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I. Pure ice crystals

1. Introduction

In addition to being a very common and important substance in nature, ice crystals show very peculiar physical and physico-chemical properties. This applies to the bulk properties of the perfect crystals and in particular to the properties due to crystal imperfections. Among the latter we can distinguish three different categories of properties:

1.1 The *self-diffusion* of oxygen, hydrogen or deuterium and substitutional impurities such as fluorine: Within the limits of error the same coefficient of diffusion has been measured for O^{18}, D and F impurities [1, 2]. This result suggests that in ice entire molecules are the migrating entities. The diffusion might take place by a vacancy or an interstitialcy mechanism. From an estimate of the energy of formation the Schottky mechanism seems to be the most likely one [3].

Recent measurements by RIEHL and DENGEL [1] of the diffusion of tritium in ice led to a somewhat lower value of the diffusion coefficient and to an activation energy which agrees with the one for the dc conductivity within the limits of error. This might perhaps indicate that the diffusion of H by the mechanism responsible for the dc conductivity is predominant.

The question of the selfdiffusion mechanism remains open, till we have more data on the behaviour of both, H and O, as a function of temperature.

1.2. The *crystal plasticity* has been studied extensively in recent years [4]. Undoubtedly these mechanical properties are to be explained by dislocation mechanisms. WEERTMAN came to the conclusion that the Eshelby-Schoeck dislocation damping mechanism can account for the steady-state creep of ice as well as ever can be expected for a dislocation theory.

1.3. The *third category* includes the dielectric and mechanical relaxation, the relaxation behaviour in proton magnetic resonance and the dc electric conductivity. In all these cases changes of the orientations of the water dipoles, i.e. rearrangements of the hydrogen atoms in the crystal structure are involved.

This subdivision of properties into categories is justified by the observation of BRILL and CAMP [5] that no correlation between plastic and dielectric dispersion properties of ice crystals exists. Theoretically it seems to be very unlikely that a dislocation mechanism would produce any changes in the hydrogen configuration [3]. The arrangement of three out of four neighbouring molecules uniquely determines the orientation of the central molecule. By the same argument it can be concluded that a vacancy mechanism does not have any influence on the H configuration of the crystal.

At present the properties of the third category are the best studied and understood and they will be discussed in the following. Most of the results to be described stem from a cooperation of Drs. A. STEINEMANN and C. JACCARD and the present author [2, 3, 6, 7].

2. Experimental

Ice crystals show a dielectric dispersion at relatively low frequencies [8]. It is a case of a pure Debye dispersion characterised by a single relaxation time τ. The dielectric constant drops from a static value ε'_s of about 100 to a high-frequency

value ε'_∞ of 3.2. The electric conductivity at high frequencies shows a large value σ'_∞ which is due to the Debye dispersion. However, at low frequencies ice does not behave as an ideal dielectric, but shows a conductivity in static fields σ'_0. It has
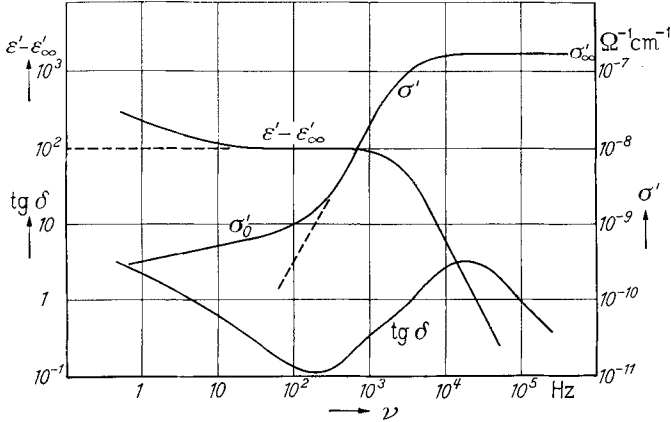

Fig. 1. Dielectric constant ($\varepsilon'_\infty - \varepsilon'$), electrical conductivity σ'_0 and loss factor tg δ of very pure ice at $-10°C$ plotted as a function of frequency (A. STEINEMANN [2]).

