

# Capture and transfer of charges by orientational defects in dipolar molecular chains

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A possible mechanism of carrier (proton and electron) capture and transport by Bjerrum defects involving establishment of a specific configuration of an electric field equal to the field of a point charge is analyzed. Finite motion of a charge around a defect on a circular orbit with its plane perpendicular to the chain axis is possible in such a field and transport together with a defect can occur along a chain. It is shown that *D* and *L* Bjerrum defects of two types can exist: a) when rotations of the neighboring molecules occur in one direction; b) when the neighboring molecules rotate in opposite directions.

## INTRODUCTION

In theoretical analysis of the motion of charges in ice and other hydrogen-bonded structures it is usual to isolate ordered chains of water (or similar) molecules, which are known as the Bernal–Fowler filaments<sup>1</sup> (Fig. 1). If a proton approaches a molecule on the extreme left in such a chain, it may form a covalent bond with an oxygen atom and the proton may be transferred from the end to the next molecule (Figs. 1a and 1b). Repetition of this process can transport the proton along a chain. The chain then assumes a position in which the transport of the next proton is no longer possible (Fig. 1c).

However, if experimentally observed currents are to be explained,<sup>2–4</sup> we must assume that such a chain returns to its initial position. If the molecule at the left-hand edge is rotated about the OH bond perpendicular to the chain axis, a *D* Bjerrum defect is created<sup>5</sup> (Fig. 1d). Subsequent rotations of all the molecules or, in other words, movement of the *D* defect restores the initial state of a chain. The same state can be attained by beginning rotation from the right-hand end of the chain and this gives rise to an *L* Bjerrum defect, which moves in the opposite direction (Fig. 1d). The next proton can move only after the Bjerrum defect moves along the chain. A similar modification of the chain results also from the motion of a proton hole, which is frequently called an OH<sup>-</sup> defect; maintenance of a current again requires the passage of a *D* or *L* defect.

It therefore follows that in hydrogen-bonded structures the current has two coupled and inseparable components. The hypothesis of such a two-stage proton conduction mechanism was first put forward by Sokolov in 1955 (Ref. 6). According to the estimates given in Ref. 7, during the first stage a proton or a hole transports only 0.64 of a proton (electron) charge, whereas during the second stage a Bjerrum defect carries the remaining 0.36 of the charge. The net result is the transport of a single charge and the chain returns to its initial position.

Elementary charge carriers in ice and similar hydrogen-bonded structures can be divided arbitrarily into two groups: ionic H<sup>+</sup> and OH<sup>-</sup> defects (a proton and a hole), which disturb the neutrality of the whole chain, and orientational (*D* and *L*) Bjerrum defects, which leave the chain on the whole neutral but alter the orientations of its parts. Numerous hypotheses of the existence of more complex ionic de-

fects of the H<sub>3</sub>O<sup>+</sup>, H<sub>5</sub>O<sub>2</sub><sup>+</sup> and similar types simply represent (in our opinion) a matter of terminology. In fact, the charge is always the same and the mobility is governed primarily by the height of the energy barrier hindering the transfer of a proton from one oxygen atom to another; the influence of protons on the neighboring molecules is of secondary importance. However, if this problem is considered in the continuum approximation, when several adjacent protons are transferred to other oxygen atoms simultaneously, the solution describes all possible ionic defects with different values of the delocalization parameter governing the width of a defect.

