The complex permittivity of ice crystals

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Résumé.

Les cristaux de glace possèdent des propriétés diélectriques très particulières. On observe une constante diélectrique statique élevée, une relaxation du type de Debye à des fréquences relativement basses et une conductivité en courant continu. On a pu montrer que ces propriétés électriques ne peuvent être interprétées théoriquement que lorsqu'on admet l'existence simultanée de défauts réticulaires typiques:

les ions H_3O^+ et OH^-, et

les défauts de valence (ou de Bjerrum).

La présente théorie tient compte de ces quatre types de défauts et de leurs propriétés de réorientation des molécules d'eau le long de leurs chemins de diffusion. La discussion des résultats montre que le temps de relaxation et la conductivité à haute fréquence sont déterminés par le mécanisme majoritaire, dans la glace pure, les défauts de valence. A cause de ce caractère prédominant assez distinct, la constante diélectrique statique ne dépend pas de la concentration et de la mobilité des défauts. Par contre, la conductivité en courant continu est due au mécanisme minoritaire des ions. Leur concentration est très faible, mais leur mobilité est extrêmement élevée, ce qui peut être expliqué par l'effet tunnel des protons le long des liaisons hydrogène.

Because of its fundamental importance for various branches of science the physical properties of ice crystals have been studied intensely in recent years at several places. New accurate measurements, the advent of new methods such as neutron diffraction [1], nuclear magnetic resonance [2] or the methods for the study of fast chemical reactions [3] and the modern concepts of crystal imperfections have led to a good understanding of many of the physical properties [4-8]. Review articles on the recent developments in ice physics may be found in [9] and [10].

1. Experimental.

The dielectric behaviour of ice crystals has attracted much interest since the first studies of the dispersion in 1924. The static permittivity has the

high value of about 100 and increases with lowering temperature. The high-frequency value $\varepsilon'_\infty = 3{,}2$ is practically temperature-independent. Ice represents one of the rare cases of a simple Debye dispersion with a single relaxation time τ. It is relatively long ($5 \cdot 10^{-5}$ sec at $-10°$ C), especially in comparison to that of liquid water. The relaxation time shows the usual exponential temperature dependence with an activation energy $E_\tau = 0{,}575$ eV. It is practically the same in the mechanical relaxation [11] and is proportional to the spin-lattice relaxation time T_1 of the proton magnetic resonance [2].

Often it is more convenient to express the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ in terms of the complex conductivity $\sigma^* = \sigma' + i\sigma''$. The relating formulae are

$$\sigma' = \omega\varepsilon_0\,\varepsilon'' \quad \text{and} \quad \sigma'' = \omega\varepsilon_0\,\varepsilon' \tag{1}$$

Therefore the real part of the conductivity σ' instead of ε'' is considered in the following.

At frequencies above the dispersion region the conductivity has a high limiting value $\sigma'_\infty = \sigma'_0 + \varepsilon_0\,(\varepsilon'_s - \varepsilon'_\infty)\,\tau$ which amounts to $1{,}6 \cdot 10^{-5}\ \Omega^{-1}\ m^{-1}$ at $-10°$ C for very pure crystals [5, 8]. The conductivity drops in the dispersion region, but does not go to zero as it would in the case of an ideal insulator. Actually it levels off at a value σ'_0 for low frequencies. This d.c. conductivity is difficult to measure, since it strongly depends on the purity of the sample and on the properties of the electrodes. If blocking electrodes are used or voltages below the dissociation potential are applied, an additional drop of σ' associated with an increase of ε' is observed at very low frequencies. This second dispersion was shown to be due to space-charge effects [4-6] and will not be considered in this paper. The best σ'_0 values for purest ice are about $10^{-7}\ \Omega^{-1}\ m^{-1}$ at $-10°$ C with an activation energy of $0{,}61$ eV [8, 12]. Micro-electrolysis experiments [13] proved the ionic caracter of the d.c. conductivity.

2. CRYSTAL STRUCTURE AND PREVIOUS THEORIES.

The ice structure consists of nearly regular oxygen tetrahedera. Every oxygen is linked to its 4 neighbours by hydrogen bonds -OH ... O-, the O-O distance being $R = 2{,}76$ Å. The observation of zero-point entropy and the neutron diffraction evidence [1] lead to the conclusion that the hydrogen

atoms are located in any one of the many possible configurations fulfilling the three Bernal-Fowler rules:

i)   the hydrogen atoms lie on the lines connecting neighbouring oxygen atoms,

ii) there is only one hydrogen atom on each such linkage;

iii) each oxygen atom has two hydrogen atoms at a short distance ($r_{OH} = 0,99\text{Å}$) and hence water molecules are preserved.

