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INTERACTION OF POINT DEFECTS IN ICE

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Abstract. The interaction of point defects in ice has been neglected for a long time. Experimental data obtained from dielectric measurements on HF-doped crystals stimulated a new evaluation of the possibility of an interaction between Bjerrum defects and ions. In a previous paper it has been shown that this leads us to assume the existence of aggregates of Bjerrum defects and ions. In this paper these aggregates and Bjerrum defects are used to explain the dielectric properties of ice, especially the temperature dependence of the product of the high and low frequency conductivity $\sigma_0\sigma_\infty$.

The interaction of Bjerrum defects and impurity molecules leads to a dependence of the concentration of Frenkel pairs on Bjerrum-defect concentration. At HF concentrations above the native Bjerrum-defect concentration the formation of a Frenkel pair is enhanced. This leads to the fast out-diffusion which has been studied in highly doped crystals by means of NMR techniques.

Résumé. *Interaction entre défauts ponctuels dans la glace.* L'interaction entre défauts ponctuels dans la glace a été négligée depuis longtemps. Des données expérimentales obtenues à partir de mesures diélectriques de cristaux dopés par HF favorisent l'idée d'une interaction possible entre défauts de Bjerrum et ions. Cela conduit à supposer l'existence d'aggrégats de défauts de Bjerrum et d'ions. Ces aggrégats et les défauts de Bjerrum sont utilisés pour expliquer les propriétés diélectriques de la glace.

L'interaction des défauts de Bjerrum et des molécules d'impuretés conduit à une dépendance de la concentration en paires de Frenkel avec celle en défaut de Bjerrum. Des concentrations en HF supérieures à celles des défauts de Bjerrum à l'équilibre augmente la formation de pairs de Frenkel. Cela conduit à la diffusion rapide qui a été étudiée dans le cas de cristaux fortement dopés, par des techniques de RMN.

Zusammenfassung. *Die Wechselwirkung von Punktfehlern in Eis.* Die Wechselwirkung zwischen Punktfehlern in Eis wurde lange Zeit vernachlässigt. Angeregt durch experimentelle Ergebnisse von dielektrischen Messungen an HF-dotierten Kristallen wurde die Möglichkeit von Wechselwirkungen zwischen Bjerrumfehlern und Ionen untersucht. Das führte in einer früheren Veröffentlichung zur Annahme, dass Aggregate aus Bjerrumfehlern und Ionen existieren. Diese Aggregate und Bjerrumfehler werden nun benutzt, um die dielektrischen Eigenschaften von Eis zu erklären, insbesondere die Temperaturabhängigkeit des Produktes der Hoch- und Niederfrequenzleitfähigkeit $\sigma_0\sigma_\infty$.

Die Wechselwirkung von Bjerrumfehlern und Fremdmolekülen führt zu einer Konzentrationsabhängigkeit der Frenkelpaare von den Bjerrumfehlern. Bei HF-Konzentrationen oberhalb der Bjerrumfehlerkonzentration im reinen Eis wird die Bildung von Frenkelpaaren verstärkt. Das führt zu der schnellen Ausdiffusion, die mit Hilfe von NMR untersucht wurde.

1. Introduction

Many of the physical properties of ice are determined by two groups of point defects: The first group, the protonic defects, result from violations of the Bernal–Fowler roules. They determine dielectric and mechanical properties. The second group, the defects in the oxygen lattice, influence spin–lattice relaxation time, the self-diffusion, and the diffusion of impurities in ice.