The transport of protons in the form of solitons was first considered in Refs. 8 and 9 and then the problem was pursued further in a number of papers (see Refs. 10–14, etc.). The soliton model of the motion of Bjerrum defects was proposed and developed in Refs. 15 and 16. The treatments given in Refs. 8–16 were concerned with the conductivity in a one-dimensional model. The question arises whether such a model satisfactorily describes a real three-dimensional system. Note that experimental determinations of the mobility are carried out along one of the crystallographic axes<sup>2</sup> and in some cases the conductivity along such an axis is up to three orders of magnitude higher than along the two other axes.<sup>4</sup> It is therefore quite permissible to assume that the motion of

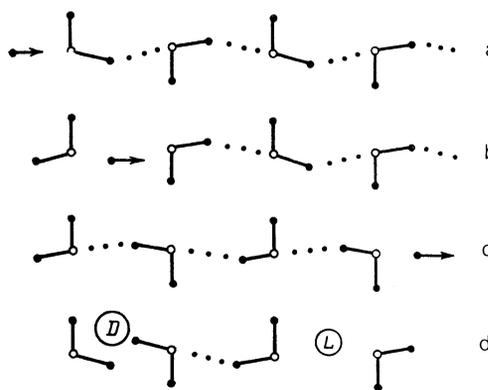


FIG. 1. Schematic representation of the motion of a proton along a chain of water molecules (a–c), and the formation of *D* and *L* Bjerrum defects (d).

ionic and orientational defects is one-dimensional, especially since an external electric field applied to a sample brings the real situation closer to the one-dimensional model.<sup>16</sup>

Recent experiments have however shown that the question of the nature of carriers and of the two-stage conduction mechanism cannot be regarded as closed. In fact, the expected evolution of hydrogen at the electrodes does not occur.<sup>17,18</sup> Therefore, we shall propose one further conduction mechanism involving charge (electron or proton) transport by Bjerrum defects. This is possible because a Bjerrum defect creates a specific electric field configuration due to the dipole moments of the chain molecules. This field forms a trap for the charged particle, which together with the Bjerrum defect, can be transported even against the direction of an external electric field if the latter is less than the field created by the molecular chain.

### SOLITON MODEL OF BJERRUM DEFECTS

Let us consider a chain of water molecules, which is the simplest example of a hydrogen-bonded chain. We assume that molecules can rotate about a fixed OH bond which is perpendicular to the chain axis. A neutral water molecule has a permanent electric dipole moment  $d = 1.87D$ . In the present model the orientation of this moment is defined by two angles:  $\theta_0$  is the constant angle between the fixed OH bond and  $\mathbf{d}$ , and  $\chi$  is the angle between the chain axis and the projection  $p = d \sin \theta_0$  of the dipole moment on a plane perpendicular to this OH bond (Fig. 2). Then the energy of the dipole-dipole interaction in the chain considered in the nearest-neighbor approximation can be described by

$$H_d = -\frac{p^2}{2a^3} \sum_n \{ \cos(\chi_{n+1} - \chi_n) + 3 \cos(\chi_{n+1} + \chi_n) \}, \quad (1)$$

where  $a$  is the chain constant.

The hydrogen bonds between the molecules (some of which can be described by the classical dipole-dipole interaction) mean that the dipole moment is in a local field with two equilibrium positions  $\chi^0 = \pi$  and  $\tilde{\chi}^0 = 0$ . This field can be described by a two-well potential with a barrier of height  $\epsilon$  between the wells:

$$H_h = \epsilon \sum_n \sin^2 \chi_n. \quad (2)$$

The rotational kinetic energy of molecules with a moment of inertia  $I$  is

$$H_k = \frac{I}{2} \sum_n \dot{\chi}_n^2. \quad (3)$$

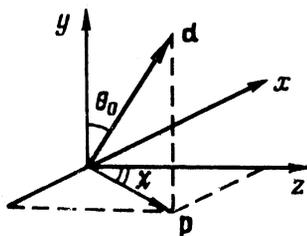


FIG. 2. Position of a dipole moment in space.

We consider fairly slow rotations of molecules when the rotation of one molecule can be transferred to the others by the dipole-dipole interaction, so that several molecules can participate simultaneously in the rotation process.

If the neighboring molecules rotate in the same way, i.e., if  $\chi_n$  and  $\chi_{n+1}$  have the same sign, then the inequality  $\chi_{n+1} - \chi_n \ll \pi$  is satisfied. In the opposite case when one molecule rotates to the left and the next one to the right, i.e., if  $\chi_n$  and  $\chi_{n+1}$  have opposite signs, the inequality  $\chi_{n+1} + \chi_n \ll \pi$  is obeyed. Let us consider these two cases.