been proved experimentally that this dc conductivity is time-independent over long periods and that it is a purely ionic conductivity [9]. Molecular hydrogen is produced at the cathode of a micro-electrolysis experiment in an amount which corresponds to the total electric charge within the limits of error of about 2%. The ratio σ'_∞/σ'_0 is roughly 300 in a high-purity crystal.
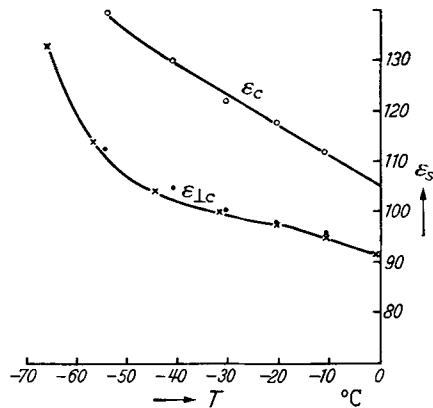

Fig. 2. Static dielectric constant of ice crystals as a function of temperature.
xx   Polycrystalline sample; AUTY and COLE [8].
oo   Single crystal; electric field parallel to c-axis } HUMBEL, JONA and SCHERRER [8].
●●   Single crystal; electric field normal to c-axis

In the actual experiment usually at very low frequencies an additional increase of the real part of the dielectric constant and additional losses are observed. This very low frequency dispersion depends on the experimental conditions and is due to space-charges [2]. The charge carriers are not or only partially discharged at the electrodes (blocking electrodes). These space-charge phenomena will not be further discussed here. Typical experimental values of the electric properties are shown on tables 1 and 2.

According to KNESER et al. [10] and to SCHILLER [11] certain elastic constants which correspond to deformations other than those of rotational symmetry, e.g. c_{44}, show a dispersion which formally can be described by the Debye expressions. The maximum of the loss factor is by more than a factor of 100 smaller than in the dielectric case, but the relaxation times are virtually the same.

Table 1. *Pure ice crystals: Typical experimental data for* $-10°C$

Dielectric constant:
  static $\varepsilon'_c = 112$ $\varepsilon'_{\perp c} = 96$
  high-frequency $\varepsilon'_\infty = 3.2$
Relaxation time: $\tau = 5 \times 10^{-5}$ sec
Electric conductivity:
  static $\sigma'_0 = 6 \times 10^{-10}$ $\Omega^{-1}cm^{-1}$★
  high-frequency $\sigma'_\infty = 1.7 \times 10^{-7}$ $\Omega^{-1}cm^{-1}$

In experiments of nuclear magnetic resonance of the protons which recently have been refined by KUME [12] and KRÜGER [13], the spin-lattice relaxation time T_1 has been observed to be proportional to the dielectric relaxation time. The line breadth, which is the reciprocal of the spin-spin relaxation time T_2, is temperature-independent below about $220°K$ and its value corresponds to the condition of the "frozen lattice". Above about $-50°C$ the line breadth decreases. This means that motional narrowing due to H atoms changing positions only occurs at temperatures near the melting point.

Table 2. *Activation energies*

	Pure ice	Solid solutions	
		$H_2O - HF$	$D_2O - DF$
Relaxation time and high-frequency conductivity	0.575 eV	0.235 eV	—
Static conductivity	0.61 eV★	0.325 eV	0.38 eV

Thus the dielectric and the mechanical as well as the spin-lattice relaxation times all have the same activation energy of 0.575 eV. These properties are associated to changes in the hydrogen arrangement as has been shown by BASS [14] theoretically for the mechanical dispersion. In this case as well as in proton magnetic resonance, rearrangements with and without net electric moment changes occur. Hence it can be concluded that there are no faster mechanisms for configuration changes than the ones determining the dielectric behaviour [3].