For the understanding of the dielectric properties two types of defects are essential, and up to a few years ago experimental results have been interpreted assuming that the concentrations of both kinds of defects are independent of each other. First doubt on this model came up in 1968 when Camp presented data (Camp and others, 1969) which indicated that a.c. and d.c. conductivities in pure ice interchange their activation energies at a temperature T_{cr} and that the product $\sigma_0\sigma_\infty$ shows an Arrhenius behaviour $\ln(\sigma_0\sigma_\infty) \propto 1/T$. These findings have been confirmed later by several authors for pure and doped ice. These data are collected by Bilgram and Gränicher (1974). Gränicher (1969) proposed as a working hypothesis that there is a cross-over where the defects interchange their predominance for the high- and the low-frequency conductivity. Such a cross-over is characterized by a vanishing configurational susceptibility $\Delta\epsilon$. In earlier experiments such a cross-over had already been observed when changing impurity concentration. In addition to this it is known that such effects also occur when changing temperature or pressure. Together with the temperature dependence of the product $\sigma_0\sigma_\infty$, this leads to a re-evaluation of the mechanisms for the creation of defects and their interactions.

2. DISSOCIATION OF H_2O IN ICE

In liquid water the dissociation of H_2O can be described by

$$2H_2O \rightleftharpoons H_3O^{+e}+OH^{-e}.$$

These ions do not exist in isolated form in water; they are surrounded by water molecules, the dipole moments of which are oriented. The enthalpy of formation of such a hydrated ion pair is 13.5 kcal/mol (57 kJ/mol) and the dissociation entropy is -27 cal/mol deg (113 J/mol deg). In ice there are four molecules surrounding an ion and their rotation is hindered. The polarization charge in ice is associated with Bjerrum defects and can diffuse away from the ion. Hence the effective charge of an ion may differ from e. The formation of an ion pair with the charge e can occur by removing one proton away from a water molecule forming thus a negative ion with a charge $-e$ and adding this proton to a neutral water molecule in ice thus forming a positive ion with the charge $+e$. This is a very artificial way of creating ions, but it has the advantage of leading to ions with a well-defined charge. Up to now the orientation of all water molecules has been fixed. The existence of an ion with the charge e seems to be quite improbable in ice because two of the surrounding water molecules have their dipole moments in an energetically unfavorable orientation. In terms of defect chemistry the reorientation of these molecules occurs by joining two L defects to the positive ion and two D defects to the negative ion. Calling q and p the effective charges of Bjerrum defects and ions respectively we can write:

$$\left.\begin{array}{lll} 2H_2O & \rightleftharpoons H_2O+P^{+e} & +H_2O-P^{+e} \\ & \rightleftharpoons (H_3O\cdot D)^{+e} & +(HO\cdot L)^{-e} \\ & \rightleftharpoons (H_3O\cdot D)^{+e}+L^{-q} & +(HO\cdot L)^{-e}+D^{+q} \\ & \rightleftharpoons (H_3O)^{+p} & +(OH)^{-p} \\ & \rightleftharpoons (H_3O)^{+p}+L^{-q} & +OH^{-p}+D^{+q} \\ & \rightleftharpoons (H_3O\cdot L)^{+(p-q)} & +(OH\cdot D)^{-(p-q)}. \end{array}\right\} \qquad (1)$$

Now the ions are surrounded by oriented water molecules. They are in an environment similar to that in liquid water. Due to the perfect lattice the polarization charges are distributed over a large region, in principle over the whole crystal. A Bjerrum defect is trapped at each ion leading to an effective defect charge of $(e-2q)$. These Bjerrum–ion (B.I.) aggregates have been postulated in an earlier paper (Bilgram and Gränicher, 1974). Ionic defects with a charge q are used in Jaccard's theory. Here the ions are surrounded by three water molecules in the proper orientation and one in the energetically unfavourable orientation. The concentration of these defects is independent of Bjerrum-defect concentration. This defect pair can not be used to explain the phenomena mentioned in Section 1 of this paper. If the B.I. aggregates are well separated from each other, their movement is determined by the reorientation of the molecules. The enthalpy of dissociation of two H_2O into $(H_3O\cdot L)^{+(p-q)}$ and $(OH\cdot D)^{-(p-q)}$ can be assumed to be similar to that in liquid water. The dissociation entropy in ice is at least as high as that in water. Hence it cannot be neglected when calculating the concentration of the B.I. aggregates. The formation enthalpy of pure Bjerrum defects generated according to

$$2N \rightleftharpoons L+D,$$

is 0.76 eV and the entropy contribution is low. The native concentration of Bjerrum defects has been determined from the doping dependence of σ_∞ and is in good agreement with the value calculated from the thermal activation energy assuming a small entropy.