1.  $\chi_{n+1} - \chi_n \ll \pi$ . In this case we have

$$\cos(\chi_{n+1} - \chi_n) \approx 1 - \frac{1}{2}(\chi_{n+1} - \chi_n)^2, \quad \cos(\chi_{n+1} + \chi_n) \approx \cos 2\chi_n.$$

Then, Eq. (1) becomes

$$H_d = \sum_n \left\{ \frac{p^2 + 2q^2}{-2a^3} + \frac{p^2}{2a^3} \left[ \frac{1}{2}(\chi_{n+1} - \chi_n)^2 - 3 \cos 2\chi_n \right] \right\}, \quad (1a)$$

$$q = d \cos \theta_0.$$

The total Hamiltonian describing the system is equal to the sum of Eqs. (1a), (2), and (3). Writing down the Hamiltonian for canonically conjugate levels  $\chi_n$  and  $I_{\dot{\chi}_n}$ , and adopting the continuum approximation, we can replace the functions of a discrete variable  $\eta$  with functions of a continuous variable  $\zeta$  in accordance with the rule

$$f_n(t) = f(\zeta, t),$$

$$f_{n\pm 1}(t) = f(\zeta, t) \pm \frac{\partial}{\partial \zeta} f(\zeta, t) + \frac{1}{2} \frac{\partial^2}{\partial \zeta^2} f(\zeta, t).$$

Consequently, the equation of motion becomes<sup>15,16</sup>

$$v_0^2 \chi_{\zeta t} - \chi_{t t} = \omega^2 \sin 2\chi, \quad (4a)$$

where  $v_0 = p/(2a^3 I)^{1/2}$  governs the velocity  $V_0 = a v_0$  with which rotations propagate along the chain, while  $\omega^2 = (\epsilon + 3p^2/a^3)I$  governs the height of the barrier between  $\chi^0 = \pi$  and  $\tilde{\chi}^0 = 0$  subject to the dipole-dipole interaction.

The solution of Eq. (4a),

$$\chi^1(\zeta - v t) = \arccos \{ \pm \text{th} [\mu (\zeta - \zeta_0 - v t)] \}, \quad (5)$$

describes the transition of all the dipoles from the initial position  $\chi^0 = \pi$  to the final position  $\tilde{\chi}^0 = 0$ , i.e., it describes the motion of an extended  $D$  defect (with the minus sign) and, conversely, the transfer of all the dipoles from  $\tilde{\chi}^0 = 0$  to  $\chi^0 = \pi$  describes the motion of an extended  $L$  defect (plus sign). Here,  $\mu = 2^{1/2} \omega / v_0 (1 - v^2/v_0^2)^{1/2}$  is a localization parameter which determines the number of molecules  $N = \pi/\mu$  which participate simultaneously in the rotation or, in other words, the size of a defect  $\Delta = aN$ . The parameter  $\zeta_0$  defines the center of a defect.

It is shown in Ref. 16 that the same expression (5) describes the motion of a defect in an external electric field in the presence of dissipation. The equation of motion is then

$$v_0^2 \chi_{\zeta t} - \chi_{t t} + \gamma \chi_t = \omega^2 \sin 2\chi + pE \sin \chi, \quad (6)$$

where  $\gamma$  is the dissipation coefficient and  $E$  is the field intensity; the velocity of a defect is no longer a free parameter, but

is determined by the parameters of the problem:

$$v_z = v_0 E (\alpha^2 + E^2)^{-1/2}, \quad (7)$$

where

$$\alpha = 2^{1/2} \eta \omega / p.$$

In an external field a  $D$  defect moves as a positively charged particle, whereas an  $L$  defect behaves as a negative particle.

