattice expansion. In contrast, the dipole density decreases, according to (4). The effect of temperature on the total polarization is determined by the aforementioned competing components; equation (5) shows that the polarization is a decreasing function of temperature.

We identify b_T , the rate of temperature variation, which may be either constant or not. The density of the current produced is

$$J(T) = \frac{d\Pi}{dt} = \Pi(T) \frac{\partial \ln \Pi(T)}{\partial T} b_T. \quad (6)$$

By integrating (5), we obtain

$$\ln \Pi(T) = \ln \Pi(T = 0) - \frac{2}{3} \int_0^T \beta(T) dT. \quad (7)$$

From equations (6) and (7), we get

$$J(T) = \frac{d\Pi}{dT} b_T = -\frac{2}{3} \beta(T) b_T \exp \left[\ln \Pi(T = 0) - \frac{2}{3} \int_0^T \beta(T) dT \right]. \quad (8)$$

We proceed with the calculation of the current density for sodium chloride doped with 100 ppm of divalent cation impurities. We assume that the crystal has been treated properly so as to have all the impurities bound to cation vacancies in nearest-neighbour lattice sites. The length of this type of dipole is $r = a/\sqrt{2}$, where $a = 5.64 \text{ \AA}$ is the lattice constant. The dipole moment is therefore $p = 6.39 \times 10^{-29} \text{ C m}$. A concentration of 100 ppm implies 10^{-4} impurities per cation site. The number of cations per unit volume is $4/a^3 = 2.23 \times 10^{28} \text{ m}^{-3}$, thus the density of the defect dipoles embedded into the matrix is $N = 2.23 \times 10^{24} \text{ m}^{-3}$. When the specimen is polarized at the temperature T_p , by an external electric field, the polarization achieved is [6]

$$\Pi = \frac{Np^2 E}{3kT_p} \quad (9)$$

where k and E are Boltzmann's constant and the intensity of the effective (local) polarizing field, respectively. Consider $T_p = 295 \text{ K}$ and an external electric field of intensity $E_{ext} = 10^6 \text{ V m}^{-1}$. The latter electric strength corresponds to the application of a voltage of 1 kV to a specimen of thickness 1 mm.

The sample's shape may adequately be visualized as a thin plate, which is normal to the external electric field. Recalling that the crystal symmetry is cubic, the local field intensity may be approximated by a Lorentz field [7]:

$$E = E_{ext} - \frac{1}{\epsilon_0} \Pi + \frac{1}{3\epsilon_0} \Pi = E_{ext} - \frac{2}{3\epsilon_0} \Pi \quad (10)$$

where ϵ_0 is the permittivity of free space. The term $-(1/\epsilon_0)\Pi$ is the depolarization field, which is determined by the shape of the specimen. However, under the constraints that the molecular sample has macroscopic dimensions and that the external field does not vary strongly over macroscopic distances, the local field is independent of the shape of the solid [8] and the depolarization term can be ignored. By employing the general form of (10) for the local field (equation (10)), the polarization achieved is $\Pi = 7 \times 10^{-7} \text{ C m}^{-2}$; the latter is the saturation polarization achieved at room temperature before a TSDC scan. Note that the omission of the depolarization term from (10), merely results in the reduction of the polarization by a factor of about 2%. In figure 1, a simulation curve of the dilatancy current density emitted when a sodium chloride crystal, with 100 ppm of dissolved defect dipoles undergoes a TSDC scan is depicted. The expansivity data were obtained from [9], while a constant heating rate of

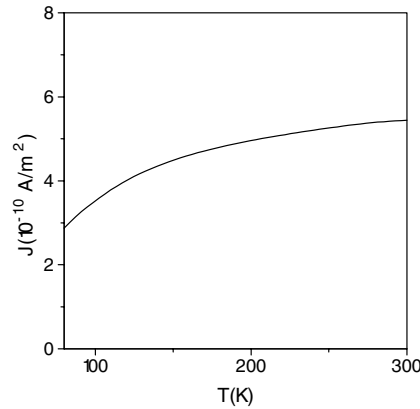


Figure 1. Simulation of the contribution of the permanent dipole dilatancy current density to the TSDC spectrum of sodium chloride doped with 100 ppm divalent cation impurities. Details are given in the text.