Using the value of the dipole moment of water measured in the vapour phase several attempts to calculate the static dielectric constant theoretically have been made. The most elaborate computation of Powles [15] with the Fröhlich theorem and under the assumption of equally probable hydrogen configurations led to a value which is about 20% lower than the experimental one. This is to be expected, since recent theoretical work by Hofacker [14] emphasises that the dipole moment is increased by hydrogen bond formation. The problem how the orientation of the water molecules changes had not to be touched in Powles' work.

It is easy to see that a crystal which strictly obeys the Bernal-Fowler rules cannot change its hydrogen arrangement and hence would not show dipole relaxation. In a recent paper [7] all potential mechanisms have been analysed. It could be shown that the time-independent d.c. conductivity of ice can only be explained, if two specific kinds of lattice imperfections occur simultaneously, though not necessarily in comparable concentrations. The violation of the third Bernal-Fowler rule leads to *ionized states* (H_3O^+ and OH^-) and the violation of the second rule to *orientational or Bjerrum defects* (doubly-occupied bonds: D-defects and vacant bonds: L-defects).

The diffusion of any one of these defects changes the orientation of the water molecules along the diffusion path in such a way that the same chain of molecules does not permit the successive passage of more than one defect of the same type. But a chain oriented e.g. by the passage of an H_3O^+ ion can be reoriented by the diffusion of a D-defect in the same or an L-defect in the opposite direction. Ionized states and Bjerrum defects are *complementary* to each other. Their concentrations in thermal equilibrium are given by the corresponding mass action laws.

A first approach toward a dynamic theory of the electric properties of ice crystals has been worked out under the assumption that only one type of defects is present at a time [4-6]. This is a useful approximation for the

interpretation of the Debye dispersion, because at high frequencies the defects perform only a few diffusion steps before the a.c. field reverses its polarity. However, for a full understanding of the electric phenomena including the d.c. conductivity all four types of defects have to be considered simultaneously and in a symmetrical way. A general theory based on these principles has been worked out [8] and is summarised in the following.

3. GENERAL THEORY.

3.1. *Effective charges.* In a stationary d.c. current the transport of one elementary charge e from one electrode to the other requires an equal number of diffusion steps of ionized states and Bjerrum defects. The energy principle leads to the relation

$$ap + 2bq = e\mathrm{R} = e\,(a + 2b)\ . \tag{2}$$

Here $a = r_{HH}$ and $b = r_{OH}$ are the distances of the proton transfer in ionized states and Bjerrum defects respectively. p and q are the corresponding effective charges, which include the contribution of the associate electron cloud movement [8] and the change of the electric potential at the proton positions due to the infrared polarisability of the molecules forming an ionized state or adjacent to a Bjerrum defect [7]. Both contributions lead to the inequality $q < e < p$.

3.2. *Transfer probabilities.* The total probability for the diffusion of a lattice imperfection from one lattice site to the neighbouring one is the product of three factors *:

i) the classical or quantummechanical transfer probability p_0^i of the proton in the double potential well of an isolated molecule pair,

ii) the modification of this probability due to an externally applied electric or mechanic stress,

iii) the geometrical transfer probability p_k^i which accounts for the actual position of the defect and the hydrogen arrangement of the neighbouring molecules in the crystal.

It is assumed that at $t = 0$ all hydrogen configurations are equally probable. E.g. the initial value p_1^+ for a proton transfer of an H_3O^+ ion

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* The index i stands for $+$, —, D or L defect.

along a bond parallel to the c-axis is $\frac{1}{4}$. If at $t = 0$ an electric field is applied, this probability becomes a function of time due to the orientation changes by defect diffusion. If j^i are the number of defects per unit area passing through a certain lattice plane (e.g. normal to c) and N_B is the number of hydrogen bonds normal to this plane, the change of the probabilities is governed by the factor

$$S = (1/N_B) \int_0^t (j^+ - j^- - j^D + j^L) \cdot dt . \qquad (3)$$

For the example given above the geometrical transfer probabilities become

$$p_1^+ = \frac{1}{4} - \frac{S}{2} \quad \text{and} \quad p_1^{+'} = \frac{1}{4} + \frac{S}{6}$$

for transfers in the direction of positive and negative values of j^i respectively. In a similar way all the different p_k^i values have been computed. S varies between 0 and $\frac{1}{2}$.