The aggregates $(H_3O\cdot L)^{p-q}$ and L defects are both able to react with D defects. Therefore the equilibrium concentration of Bjerrum–ion aggregates is not independent of Bjerrum-defect concentration. Thus in HF-doped ice with medium or low HF concentrations the equilibrium equation is

$$(C_l + \kappa C_{bi})\, C_d = K_0. \tag{2}$$

Here κ is a coefficient which relates the recombination rate of D defects and Bjerrum–ion aggregates with the recombination rate of D and L defects. We assume κ to be about 1.

3. DISSOCIATION OF HF IN ICE

An HF molecule which substitutes for an H_2O molecule in the ice structure introduces an L defect into the ice. Together with one water molecule, the HF can dissociate and form an ion pair. In a third process using two water molecules the L defect influences the self-dissociation of H_2O.

$$\mathrm{HF \cdot L} \rightleftharpoons \mathrm{HF}^{+q} + \mathrm{L}^{-q}, \tag{3}$$

$$\mathrm{HF \cdot L} + \mathrm{H_2O} \rightleftharpoons (\mathrm{H_3O \cdot L})^{+(p-q)} + \mathrm{F}^{-(p-q)}, \tag{4}$$

$$\mathrm{HF \cdot L} + 2\mathrm{H_2O} \rightleftharpoons (\mathrm{H_3O \cdot L})^{p-q} + (\mathrm{OH})^{-p} + \mathrm{HF}^{+q}. \tag{5}$$

These equilibria have to be combined with the native defect-generation processes discussed in Section 2. Process (3) will be dominant at low temperatures. Each HF molecule introduces an L defect which is liberated easily. At high temperatures independent of whether Process (4) or (5) predominates, HF introduces B.I. aggregates which lead to a reduction of free L defects according to Equilibrium (2). Hence at high temperatures and low HF concentrations, Bjerrum defects are majority carriers (the case of pure ice), with an increasing HF concentration the native L-defect population will decrease and the aggregated state becomes the majority carrier. Finally at high concentrations the degree of dissociation decreases and hence Bjerrum defects become majority again. This change of majority character on varying impurity concentration has been observed already by Steinemann (1957). The occurrence of cross-overs by changing temperature can be understood on the same grounds. Regarding a crystal with HF concentration C_{HF} below the native Bjerrum concentration at 0°C, then at low temperatures Bjerrum–ion aggregates are in the majority. With increasing temperature the first cross-over is reached and Bjerrum defects become dominant. According to Equation (2) the concentration of B.I. aggregates decreases with increasing L-defect concentration, i.e. with increasing temperature.

4. DEFECT PROPERTIES

The properties of Bjerrum defects and B.I. aggregates can be determined from the high-frequency conductivity (Bilgram and Gränicher, 1974).

$$\sigma_\infty = C_{bi}\mu_{bi}(p-q) + C_l\mu_l q, \tag{6}$$

where C_l, μ_l, and C_{bi}, μ_{bi} are the concentrations and mobilities of L defects and B.I. aggregates respectively. In doped crystals, if one of these two defect types is in a majority and the contribution of the other one can be neglected, σ_∞ is given by

$$\left.\begin{array}{l} \sigma_\infty = C_{bi}\mu_{bi}(p-q), \\ \text{or} \\ \sigma_\infty = C_l\mu_l q. \end{array}\right\} \tag{7}$$