2. We now consider a different case of mutual orientation of the neighboring molecules in the course of rotation:

$$\chi_{n+1} + \chi_n \ll \pi.$$

Now it is convenient to adopt a new unknown  $\varphi_n$  whose sign depends on the molecule number:

$$\chi_n = (-1)^n \varphi_n. \quad (8)$$

We then find that

$$\begin{aligned} \cos(\chi_{n+1} - \chi_n) &= \cos(\varphi_{n+1} + \varphi_n) \approx \cos 2\varphi_n, \\ \cos(\chi_{n+1} + \chi_n) &= \cos(\varphi_{n+1} - \varphi_n) \approx 1 - \frac{1}{2}(\varphi_{n+1} - \varphi_n)^2, \end{aligned}$$

and

$$H_d = \sum_n \left\{ \frac{3p^2 + 2q^2}{-2a^2} + \frac{3p^2}{2a^3} \left[ \frac{1}{2}(\varphi_{n+1} - \varphi_n)^2 - \frac{1}{3} \cos 2\varphi_n \right] \right\}. \quad (1b)$$

The equation of motion can then be of the same form as in the preceding case:

$$\tilde{v}_0^2 \varphi_{tt} - \varphi_{tt} = \tilde{\omega}^2 \sin 2\varphi, \quad (4b)$$

but the parameters are now different:

$$\tilde{v}_0 = \left( \frac{3p^2}{2a^2 I} \right)^{1/2}, \quad \tilde{\omega}^2 = \frac{1}{I} \left( \epsilon + \frac{p^2}{a^3} \right).$$

Its solution is naturally of the same form as in the first case, but real rotations of the neighboring molecules in a chain occur in different directions when we allow for Eq. (8).

We can compare the Bjerrum defect energies in these two cases. We can define the energy of a defect as the difference between the energy of a chain in the absence of a defect and one with a defect:

$$\Delta H_{1,2} = - \frac{2p^2 + q^2}{a^3} - (H_d + H_h + H_k). \quad (9)$$

In both cases the energy of the defect can be described by

$$\Delta H_{1,2} = \mu_{1,2} I (v^2 + v_{1,2}^2) + \frac{2I}{\mu_{1,2}} \omega_{1,2}^2, \quad (9a)$$

where

$$\begin{aligned} \mu_1 &= \frac{2^{1/2} \omega}{(v_0^2 - v^2)^{1/2}}, \quad \mu_2 = \frac{2^{1/2} \tilde{\omega}}{(\tilde{v}_0^2 - v^2)^{1/2}}, \\ v_1^2 &= v_0^2, \quad v_2^2 = \tilde{v}_0^2 = 3v_0^2, \\ \omega_1^2 &= \omega^2 = \frac{\epsilon}{I} + 3v_0^2, \\ \omega_2^2 &= \tilde{\omega}^2 = \omega^2 - v_0^2 = \frac{\epsilon}{I} + 2v_0^2. \end{aligned} \quad (10)$$

Comparing these energies, we find that

$$\begin{aligned} \Delta H_1 &< \Delta H_2 \text{ for } v^2 < v_c^2, \\ \Delta H_1 &> \Delta H_2 \text{ for } v^2 > v_c^2, \end{aligned}$$

where

$$v_c^2 = v_0^2 \frac{9Iv_0^2 + 6\epsilon}{15Iv_0^2 + 8\epsilon}. \quad (11)$$

Consequently, below a certain critical velocity  $v_c$  the preferred process is the formation of  $D$  and  $L$  defects of the first type, while above it the defects are of the second type.

## ELECTRIC FIELD OF BJERRUM DEFECTS

We shall first consider the field of Bjerrum defects on the basis of general physical considerations.

At any point in space the density of a field  $E$  can be resolved into transverse  $E_{\perp}$  and longitudinal  $E_{\parallel}$  components; along the dipole axis and along an axis passing through the center of the dipole at right angles to it, we have  $E_{\perp} = 0$ . In the case of an infinite chain of identically oriented dipoles the transverse components of all the dipoles cancel at every point and only the longitudinal component remains. However, a Bjerrum defect essentially separates an unoriented part of a chain from one which has been reoriented, i.e., it divides the chain into two parts with opposite orientations of the dipoles and, consequently, the electric field in these parts has opposite directions.