3. The positions of hydrogen in the ice lattice

It has been known for some time from X-ray analysis that each oxygen atom is surrounded by four neighbours which form a very nearly ideal tetrahedron. The

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★ M. EIGEN, L. DE MAEYER and H. C. SPATZ presented at the Colloquium on the Physics of Ice Crystals, Erlenbach-Zürich 1962 new and apparently more reliable values obtained by four-probe measurements:
$\sigma'_0 = 1.0 \times 10^{-9}$ $\Omega^{-1}cm^{-1}$ ($\pm 15\%$) at $-10°C$ and an activation energy of 0.480 ± 0.065 eV.

$O - O$ distance R is 2.76 Å. All oxygen atoms are linked by hydrogen bonds which are governed by the following *Bernal-Fowler* rules [15]:

i) On each line connecting neighbouring O atoms there is only one H atom.

ii) Always two H atoms are close to one O atom at a distance of $b = 0.99$ Å. Hence water molecules are preserved in the structure.

These rules permit 6 orientations of the dipole moment of every water molecule. But according to PAULING [16] the number of hydrogen configurations of a crystal of N molecules reduces to $(3/2)^N$. From neutron diffraction on D_2O single crystals PETERSON and LEVY [17] have concluded that PAULING's model is the correct long-range description of the structure. This means that all configurations allowed by BF rules occur with about equal probability under normal conditions.

Fig. 3. Arrangement of water molecules in hexagonal ice crystals. The open circles represent oxygen atoms, the full circles hydrogen

The conclusion drawn from the properties of section 1.3, shows that PAULING's half-hydrogen model is observed in diffraction due to a *space* average rather than a time average. From the observation of zero-point entropy and the neutron diffraction data follows that no ordering occurs on cooling to very low temperatures. In the framework of the present concepts this is based on the fact that the relaxation time for configuration changes becomes very long at temperatures below those of liquid air [3].
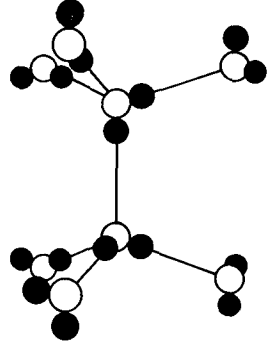
4. Mechanisms of hydrogen rearrangements

It has been demonstrated [18, 3] that the electrical properties of ice crystals can only be accounted for by assuming two kinds of very specific point imperfections:

— Ion-states: H_3O^+ and OH^- and

— Bjerrum's orientational defects.

In analogy to liquid water it seems rather natural to assume a self-dissociation of water in ice too, according to the equation

$$2 H_2O \rightleftharpoons H_3O^+ + OH^-. \tag{1}$$
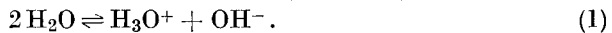
These ion-states are generated by a *translational* motion of a proton along the hydrogen bond to a neighbouring molecule, thus violating the second Bernal-Fowler rule. Once formed, the ion-states are able to diffuse in the lattice by similar translational jumps through a distance $a = 0.78$ Å. We call these defects *ion-states* rather than ions, because they do not move bodily in the lattice. But as they move in the lattice, they change the orientation of the water molecules along the diffusion path.

However, the existence of these ion-states alone is not sufficient to explain the time-independence of the dc conductivity σ_0'. With no other mechanism present, the ice lattice would polarise sooner or later upon the application of an electric
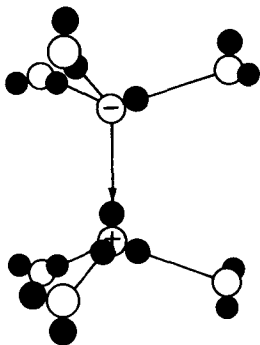

Fig. 4. Formation of a pair of ion-states by the translation of a proton along the hydrogen bond
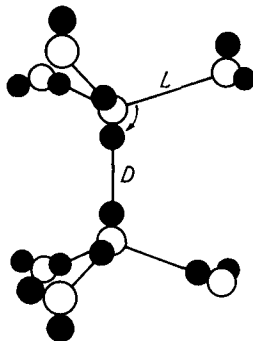
Fig. 5. Formation of a pair of Bjerrum defects by a rotational motion of a proton within the same molecule

field and then no further current could flow. From this follows that we have to postulate a second, motionally independent mechanism which, too, permits re-orientations of the molecules.