These two equations are only valid if one defect species can be neglected and does not influence the concentration of the other one. A criterion for the validity of Equation (7) can be obtained from $\Delta\epsilon$. As $\Delta\epsilon$ is proportional to the difference in the defect currents, one of them can be neglected if $\Delta\epsilon$ has a maximum. For the evaluation of σ_∞ data obtained not at maximum $\Delta\epsilon$, Equation (6) has to be used. The defect concentrations are known only for the extreme cases as the equilibrium constants are not known. Therefore data obtained under other conditions than at extreme $\Delta\epsilon$ cannot be used for the determination of defect properties. Bjerrum defects as well as Bjerrum–ion aggregates can be majority carriers depending on HF concentration and temperature. Using crystals with different dopant concentrations, $\Delta\epsilon_{\max}$ will be found at different temperatures for both majority regions. From σ_∞ measurements it is possible to obtain the products $\mu_{\mathrm{bi}}(p-q)$ and $\mu_{\mathrm{l}}q$ and their temperature dependence. At the cross-over the defect currents are in balance, hence $\Delta\epsilon$ vanishes there. At the cross-over it is possible to measure the apparant mobility μ_{c} of defects with charge e:

$$\sigma_\infty \text{ (at cross-over)} = \tfrac{1}{2}C_{\mathrm{HF}}\mu_{\mathrm{c}}e.$$

Using the conductivity at the cross-over, the temperature dependence of $\mu_{\mathrm{c}}e$ can be obtained if crystals with differing impurity concentrations are used. The data obtained from the experiments can be fitted in such a way that

$$\mu_{\mathrm{bi}}(p-q)+2\mu_{\mathrm{l}}q = \mu_{\mathrm{c}}e. \tag{8}$$

Using

$$p+q = e,$$

it can be concluded that

$$\mu_{\mathrm{bi}} = \mu_{\mathrm{l}} = \mu_{\mathrm{c}} = \mu.$$

All defects thus have the same mobility. The process determining the mobility is the reorientation of water molecules. The activation energy of defect mobility is 0.24 eV. The effective charges are $4q > p > 3q$. The quantities which are important in d.c. conductivity are $(p-q) > e/2 > 2q$.

Low-frequency conductivity σ_0 can only be determined less precisely than σ_∞. It is given by

$$\frac{e^2}{\sigma_0} = \frac{(p-q)^2}{C_{\mathrm{bi}}\mu_{\mathrm{bi}}(p-q)}+\frac{(2q)^2}{C_{\mathrm{l}}\mu_{\mathrm{l}}q}, \tag{9}$$

σ_0 being determined by the minority carrier. If the aggregates are minority carrier, e.g. at low HF concentrations and high temperatures

$$\sigma_0 \propto \mu_{\mathrm{bi}}C_{\mathrm{bi}}.$$

There are two contributions to the temperature dependence of σ_0: μ_{bi} increases with increasing temperature but C_{bi} decreases if L-defect concentration is increasing with temperature. This is the case at high temperature and low concentrations as discussed in Section 3. For these conditions a very weak temperature dependence of σ_0 can be observed.

5. The temperature dependence of the product $\sigma_0\sigma_\infty$

All the defect equilibria discussed above are based on the interaction of L defects and B.I. aggregates. This is an important difference from earlier theories. The dependence of the concentrations of these two defects on HF concentration is not trivial. But there is an elegant new way to obtain information on the concentration product $C_{\mathrm{bi}}C_{\mathrm{l}}$ since it is a simple function of $\sigma_0\sigma_\infty$. The high- and low-frequency conductivities are given by Equations (6) and (9).

For the product of the two conductivities which can be measured we obtain:

$$\sigma_0\sigma_\infty = e^2C_{\mathrm{bi}}C_{\mathrm{l}}\mu^2\,\frac{C_{\mathrm{bi}}(p-q)+C_{\mathrm{l}}q}{C_{\mathrm{bi}}4q+C_{\mathrm{l}}(p-q)} = e^2C_{\mathrm{bi}}C_{\mathrm{l}}\mu^2Q.$$

Using $p:q = 3:1$, the quantity Q can be estimated and for all concentrations: $Q = \frac{1}{2}$.