A  $D$  defect creates a field similar to the field of a point positive charge and, consequently, it attracts an electron, whereas an  $L$  defect is the field of a negative charge and can attract a proton.

This qualitative conclusion may be supported by numerical calculations. In fact, if we consider the field of the  $n$ th dipole

$$E_n = - \frac{\mathbf{d}_n}{r_n^3} + 3(\mathbf{d}_n \mathbf{r}_n) \frac{\mathbf{r}_n}{r_n^5} \quad (12)$$

in the  $xz$  plane, then at a point  $(x, z)$  with the coordinates  $(0, z_n)$  of the dipole, we find

$$\begin{aligned} \mathbf{r}_n &= \{x, 0, z - z_n\}, \quad r_n = [x^2 + (z - z_n)^2]^{1/2}, \\ \mathbf{d}_n &= \{p \sin \chi_n, 0, p \cos \chi_n\}, \end{aligned} \quad (13)$$

where the components of the field (12) can be written in the form

$$E_n^x(x, z) = - \frac{p}{r_n^3} \sin \chi_n + 3p [(z - z_n) \cos \chi_n + x \sin \chi_n] \frac{x}{r_n^5}, \quad (12a)$$

$$E_n^z(x, z) = - \frac{p}{r_n^3} \cos \chi_n + 3p [(z - z_n) \cos \chi_n + x \sin \chi_n] \frac{z - z_n}{r_n^5}. \quad (12b)$$

Hence, we can see directly that if all the dipoles are oriented in the same way, then  $E_n^z(\chi_n = 0) = -E_n^z(\chi_n = \pi)$ . Therefore, if the two parts of the chain have opposite orientations, which is true of a chain with a Bjerrum defect, they create oppositely directed fields and can therefore attract corresponding charges to a defect.

The field of the whole chain is essentially the sum of the fields of all the dipoles. Therefore, if we sum over  $n$ , we obtain transverse and longitudinal components of the field and in Eq. (5) for  $\chi(\xi - vt)$  we have to return to a discrete representation  $\xi \rightarrow n$  when  $\xi_0 = n_0 = 0$ :

$$\chi(\xi - vt) \rightarrow \chi_n(t) = \arccos \{ \pm \text{th} [\mu(n - vt)] \}. \quad (5a)$$

It therefore follows from Eqs. (5a), (12a), and (12b) that

$$E_{\perp}(x, z) = \sum_n E_n^z = \pm p \sum_n \left\{ \frac{\text{sech}[\mu(n - vt)]}{-r_n^3} + \frac{3x}{r_n^5} \left[ (z - z_n) \text{th}[\mu(n - vt)] + x \text{sech}[\mu(n - vt)] \right] \right\}, \quad (14a)$$

$$E_{\parallel}(x, z) = \sum_n E_n^z = \pm p \sum_n \left\{ \frac{\text{th}[\mu(n - vt)]}{-r_n^3} + \frac{3(z - z_n)}{r_n^5} \left[ (z - z_n) \text{th}[\mu(n - vt)] + x \text{sech}[\mu(n - vt)] \right] \right\}, \quad (14b)$$

where the plus and minus signs correspond to the  $L$  and  $D$  defects, respectively.