$b_T = 0.1 \text{ K s}^{-1}$ is employed. The signal may augment by an order of magnitude, in the extreme case of $E = 10^7 \text{ V m}^{-1}$. Since $(\partial \ln \Pi(T)/\partial T)_P < 0$, the dipole polarization is reduced on increasing the temperature, and subsequently the dilatancy current is actually a depolarization one.

2.2. Current emitted on pressure variation

We regard pressure as the unique independent variable of equation (1). Recalling that

$$3 \left. \frac{\partial \ln a}{\partial P} \right|_T = \left. \frac{\partial \ln V}{\partial P} \right|_T \equiv -\chi_T(P) \quad (11)$$

where $\chi_T(P)$ denotes the isothermal compressibility, we obtain the reduced variation of the dipole moment on pressure:

$$\left. \frac{\partial \ln p(P)}{\partial P} \right|_T = -\frac{1}{3} \chi_T(P). \quad (12)$$

The density N of the dipole centres follows the volume change on pressure:

$$\left. \frac{\partial \ln N}{\partial P} \right|_T = -\left. \frac{\partial \ln V}{\partial P} \right|_T \equiv \chi_T(P). \quad (13)$$

The dipole moment reduces on pressurization, according to equation (12), as pressure brings the lattice points closer together and reduces the dipole length. In contrast, this effect results in an increase of the dipole density, as equation (13) shows. Taking the logarithm of equation (1), differentiating with respect to pressure and using equations (12) and (13), we obtain

$$\left(\left. \frac{\partial \ln \Pi(P)}{\partial P} \right) \right)_T = \frac{2}{3} \chi_T(P). \quad (14)$$

It is obvious that the polarization increases on pressurization; the dipole concentration increment (equation (13)) is stronger with reduction of the dipole's length (equation (12)). It is an adequate approximation to assume that the variation of the isothermal bulk modulus B (which is defined as the inverse of the isothermal compressibility) upon pressure is linear:

$$B(P) = B_0 + \left(\left. \frac{\partial B}{\partial P} \right) \right)_T P \quad (15)$$

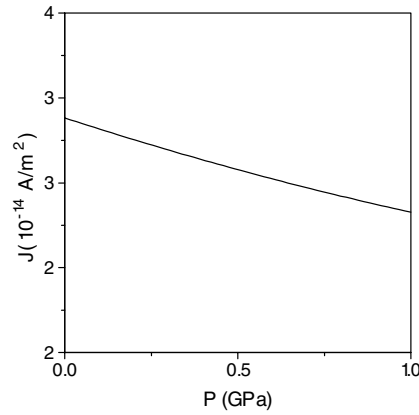


Figure 2. The dilatancy current density contribution to the PSDC spectrum calculated for sodium chloride doped with 100 ppm divalent cation impurities.

where B_0 is the zero-pressure (which is considered as the ambient pressure) value of the bulk modulus and $(\partial B/\partial P)_T$ holds approximately a constant value.

Labelling $\chi_T(P) \equiv 1/B(P)$, the integration of (14) yields

$$\ln \Pi(P) = \ln \Pi(P=0) + \frac{2}{3} \left(\frac{\partial B}{\partial P} \right)_T^{-1} \left[\ln \left(B_0 + \left(\frac{\partial B}{\partial P} \right)_T P \right) - \ln B_0 \right]. \quad (16)$$

The current density is

$$J = \frac{d\Pi}{dt} = \Pi(P) \frac{\partial \ln \Pi(P)}{\partial P} b_P \quad (17)$$

where b_P denotes the pressure rate. Specifying $b_P = \text{constant}$, from (16) and (17), we obtain an analytical expression for the pressure produced current density, within the linear approximation of the $B(P)$ variation (see equation (15)):

$$J(P) = -\frac{2}{3} b_P \left(B_0 + \left(\frac{\partial B}{\partial P} \right)_T P \right)^{-1} \times \exp \left\{ \ln \Pi(P=0) + \frac{2}{3} \left(\frac{\partial B}{\partial P} \right)_T^{-1} \left[\ln \left(B_0 + \left(\frac{\partial B}{\partial P} \right)_T P \right) - \ln B_0 \right] \right\}. \quad (18)$$

The latter equation is a monotonic function of pressure.