Hence

$$\sigma_0\sigma_\infty = \tfrac{1}{2}e^2C_{\mathrm{bi}}C_{\mathrm{l}}\mu^2.$$

The temperature dependence of $\sigma_0\sigma_\infty$ can be plotted in an Arrhenius plot, and the apparent activation energy consists of a contribution from the mobility $E_\mu = 0.24$ eV and one from the temperature dependence of the concentrations. The temperature dependence of the defect concentrations vanishes if

(i) the HF concentration is so low that HF dissociates at all temperatures, that means the crystal does not reach a second cross-over; and

(ii) the intrinsic defect concentrations are below the foreign concentrations and only extrinsic defects contribute to the conductivity.

For temperatures below $-10°C$ these two conditions are fulfilled for 5×10^{-6} mol/l $> C_{HF} > 10^{-6}$ mol/l. At this concentration an activation energy of $2E_{\mu} = 0.48$ eV has to be expected. At higher HF concentrations as well as at lower concentrations the apparent activation energy will be higher because of the increasing defect concentrations with increasing temperature due to dissociation of HF or of water molecules, respectively.

This has been found by Glen (1973). He observed a minimum activation energy of 0.49 eV for an HF concentration of 3×10^{-6} mol/l. This experimental result demonstrates that it is the concentration product $C_{l}C_{bi}$ that shows an Arrhenius behaviour and not the individual concentrations. In addition to that the measured activation energy gives additional support for the hypothesis that both types of defect which are active in dielectric processes in ice have the same propagation mechanism.

6. Diffusion of HF

If HF concentration exceeds 1 p.p.m. (for experiments near to the melting point) the diffusion of HF in ice has been found to be much faster (by about a factor 10^5) than the self-diffusion. At low HF concentrations a diffusion constant similar to the value for self-diffusion has been found (Bilgram and others, 1976). If crystals are stored, the HF concentration decreases with time. Two stages of out-diffusion can be observed: a first one with high impurity loss lasting a few days and a second one where HF concentration is nearly constant for months. NMR experiments have shown, that during out-diffusion two well-defined concentration regions exist in the crystal. This is not to be expected if diffusion is determined by Fick's law.

It is generally agreed, that self diffusion occurs by a vacancy mechanism and that at low concentrations HF diffuses in the same way. Two processes can be considered for the high-concentration case:

(i) doped crystals usually have a higher dislocation density than pure crystals, therefore it can be assumed that in doped crystals HF diffusion occurs along dislocations.

(ii) HF in doped crystals diffuses by an interstitial mechanism. Due to the concentration dependence of the chemical potential of HF in ice, interstitial molecules exist only in ice at concentrations above the intrinsic Bjerrum concentration (1 p.p.m. at the melting point).

In the first model diffusion increases due to a decrease of crystal perfection by doping. The second model assumes that the diffusion constant changes due to a change in defect chemistry at a typical HF concentration. There is an experiment which can distinguish between these two models: It is possible to compare the diffusion of molecules which do not influence defect chemistry in a pure (perfect) crystal and in a doped crystal (with dislocations). Such experiments have been done by measuring self-diffusion in pure and doped crystals. No influence of doping and crystal perfection has been found. Thus it can be concluded that dislocations are not responsible for the observed change of diffusion constant.