3.3. *Form of the solution.* The expressions for the defect currents j^i can be cast in a system of four differential equations. Since we are interested in the periodic solutions and assuming a homogenous defect distribution, one obtains the following four equations for the RMS values of the variables j^i and the external field F

$$j^i = \pm n^i \, \mu^i \, F \pm \Omega^i \, n^i \, (j^+ - j^- - j^D + j^L)/i\omega \qquad (4)$$

where n^i are the defect concentrations, $\mu^{\pm} = apRp_0^{\pm}/6kT$ and $\mu^L = 2bqRp_0^L/9kT$ are the mobilities and the $\Omega^i = \text{const.} \cdot p_0^i$ describe the interaction between the four types of defects. Defining σ^i as the specific high-frequency conductivities $\sigma^{\pm} = apn^{\pm} \, \mu^{\pm}/R$ and $\sigma^L = 2bqn^L \, \mu^L/R$, the equations can be solved and take the form of a Debye dispersion:

$$\sigma^* = \sigma_0' + \frac{\sigma_\infty' - \sigma_0'}{1 + 1/i\omega\tau} \qquad (5)$$

where

$$\sigma_\infty' = \sigma^+ + \sigma^- + \sigma^D + \sigma^L \qquad (6)$$

$$1/\sigma_0' = A_1/(\sigma^+ + \sigma^-) + A_2/(\sigma^D + \sigma^L) , \qquad (7)$$

and

$$1/\tau = A_3[(\sigma^+ + \sigma^-)\, A_4 + (\sigma^D + \sigma^L)\, A_5]\,. \qquad (8)$$

Using equation (1) one obtains for the static permittivity

$$\varepsilon_s' = \varepsilon_\infty' + A_6 \frac{[(\sigma^+ + \sigma^-)\, A_7 - (\sigma^D + \sigma^L)\, A_8][(\sigma^+ + \sigma^-)\, A_9 - (\sigma^D + \sigma^L)\, A_{10}]}{[(\sigma^+ + \sigma^-)\, A_4 + (\sigma^D + \sigma^L)\, A_5]^2}\,. \qquad (9)$$

The positive constants A_l contain numerical factors, universal constants and the quantities a, b, p, q and R.

3.4. *Discussion.* As shown in § 1 σ_∞' and σ_0' differ by a factor of 160 in very pure crystals. This means—by comparison of equations (6) and (7)— that one of the two kinds of lattice imperfections clearly predominates and thus determines σ_∞', τ and ε_s'. In this case the static dielectric constant is independent of the concentration and of the mobility of the majority defects, but depends on the quantities ocurring in the factors A_l. The effective charges p and q have not been calculated theoretically so far. Since the detailed analysis of the electric measurements on mixed crystals of ice and hydrofluoric acid [6, 8] leads to the conclusion that actually the *Bjerrum defects* provide the *majority mechanism* in pure ice, the effective charges can be determined empirically with the aid of equation (9). The results are $p = 2{,}0\,e$ and $q = 0{,}6\,e$, where e is the elementary charge. These values seem to be very reasonable and are in agreement with the inequality of § 3.1.

As equation (7) shows, the d.c. conductivity is determined by the *minority defects* which actually are the ionized states in pure ice. For the mobility of the ions very high values of $10^{-5}\ m^2/Vs$ have been measured recently [3]. They are in agreement with the calculations of quantum-mechanical tunnelling of protons as diffusion mechanism of ionized states. Thus ice may well be called a *protonic semiconductor*.

In ice-HF mixed crystals the conductivities $(\sigma^+ + \sigma^-)$ and $(\sigma^D + \sigma^L)$ may be such that one of the brackets in equation (9) cancels. The static dielectric constant then equals ε_∞'. Such cases of *pure conductance* have been observed and correspond to the two minima in the study of the dielectric constant as a function of the fluorine content [6].

As shown in details in [8] the theory describes quantitatively all known electric properties of ice and ice-HF mixed crystals. Further experiments to test the theory are in progress.

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