For sodium chloride, we take the saturation polarization value $\Pi = 7 \times 10^{-7} \text{ C m}^{-2}$, which was estimated in section 2.1. From [10] we obtain $B_0 = 2.384 \times 10^{10} \text{ Pa}$ and $(\partial B/\partial P)_T = 5.35$ and, subsequently, the theoretical PSDC density was calculated via equation (18). The simulation curve is displayed in figure 2 for a typical pressure rate $b_P = 1.7 \times 10^3 \text{ Pa s}^{-1}$. Note that $(\partial \ln \Pi(P)/\partial P)_T > 0$, i.e. in the PSDC paradigm the pressure reduction diminishes the dipolar polarization. Therefore, the aforementioned dilatancy current is a depolarization current.

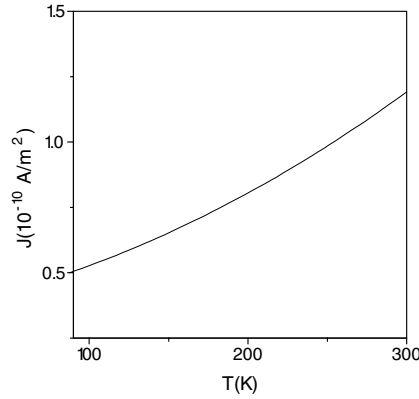


Figure 3. Simulation of the TSPC dilatancy current due to dilatancy effects on the ionic polarization in sodium chloride, under the action of a 10^6 V m^{-1} external electric field. The heating rate is 0.1 K s^{-1} .

3. Ionic (induced) polarization

3.1. Current produced on temperature variation

The induced (ionic) polarization Π is proportional to the density of the induced dipoles N , the polarizability α_p and the intensity of the local electric field E :

$$\Pi(T, P) = N(T, P)\alpha_p(T, P)E(T, P). \quad (19)$$

In the present section, we shall only consider the isobaric case. In the literature, we find the following expression for the polarizability [11]:

$$\alpha_p = ce^{*2}B^{-1}a^{-1} \quad (20)$$

where c is a constant, which is approximately equal to two-thirds for alkali halides [12] and e^* denotes the Sziget effective charge. Moreover, we consider the local field, which determines the induced dipole moment, as a Lorentz one, like that represented previously by equation (10).

By replacing equations (10) and (20) in equation (19), and taking the derivative of the logarithm with respect to temperature, and with the help of equations (2) and (4), we get

$$\left(\frac{\partial \ln \Pi}{\partial T}\right)_p = \left(1 - \frac{2N(T)\alpha_p(T)}{X}\right) \left\{ 2\left(\frac{\partial \ln e^*}{\partial T}\right)_p - \frac{4}{3}\beta(T) - \left(\frac{\partial \ln B(T)}{\partial T}\right)_p \right\} \quad (21)$$

where $X = 3\epsilon_0 + 2N(T, P)\alpha_p(T, P)$. The current density emitted is

$$J(T) = \frac{d\Pi}{dt} = b_T \frac{d\Pi}{dT} = b_T \left(\frac{\partial \ln \Pi}{\partial T}\right)_p \Pi(T). \quad (22)$$

We now work on a numerical estimate for sodium chloride. The density of cations (or ions), which is identical to that of the induced dipoles, is $4/a^3$, where a denotes the lattice constant. The lattice constant varies with temperature as $a(T) = a(T=0) \exp \int_0^T \frac{1}{3}\beta(T) dT$, where $\beta(T)$ is provided by [9]. We neglect the curvature of the $B(T)$ plot observed in the quantum limit, as well as the high-temperature region where anharmonic effects are strong enough; hence, the isothermal bulk modulus can be expressed as a linear function of temperature:

$$B(T) = B_0^{SL} + \left(\frac{\partial B}{\partial T}\right)_p T \quad (23)$$

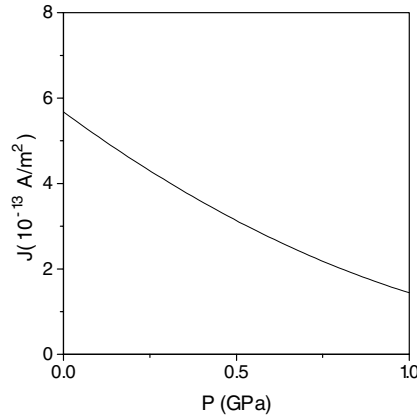


Figure 4. Simulation of the PSC component of the dilatancy current of the ionic polarization in sodium chloride under the action of a 10^6 V m^{-1} external electric field. The pressure rate is $-1.7 \times 10^3 \text{ Pa K}^{-1}$.

