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PSEUDOPIEZOELECTRIC EFFECTS IN ICE

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Abstract

Observations of the electromagnetic radiation emitted by glaciers and sea ice suggest the existence of pseudopiezoeffects in natural ice Ih. This work deals with the theoretical prediction and experimental detection of pseudopiezoelectric effects in ice, manifested in the presence of gradients of elastic stresses, temperature and impurity concentration.

In a number of natural phenomena, e.g., in the preparation for drift and in the drift of temporary ice, in the displacement of sea ice and during compression of ice fields one can observe electromagnetic radiations emitted from the regions of ice mass which are acted upon by variable elastic stresses [1]. Here, usually, a maximum of the radiation energy appears to be close to Debye frequencies of relaxation of ice. These observations indicate the existence of electric polarization phenomena occurring under the action of elastic stresses in natural ice Ih, that is piezoeffects. But a standard piezoelectric polarization $P_i$ of a solid can be observed only for the structures which have no symmetry center, and can be described by the expression

$$P_i = d_{ijk} \varepsilon_{jk}$$

where $d_{ijk}$ is a piezoconstant tensor, and $\varepsilon_{jk}$ is a deformation tensor. Natural ice (Ih) due to disorder in its proton subsystem has a kind of a "statistical" symmetry center and, therefore, a usual piezoeffect is not observed in it. This symmetry center, however, can be destroyed in the following cases:

1) $\text{grad} \left( \frac{1}{2} \varepsilon_{ii} \right) \neq 0$ i.e. when there is a compression or extension gradient

2) $\text{grad} T \neq 0$ which takes place in the presence of thermal fluxes through ice

3) $\text{grad} C \neq 0$ i.e. in the case of an inhomogeneous impurity distribution over the ice bulk

4) $E \neq 0$ i.e. when an external electric field is applied to ice

5) $\text{grad} (B)^2 \neq 0$ i.e. in non-uniform magnetic fields.
In the present paper we have considered theoretically and observed experimentally the effects 1-4.

**Theoretical consideration**

There are experimental indications that the volumes occupied by ions (H,O$^+$ and OH$^-$) and Bjerrum defects (L- and D-) in ice are different from those, occupied by water molecules in the ice lattice [2]. As a consequence their energy must depend on the pressure ($E = \frac{3}{2} \epsilon_{ij}$), and in the presence of the pressure gradient these defects will be moving along grad ($\frac{3}{2} \epsilon_{ij}$), the same as an air bubble comes to the surface in liquids. Inasmuch as ionic and Bjerrum defects possess an electric charge, their directed motion can cause electric current and polarization of ice. In the first (linear) approximation the energy of the defect, W, in the field of elastic deformations is given as:

$$W_i = W_0 - \alpha_i \left( \frac{3}{2} \epsilon_{ij} \right)$$

where $i = 1, 2, 3, 4$ for H,O$^+$, OH$^-$, O$^-$, and L-defects, respectively. The force acting on the defect from the side of the elastic stress field:

$$\vec{F}_i = \alpha_i \, \text{grad} \left( \frac{3}{2} \epsilon_{ij} \right)$$

The flux of the i-th type defects is described by the equation:

$$\vec{J}_i = (e_i \vec{E} - \eta_i \vec{P} + \alpha_i \text{grad} \left( \frac{3}{2} \epsilon_{ij} \right)) \frac{\mu_i n_i}{\epsilon_i l} - \frac{k_B T \mu_i}{\epsilon_i} \text{grad} (n_i)$$

where the configurational vector $\vec{\omega}$:

$$\vec{\omega} = \frac{t}{\sum_i n_i \vec{J}_i \, dt}$$

$e_i$, $\mu_i$, $n_i$ - are the charge, the mobility and the concentration of the i-th type defects, respectively

$$\eta_i = (1, -1, -1, 1)$$

$\vec{P} = 3.85 \, \kappa_{\theta} \rho_{\theta}; \Omega_{\theta} = 2.76 \, \AA$

and $E$ is the strength of the electric field.

Combined with the Poisson equation:

$$\text{div} \vec{E} = \frac{1}{\epsilon_0 \epsilon_\infty} \sum_i e_i (n_i - n_{i0})$$

eq.(4-6) describe fully this pseudopiezoeffect. $\epsilon_\infty \approx 3.2$, $\epsilon_0$ is the dielectric permittivity of vacuum. Consider several specific solutions of this system.

$$\text{grad} \left( \sum_i \epsilon_{ij} \right) = \text{const}$$

For an ice sample with unclosed surfaces in a stationary situation an electric field $\vec{E}$ occurs along grad ($\sum \epsilon_{ij}$).

In the case of one type of charge carriers

$$\vec{E} = \frac{\alpha_i \text{grad} \left( \frac{3}{2} \epsilon_{ij} \right)}{(\epsilon_i + \epsilon_\infty \epsilon_\infty)}$$
In the case of two types of charge carriers ($H_2O^+$ and L defects)

$$\vec{E} = \frac{(\lambda_u - \lambda_1) \nabla \epsilon}{\epsilon}$$

(9)

where $e$ is the charge of the proton.