This second kind of imperfections of the H network are the orientational defects first introduced by BJERRUM [18]. They arise from violations of the first BF rule. A proton can make a *rotational* motion within the electron cloud of its own molecule to a neighbouring bond. Thus a doubly-occupied bond (D-defect) and a vacant bond (L-defect) are generated. This can be formulated as a reversible reaction calling normal bonds N:

$$2\,\mathrm{N} \rightleftharpoons \mathrm{D} + \mathrm{L}, \tag{2}$$

for which the law of mass action can be applied. Here again it is true that the same kind of motion responsible for the formation of the defects also enables the diffusion of the defects in the lattice. The diffusion of these defects produces re-orientations of molecules too. Bjerrum defects have the required complementary properties: e.g. a chain of molecules polarised by the diffusion of an H_3O^+ ion-state will be brought back to its original configuration by the diffusion of an D-defect in the same or an L-defect in the opposite direction. For a complete theoretical description of the electric properties of ice it is necessary to consider the coexistence of the four species of defects.

The actual structures of the defects are not known, the figures 4 and 5 being only schematic of course. For the Bjerrum defects the only postulate of the theory is the property of reorienting water molecules by defect diffusion by proton motions other than the translations occurring with ion-states. COHAN et al. [19] discussed a structure for the D-defect in which the molecules forming the defect are rotated bodily relative to the usual bond directions such as to decrease the H — H repulsion. Recently DUNITZ [20] proposed another model, in which in the step of generation the proton would move only about half way to a relatively

highly symmetric position. Each diffusion step of a D-defect would then involve the motions of both neighbouring protons. Both models comply with the postulate of the theory and lead to the correct order of magnitude of the energy of formation.

5. Theoretical

The general form of the theory on the bases described above has been worked out by JACCARD [6]:

When a defect diffuses, a certain effective charge is transported. It differs from the charge of the proton due to the associate electron cloud movement and the variation of the potential at the H sites caused by the polarisability of neighbouring molecules. Both contributions lead to the inequality that the effective charge of Bjerrum defect q is smaller and the charge p of the ion-states is larger than the elementary charge [3, 6]:

$$q < e < p. \tag{3}$$

According to the energy principle the relation

$$a p + 2 b q = e R = e (a + 2 b) \tag{4}$$

must hold. Therefore, only one of the effective charges is an unknown parameter of the theory.

Another basic quantity is the transfer probability for the diffusion of a defect. There are three factors to be considered:

i) the classical or quantum-mechanical transfer probability $\mathscr{P}_0^i$ of the proton in the double potential well of two neighbouring lattice sites.

ii) the modification of this probability due to the external electric field or mechanical stress,

iii) the geometrical transfer probability which accounts for the actual position of the defect and the hydrogen arrangement of the neighbouring molecules. This last term is rather tedious to compute. It depends on the state of polarisation of the molecules due to the prehistory of the diffusion of defects.

Considering bonds intersecting planes normal to the applied electric fields, it is possible to write down four differential equations for the defect currents[*]. Assuming a homogeneous defect distribution the system of equations can be solved for periodic, stationary solutions. Defining the specific conductivities as

$$\sigma^{\pm} = n^{\pm} \mu^{\pm} p \, a / R \tag{5}$$

$$\sigma^{\mathrm{D}}_{\mathrm{L}} = n^{\mathrm{D}}_{\mathrm{L}} \mu^{\mathrm{D}}_{\mathrm{L}} q \, 2 \, b / R \tag{6}$$

where n^i are the concentrations and μ^i the mobilities:

$$\mu^{\pm} = \mathscr{P}_0^{\pm} a \, p \, R / 6 \, k \, T \tag{7}$$

$$\mu^{\mathrm{D}}_{\mathrm{L}} = \mathscr{P}_0^{\mathrm{D}}_{\mathrm{L}} 2 \, b \, q \, R / 9 \, k \, T , \tag{8}$$

a final expression can be derived for the electric conductivity. It consists of two terms: a frequency independent dc conductivity σ_0', and a term which has the

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[*] Higher order correlations due to the puckered hexagons formed by the water molecules are not considered.

form of the Debye dispersion for the complex number σ^*. The characteristic quantities of the dispersion: the hf conductivity σ'_∞, the relaxation time τ and the static dielectric constant ε'_s can be extracted. They depend on all the specific conductivities and constants like a, b, p, q and R.