where B_0^{SL} is the intercept of the linear part of the $B(T)$ plot with the vertical axis. From [10], we get $B_0^{SL} = 2.843 \times 10^{10} \text{ Pa}$ and $(\partial B/\partial T)_P = -1.583 \times 10^7 \text{ Pa K}^{-1}$. The effective electric charge is $e^* = 0.77e$, where e denotes the electron's charge density and $(\partial \ln e^*/\partial T)_P = 2.48 \times 10^{-5} \text{ K}^{-1}$ [13]. In figure 3, the simulation of the dilatancy current density in the TSPC experiment is shown. The external field intensity is $E = 10^6 \text{ V m}^{-1}$ and the heating rate is 0.1 K s^{-1} . $(\partial \ln \Pi/\partial T)_P$ is negative, so, on increasing the temperature during the TSPC scan, the ionic polarization is reduced and the dilatancy current is characterized as a depolarization component in the dielectric spectrum. The intensity of the signal is worth noting, in comparison with the aforementioned types of dilatancy currents.

3.2. Current produced on pressure variation

We regard pressure as the unique independent variable of equation (19). Taking the logarithm and differentiating with respect to pressure, in combination with equations (11) and (13), we obtain

$$\left(\frac{\partial \ln \Pi}{\partial P}\right)_T = \left(1 - \frac{2N(P)\alpha_p(P)}{X}\right) \left\{ 2\left(\frac{\partial \ln e^*}{\partial P}\right)_T + \frac{4}{3}\chi_T(P) - \left(\frac{\partial \ln B(P)}{\partial P}\right)_T \right\} \quad (24)$$

where $X = 3\varepsilon_0 + 2N(T, P)\alpha_p(T, P)$.

The current density which stems from the pressure change is

$$J(P) = \frac{d\Pi}{dt} = b_P \frac{d\Pi}{dP} = b_P \left(\frac{\partial \ln \Pi(P)}{\partial P}\right)_T \Pi(P). \quad (25)$$

For sodium chloride, the linear $B(P)$ relationship presented in section 2.2 is valid. The lattice constant is given by $a(P) = a(P=0)[\exp \int_0^P \chi_T(P) dP]^{1/3}$. In order to estimate the pressure dependence of the Szigeti effective charge, we employ the following relation [13]:

$$\left(\frac{\partial \ln e^*}{\partial P}\right)_T = -\frac{V}{B} \left(\frac{d \ln e^*}{dV}\right)_T \quad (26)$$

where V is the volume per unit cell. The latter equation may be rewritten in the following form:

$$\left(\frac{\partial \ln e^*}{\partial P}\right)_T = -\frac{\chi_T}{\beta} \left[\beta V \left(\frac{d \ln e^*}{dV}\right)_T \right]. \quad (27)$$

By replacing in the latter equation the value $\beta V(d \ln e^*/dV)_T = 4.32 \times 10^{-5} \text{ K}^{-1}$, which is reported in [13], we get $(\partial \ln e^*/\partial P)_T \cong -1.8 \times 10^{-13} \text{ Pa}^{-1}$. Equation (25) yields the theoretical PSPC, which is depicted in figure 4, for a pressure rate $b_P = -1.7 \times 10^3 \text{ Pa s}^{-1}$. Since $(\partial \ln \Pi/\partial P)_T > 0$, in the aforementioned PSPC experiment, the ionic polarization is reduced on decreasing the pressure, and, therefore, the dilatancy current appears as a depolarization current.

4. Conclusions

In the present work, we showed that the expansion or contraction of a *polarized* dielectric, due to temperature or pressure variation, induces an electric current. The origin of the signal is entirely different from that produced by dipole rotation or space charge motion. The expressions for the polarization (or depolarization) currents were extracted, regarding the simple case of a cubic ionic crystal with divalent cation impurities. Numerical calculations of the current density for the above-mentioned system, were carried out corresponding to different polarization and depolarization experiments. The most intense signal is associated with the ionic polarization change on temperature modification. The phenomenon is expected to be more spectacular in electrets or composite materials exhibiting larger dielectric constants than that of an ionic crystal.

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