The first hint for the interpretation of the diffusion process by means of point-defect chemistry came from the out-diffusion experiments. It has been found, that the high-concentration process stops at the intrinsic Bjerrum defect concentration C_L. This limiting concentration decreases with decreasing temperature. Below this concentration, the chemical potential of HF decreases as it is no longer necessary to introduce a Bjerrum defect with each HF molecule. At low HF concentrations $C_{HF} < C_l, C_d$ the number of Bjerrum defects changes only very little after the addition of L defects. $C_l + C_d \approx$ const. There is a sudden increase in the chemical potential of HF in ice and in the vapor pressure of HF in equilibrium with doped ice as soon as the HF concentration in ice exceeds the value C_L. Above C_L the formation energy for a pair consisting of an interstitial HF and a vacancy is lower than the formation energy of a Schottky defect in pure ice. Therefore the concentration of interstitial HF molecules increases at this typical concentration and gives rise to the onset of the high-diffusivity process. An HF molecule which is at an interstitial site can move easily out of the crystal and only a small driving force is necessary. During out-diffusion there is only a very small gradient in the outer part of the crystal which has lost its high concentration already. This explains the occurrence of two discrete concentrations in the crystal, the initial HF concentration and C_L. The out-diffusion of HF is an example of an interaction of protonic defects with defects in the oxygen lattice which determine the diffusion processes in ice. The concentrations of oxygen-lattice defects are strongly influenced by the concentration of protonic defects which determine the chemical potential of impurity atoms in the ice structure.

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DISCUSSION

J. W. GLEN: How can an ion–L-defect (B.I.) pair be more mobile than the L defect, since in order to move at all another L defect has to move up to a neighbouring water molecule to which a proton then tunnels? If this is correct, an L defect moves past to give a single step of the B.I. pair.

J. H. BILGRAM: Bjerrum defects and ion states are a means for book-keeping of the protonic motion through the ice. The structures of these defects are not known.

In this paper it has been assumed that the four water molecules which surround an ion are in the energetically favourable orientation. In ice this is only possible if an L-defect is associated to the ion. The orientation of additional water molecules around the aggregate can be done without trapping of additional Bjerrum defects. This cloud can move through the lattice by rotation of water molecules. Bjerrum defects carry an effective charge. There is no reason to assume that they are not surrounded by a polarization cloud. The movement of Bjerrum defects is also limited by the rotation of water molecules. Therefore both types of defects have the same mobility. This can be deduced from the experimental data. Each protonic defect which moves through the ice produces a polarization trace. The "book-keeping" has to show that this trace can be eliminated by the movement of a different defect which moves in the opposite direction. For each step of an ion with charge p an L-defect has to do a step into the opposite direction. For each step of an aggregate an L-defect has to move two steps. This occurs, e.g. if an L defect passes by an aggregate.

M. Hubmann: When the electrical properties are explained by means of B.I.-aggregates some difficulties are encountered. This concerns the way they move. One can assume that: (a) The ions are immobile. In this case the aggregates can change their site only when they are met by an L-defect. As a consequence the mobility μ_{BI} is proportional to the concentration of the L-defects. (For a detailed discussion see Hubmann (unpublished).) (b) The ions are mobile and form loosely-bound aggregates. In this case one must keep trace of the un-aggregated ions. It is possible to extend the formalism of Jaccard to include other defects too (Hubmann, unpublished).

The results are in this case:

$$\sigma_\infty = \sigma_\pm + \sigma_{DL} + \sigma_{BI},$$

$$1/\tau \propto T(\sigma_\pm/e_\pm{}^2 + \sigma_{DL}/e_{DL}{}^2 + 4\sigma_{BI}/e_{BI}{}^2).$$

There is no additional dispersion.

The cross-over condition is

$$\sigma_\pm/e_\pm - \sigma_{DL}/e_{DL} + 2\sigma/e_{BI} = 0.$$

The additional terms, which appear in the expressions above must be discussed too. It is questionable whether the requirements from (a) or (b) can be brought into agreement with experiment.

Bilgram: I do not think that it is possible to calculate the mobility of protonic defects in ice as long as their structure is not known. One of the few facts we know about these defects is that they are charged. This should not be neglected as has been done in the calculation by Dr Hubmann. Ionic states with a less perfect polarization cloud than Bjerrum–ion aggregates have a higher effective charge than the aggregates. They have also a higher energy of formation and hence they can be neglected.