The fairly large ratio σ'_∞/σ'_0 shows that one kind of defects must be predominant. The analysis of the investigations on ice-HF mixed crystals to be described subsequently led to the conclusion that the Bjerrum defects provide the majority mechanism and hence determine the values for σ'_∞ and τ. The ion-states, on the other hand, are rate-determining for the dc conductivity. The final expressions specialised for the case of pure ice, where we can assume that

$$(\sigma^L + \sigma^D) \gg (\sigma^+ + \sigma^-),$$

are as follows:

$$\sigma'_\infty = (\sigma^L + \sigma^D), \tag{9}$$

$$\sigma'_0 = (\sigma^+ + \sigma^-)\, e^2\, R^2\, (1 + 10\, q\, b/27\, e\, R)/p^2\, a^2 \tag{10}$$

$$1/\tau = (\sigma^L + \sigma^D)\, 3\sqrt{3}\, R^3\, k\, T/4\, q^2\, b^2 \tag{11}$$

$$\varepsilon'_s = \varepsilon'_\infty + 4\, q^2\, b^2/3\sqrt{3}\, \varepsilon_0\, R^3\, k\, T. \tag{12}$$

Under these circumstances the static dielectric constant becomes independent of the specific conductivities, i.e. independent of the concentrations and the mobilities of all the defects. The last equation (12) can be used to calculate the effective charge q, since all other quantities are known experimentally. In agreement with the inequality (3) the values $q = 0.6\,e$ and $p = 2.0\,e$ were found.

Using the experimental data given e.g. in tables 1 and 2, the derived data shown in table 3 can be evaluated. The values are taken from references [6] and [2] and, where indicated, from [21]. In pure ice the concentration of ion-states is lower than the one for Bjerrum defects by a factor of about 10^5. The self-dissociation in ice is considerably smaller than in liquid water, since the effective dielectric constant has a value close to 3.2 rather than a value of 80 as in the liquid. The very low ionic concentration is compensated somewhat by a very high mobility [21], which can be accounted for by tunneling of the protons along the hydrogen bonds.

Table 3. *Pure ice: Derived data for* $-10°$C

	Bjerrum defects	Ion-states
Reaction equation	$2\,\mathrm{N} \rightleftharpoons \mathrm{D} + \mathrm{L}$	$2\,\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{OH^-}$
Energy of formation	0.68 ± 0.04 eV	$\begin{cases} 1.2\ \pm 0.1\ \ \text{eV} \\ 0.96 \pm 0.13\ \text{eV } [21] \end{cases}$
Concentration of defects	7×10^{15} cm^{-3}	8×10^{10} cm^{-3} [21]
Activation energy of diffusion	0.235 ± 0.01 eV	≈ 0 (tunneling)
Transition probability	2×10^{11} sec^{-1}	6×10^{13} sec^{-1}
Mobility (in cm^2/Vsec)	$\mu^L = 2 \times 10^{-4}$	$\mu^+ = 7.5 \times 10^{-2}$ [21]
Mobility ratio	$\mu^L/\mu^D \gtrsim 1$	$\mu^+/\mu^- = 10$ to 100 [21]
Effective charge	$0.6\,e$	$2.0\,e$

For comparison: Number of molecules per unit volume 3×10^{22} cm^{-3}

II. Behaviour of ice-HF solid solutions

1. Introduction

For quite a number of substances (salts, acids, bases) investigations [2, 22] have been made in order to find out whether they form solid solutions with ice. Even in cases where a real solubility could be established, the concentrations in the ice were usually low, but nevertheless the electric properties of the ice were found to change drastically. The best and most reproducible results have been obtained with NH_4F, HF and NH_3. The ease with which these impurities enter the ice lattice decreases in the order given. The highest concentrations reached in these cases were of the order of 10^{-2} molar solution which corresponds to a molar ratio of $1:5'000$. Above this limiting concentration the crystals are disturbed and bubbles appear.