We have also found the solution for the ice samples supplied to real measuring devices, for the case of the application of oscillating or pulsed deformations. These solutions were used for processing the experimental results. However, even finite formulae, describing these cases, consume two pages, we therefore, do not present them here. In the cases of the effects (2-4), the electric polarization of the ice samples arises either due to thermoelectric effect (grad $T \neq 0$) or redistribution of the space charge in the course of diffusion in inhomogeneously doped samples of ice (grad $C \neq 0$) or during the current flow through ice ($E \neq 0$). On each particular case the elastic deformation of ice reverses its polarization $P$ and is followed by dissipation of the energy of the electromagnetic fields. This dissipation can be observed as electromagnetic radiation or else, (if the samples incorporate electrodes) in the form of oscillating potential difference. In this case at frequencies $\omega \gg \omega_0$ the charge carriers have no time to get redistributed in the bulk of the deformed ice and, in the first approximation, the oscillating part of the polarization $P_{AC} = \epsilon E$, where $\epsilon$ is a strain. At frequencies $\omega \lesssim \omega_0$ one has to allow for the fact that the AC voltage arising at the elastic oscillations is applied to the bulk of ice whose electric conductivity and dielectric permittivity have a complicated frequency dependence [7].

Experiment

The experimental techniques and the equipment used by us for the investigation of the electromechanical polarization occurring at inhomogeneous deformations (grad $\nabla \epsilon \neq 0$) were, principally, analogous to those described in the work [6]. The main difference consisted in the application of pulsed loadings, the duration of the front being $\approx 0.8$ ms. The sample dimensions were also changed to $25 \times 10 \times 1$ mm$^3$. Besides pure melt-grown ice we employed ice grown from the gas phase, and the samples doped with HF and HCl, the concentrations $10^{-9}$ - $10^{-3}$ M/l. A DL 102 Point Averager was used to isolate the signals from the noises.

Figure 1 presents typical time diagrams of the pseudopiezoeffect signal for the sample doped with HF ($10^{-7}$ M/l) at several temperatures. At temperatures $T < -50^\circ$C the effect reverses its sign, and near the transition temperature the competition of the two mechanisms is clearly seen. The investigations of $\sigma$ and $c$ dispersion in the same samples shows that at $T \approx -50^\circ$C the "crossover" phenomenon is observed, so that at higher temperatures the majority carriers are L defects whereas at lower temperatures $H_2O^+$ ions.

Fig.1: Time diagram of the potential difference $V$ at bending of a thin ice sample measuring $25 \times 10 \times 1$ mm$^3$; the amplitude of the displacement of the sample upper end is 48 $\mu$m. The input capacity and resistance of the measuring device correspond to 140 pF and $10^6$ Ohm respectively. The sample was doped with HF, the concentration being $10^{-7}$ M/l.
The solution of the system of equations (4-6), which are time-dependent, for the case of $\text{H}_2\text{O}^+$ ions and L defects, with respect to the potential difference, $V$, at the input of the measuring device with an input resistivity and capacity $R$ and $C$, respectively, yields

$$V = V_1 \exp(-\omega_1 t) + V_2 \exp(-\omega_2 t)$$

$$V_1 = \mathcal{L}_4 \text{grad} \left( \frac{2}{3} \varepsilon_{ijj} \right) / (e_3 + e_3 Z \omega_D)$$

$$V_2 = \mathcal{L}_4 (L - L_1) \text{grad} \left( \frac{3}{2} \varepsilon_{ijj} \right) e / e_1^2 \left( \frac{2 \sigma_1}{\sigma_3} + \frac{e_3^2}{e_1^2} \right)$$

$$\frac{1}{Z} = \frac{1}{C} \left[ \frac{1}{R} + \frac{S}{L} (\sigma_1^2 + \sigma_4^2) \right]$$

$$\omega_1 = \omega_D + \frac{1}{Z}; \quad \omega_2 = \omega_D / CR(\omega_D + \frac{1}{Z})$$

$$\sigma_1 = e_1 / \mu_1 n_1; \quad \sigma_4 = e_3 / \mu_4 n_4; \quad \sigma_3 = e^2 / \left( \frac{e_3^2}{\sigma_1^2} + \frac{e_1^2}{\sigma_4^2} \right)$$

$$\omega_D = \varphi \left( \frac{\sigma_1}{e_1^2} + \frac{\sigma_4}{e_3^2} \right); \quad S = 250 \text{mm}^2; L = 1 \text{mm}$$

$\omega_D$ is the Debye frequency, $\alpha_1$ were determined from the eq.(10-14) and the experimental data. Fig.2 shows the temperature dependence of $\alpha_1$. With $T > -20^\circ\text{C}$, $\alpha_1$ is related to L defects, with $T < -70^\circ\text{C}$ to $\text{H}_2\text{O}^+$ ions.

Fig.2 : Temperature dependence of the pseudopiezoeffect constant $\alpha$. The HF concentration is $10^{-7}$ m/1.
The obtained α₁ and α₄ correspond to larger specific volumes of H₂O⁺ and L defects as compared with that of water molecule. The effects (2)-(4), too were observed experimentally. To excite oscillating homogeneous deformations in the frequency range of 5-10000 Hz, we employed a vibrator 513-A (Shin Nippon Seiki Co.,Ltd) and a magnetodynamic system, described elsewhere [6]. With frequencies ω > ω₀, the observed AC voltages were close to the value of εV, where ε is a deformation amplitude (ε = 10⁻⁵-10⁻⁷), and V is a constant potential difference caused by grad (T), grad (c) or an external field E. With ω < ω₀, the dispersion of the signal amplitudes were observed at the same frequencies as that in the spectra of the electric properties. In the experimental investigations of the effect (2) an active part was taken by doctor Sato. The authors express their deep gratitude to him. The authors are also thankful to the Japan Society for the Promotion of Science whose financial support aided in the accomplishment of this combined work.

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