J. G. Paren: In lightly doped HF ice at high temperatures the d.c. conductivity is nearly independent of temperature. I do not understand why you interpret this in terms of Bjerrum–ion complexes which you claim have a mobility similar to that of L-defects. Surely H_3O^+ ions can better fit the evidence, their number being equal to the HF concentration. In this way the temperature-independent conductivity can be presumed to be due to quantum-mechanical tunnelling.

Bilgram: At high temperatures and low concentrations of HF the analysis of Camplin and others (1978) obtains the same mobility for Bjerrum defects and ionic states. This is in agreement with the evaluation presented in this paper. It is very hard to believe that the rotation of water molecules and a quantum-mechanical tunnelling process will lead to the same mobility. In addition a model has to explain the occurrence to two cross-overs by changing temperature. This has been observed by Ruepp (1973, fig. 4). If the mobilities at high temperatures are determined, then in the paper presented here no fitted parameters are necessary for the determination of the temperature dependence of the mobilities. The $\Delta\epsilon$ values taken from the experiment determine the σ_∞ values which have to be used for the mobility calculation. No equilibrium constants are involved.

R. Taubenberger: Do you take the data of Camp and others (1969), Schenk (unpublished), Von Hippel and others (1972), and Camplin and Glen (1973) as a proof of going through cross-overs in the sense of the Jaccard model?

Bilgram: Yes, in the sense that defect currents are equal at the cross-over.

Taubenberger: You give now $p : q : e = 3 : 1 : 4$, which means with Jaccard's equation for σ_0 that $4/\sigma_0 = (1/\sigma_L) + (1/\sigma_{BI})$, that is you had the symmetrical case where Jaccard's $\Gamma(\Sigma)$ representation degenerates to a single branch $\Gamma \propto (1 - \Sigma)$, which is in strong contradiction to measured data of Hubmann (1978), A. H. Runck (private communication in 1973), and Camplin and others (1978). Could you comment on this discrepancy? Furthermore with your special choice for p/q you have trivially $\sigma_0\sigma_\infty = \frac{1}{2}e^2C_{\text{BI}}C_{\text{L}}/\mu^2$ for all concentration ratios $C_{\text{L}}/C_{\text{BI}}$ so there is nothing specific to argue for three different cases.

Bilgram: The model I use is a phenomenological one. It uses the data of Camplin, Runck, and Hubmann. It is in agreement with these *measured* data. The corresponding microscopic quantities used in Jaccard's theory have not yet been calculated. $\Gamma(\Sigma)$ is not a measured quantity.

Taubenberger: According to your figure 5 in Bilgram and Gränicher (1974), it is hardly believable that the C_{BI}-majority in the *m*-region should be sufficient to account for the high $\Delta\epsilon$-values found in the ionic branch or at least sufficient for your q/p ratio that would imply $\Delta\epsilon_{\text{max}}$ (ionic) $\approx$ $\Delta\epsilon_{\text{max}}$ (Bjerrum) $=$ $\Delta\epsilon$ (pure). Could you comment on this difficulty?

Bilgram: The figure you refer to is a qualitative one. It illustrates the occurrence of two cross-overs. It is not supposed to be used for quantitative calculations.

Taubenberger: Are you aware of the fact that neither the behaviour of $\sigma_0(1/T)$ nor that of $[\sigma_0-\sigma_\infty](1/T)$ are specific for Jaccard's model and that for Jaccard's model one should have an S-shaped deviation from an Arrhenius straight line that is given by p/q, except for your specific choice, and that this deviation should therefore be the same for all samples, which is not the case?

Bilgram: With the $p:q$ ratio which I have found from the experiments the data can be fitted. A different $p:q$ ratio may give rise to a more difficult picture.

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