The ionic and atomic radii of fluorine and nitrogen are very similar to oxygen. Therefore, it might be expected that *substitutional* mixed crystals are formed, HF and NH_3 replacing water molecules. If this is the case the impurities influence the equilibria of the lattice imperfections discussed in part I. The agreement between the theoretical expectations and experiments is conclusive evidence that the assumption of substitution is justified [2, 6].

2. Extension of the theory to mixed crystals

The substitution of water molecules by HF and NH_3 produces a deficiency and excess of protons respectively, i.e. one L- or one D-defect per molecule is introduced. NH_4F leaves the total proton number unchanged, but in fact rather complicated equilibria are to be expected.

The following discussion is for HF on which most of the measurements have been done. The same statements are expected to hold for NH_3 by changing L to D and $+$ to $-$ ion-states.

Bjerrum defects: To the concentration of the thermally formed defects we have to add an impurity L concentration equal to the concentration of the HF. Up to now, no association/dissociation equilibria between HF molecules and L-defects had to be considered, however, at very low temperatures this might be necessary. The law of mass action for the reaction (2)

$$n_L \cdot n_D = k \cdot \exp\left(-E_0/k\,T\right) \tag{13}$$

shows that n_L increases with rising HF content. In the limit of fairly high concentrations n_L becomes equal to the HF concentration, whereas n_D drops to zero.

Ion-states: As in liquid water there will be a dissociation according to the equation

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-. \tag{14}$$

The H_3O^+ concentration from this reaction adds to the one of the self-dissociation of the water molecules according to equation (1). In this case the positive ion-state concentration increases with rising HF concentration too, but ultimately only as $\sqrt{n_{HF}}$, while the negative ion-states die out.

In short, the specific conductivities of all the defects vary with the impurity concentration and will show a different temperature dependence form the one in pure ice. At high concentrations finally the L-defects must win and become the majority mechanism due to their higher power of the concentration dependence.

3. Experimental results [2, 6]

For HF concentrations below 5×10^{15} cm^{-3} (10^{-5} molar) no influence on the electric behaviour could be detected. This limit corresponds to the concentration of Bjerrum defects in pure crystals as shown on table 3 (7×10^{15} cm^{-3}). With increasing HF concentration the low frequency space-charge dispersion becomes rapidly mighty and shifts toward higher frequencies. There are concentrations where the two dispersions merge together, but at still higher concentrations the Debye dispersion emerges again. Thus for most mixtures it has been possible to determine the characteristic values of the Debye dispersion graphically from the measured curves.

The dispersion frequency $1/\tau$ is characteristic for the majority mechanism. Above 10^{-5} m-HF there is a concentration range where $1/\tau$ varies as $\sqrt{n_{HF}}$ followed by a region of proportionality at high concentration. This region becomes much broader at low temperatures, i.e. at $-54°$C as measurements of σ'_∞ show. Evidently these are the conditions where L-defects are in majority.

The dc conductivity σ'_0 depending on the minority defects shows an increase proportional to $\sqrt{n_{HF}}$ over the range 10^{-5} up to the limit of 10^{-2} m. The ratio σ'_∞/σ'_0 goes through a minimum at medium concentrations.
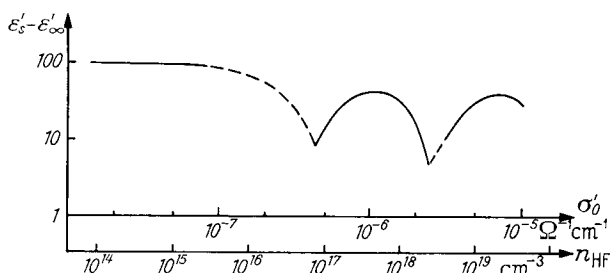

Fig. 6. Dipolar contribution to the dielectric constant ($\epsilon'_s - \epsilon'_\infty$) at $-10°$C plotted as a function of the dc conductivity σ'_0 and of the concentration of HF. (A. STEINEMANN [2].)

The static dielectric constant of the Debye dispersion starts to decrease above 10^{-5} m, passes through two minima where it drops to about the hf value 3.2. At high concentrations there is again an increase until the limit of miscibility is reached.

The typical behaviour of these quantities is compatible with the following explanation: *In pure ice Bjerrum defects provide the majority-mechanism.* In the region between the minima of the static dielectric constant and of ($\sigma'_\infty - \sigma'_0$) there is a slight predominence of the H_3O^+ ion-states. At high concentrations, above the second minimum, the L-defects overtake and clearly become majority.

The two minima of the static dielectric constant correspond to conditions of *pure conduction*. This means that the ratio of the specific conductivities $(\sigma^L + \sigma^D)/(\sigma^+ + \sigma^-)$ is such that no net dipolar polarisation of the crystal results. The relaxation time, in contrast, is not affected by this special situation.

The theory in its present form is in good agreement with all known facts including details like the minima of the static dielectric constant. However, more precise measurements of characteristic data on the same crystal specimen will be needed to test the theory more thoroughly.

III. Concluding remarks and discussion

1. Thermoelectric effect

Recently JACCARD generalized his theory to the case of non-vanishing temperature and defect gradients (to be published in this journal). Thermoelectric effects have been measured by LATHAM and MASON [23] and have been brought in connection with thunderstorm electricity. The charge-separation during the freezing of water (Costa-Ribeiro effect) too is basically due to the fact that defects of opposite signs show unequal mobilities.

Further investigations of these effects seem to be promising.

2. Saturation current and dissociation field effect

In a strong electric dc field the static conductivity shows saturation, since the field depletes the crystal of all charge-carriers. The ion-states freshly produced by the dissociation according to equation (1) leave the crystal in a short time. This means that the saturation current is limited by the rate of dissociation. In addition the field itself has an influence on the dissociation (Wien effect).

These properties have been studied extensively by EIGEN et al. [21] on H_2O and D_2O ice. For ordinary ice the rate constant of dissociation is 3.2×10^{-9} sec^{-1} ($\pm 10\%$) at $-10°C$ with an activation energy of 0.98 ± 0.13 eV. From the relaxation of the dissociation field effect the rate constant of recombination could be deduced as 0.86×10^{13} (mole.sec)$^{-1}$. The equilibrium constant in the law of mass action becomes 3.8×10^{-22} mole/lit.

3. Theoretical work by ONSAGER and DUPUIS [24]

Starting from the same bases as JACCARD, ONSAGER and DUPUIS independently had developed a theory of the electrical properties of ice. They consider in details the interactions among the defects including the effect of the polarisability of the crystal lattice in a generalized Debye-Hückel theory. The result is that the charges of the ion-states as the minority carriers are screened by Bjerrum defects, the screening radius being a few hundred Ångströms.

In addition they discuss associations of ion-states and Bjerrum defects leading to *sessile* ions. They argue that about 1/3 of the positive ions could be sessile and that this might be essential for the interpretation of the mixed crystal data (L. ONSAGER and T. J. DOUGHERTY, forthcoming paper).

The Onsager-Dupuis theory is in good agreement with the dissociation field effect data of EIGEN et al. [21].

4. Outlook

The ion-states in ice have mobilities which are by about two orders of magnitude bigger than the ones for usual ionic conductors. This suggests to use the term

proton-conductivity for ice. Stimulated by the analogy to semiconductors even a "band theory of protonic conduction" has been worked out recently [25]. The correct value for the mobility could be calculated. However, the proton bands turned out as very narrow which casts some doubts on the usefulness of such an approach.

Hydrogen bond systems occur in many other crystals e.g. in the ferroelectric KH_2PO_4 and in biological tissues such as the nerves where protolytic reactions seem to be important. Therefore, it can be expected that the ideas developed for ice will prove to be fundamental for these other cases too. It is felt that the basic properties of ice crystals are understood in principle by now, though in the details much remains to be done both from the theoretical and experimental point of view.

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