In numerical calculations it is preferable to adopt dimensionless variables and consider the fields at points which are multiples of the chain length so that

$$k = \frac{x}{a}, \quad m = \frac{z}{a}, \quad n = \frac{z_n}{a} \quad (15)$$

are integers and the dimensionless expressions (14a) and (14b) become

$$\begin{aligned} E_{\perp}^{\pm}(k, m) &= \pm \sum_n \left\{ \frac{\text{sech}[\mu(n - vt)]}{-\rho_n^3} + \frac{3k}{\rho_n^5} \left[ k \text{sech}[\mu(n - vt)] + (m - n) \text{th}[\mu(n - vt)] \right] \right\}, \\ E_{\parallel}^{\pm}(k, m) &= \pm \sum_n \left\{ \frac{\text{th}[\mu(n - vt)]}{-\rho_n^3} + \frac{3(m - n)}{\rho_n^5} \left[ k \text{sech}[\mu(n - vt)] + (m - n) \text{th}[\mu(n - vt)] \right] \right\}, \end{aligned} \quad (16)$$

where  $\rho_n = [k^2 + (m - n)^2]^{1/2}$ , and are related to real fields by the expressions

$$E_{\perp}^{\pm} = \frac{d}{a^3} \tilde{E}_{\perp}^{\pm}, \quad E_{\parallel}^{\pm} = \frac{d}{a^3} \tilde{E}_{\parallel}^{\pm}. \quad (17)$$

These expressions have just one parameter  $\mu$  determined by the characteristics of the chain and related to the defect dimensions; it is therefore sufficient to select its numerical value so as to satisfy the continuum approximation:  $N = \pi/\mu \gg 1$ . We can show that the values of (16) for  $\mu = 1$  ( $N \approx 3$ ) are practically indistinguishable from those for  $\mu = 0.5$  ( $N \approx 6$ ), as shown in Fig. 4. The same numerical value of  $\mu$  lying within the interval 0.5–1.0 can be obtained if we calculate  $\mu$  from the chain parameters  $d$ ,  $I$ , and  $\epsilon$  (Ref. 15) determined experimentally. We therefore describe calculations carried out on the assumption that  $\mu = 0.5$ .

Figure 4 shows the quantities  $\tilde{E}_{\perp}^{\pm}$  and  $\tilde{E}_{\parallel}^{\pm}$  at a distance  $50a$  ( $k = 50$ ) from the chain in the case of an  $L$  defect located at the chain center ( $v = 0$ ). In the case of a  $D$  defect the

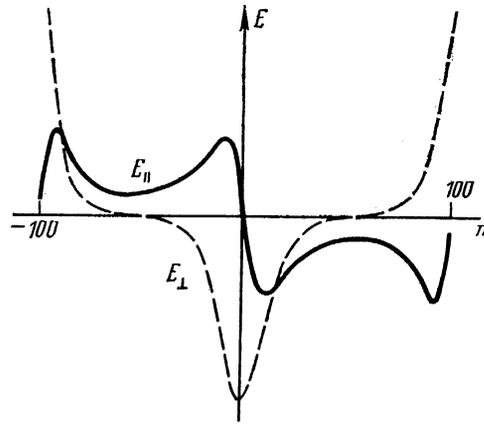


FIG. 3. Sharp peaks of the  $E_{\parallel}$  and  $E_{\perp}$  components in the region of a defect and at the ends of a chain at short distances from the chain;  $k = 10$ ,  $\mu = 0.5$ .

signs of all the fields are reversed. It is clear from Fig. 3 that the longitudinal component  $E_{\parallel}^{\pm}$  has different signs in different parts of the chain. This creates a field which can transport a positive charge (for example, a proton) toward the center of the chain, i.e., to the  $L$  defect. The transverse component  $E_{\perp}^{\pm}$  is directed so that it also facilitates the motion of the proton toward the  $L$  defect, and we can see that a reduction in the localization weakens  $E_{\perp}^{\pm}$  (Fig. 4). This is easily understood if we bear in mind that in the region of this defect the dipoles, are roughly speaking, directed at right-angles to the chain axis. In this case the field created by the dipoles is opposite to the field produced by the rest of the chain in one direction ( $k = 50$ ) and is equal to its field in the other direction ( $k = -50$ ). This is supported by the result of quantitative calculations. For example, Fig. 4 shows that  $E_{\perp}^{\pm}$  for  $k = -50$  has a larger absolute value and is directed opposite to the field  $E_{\perp}^{\pm}$  when  $k = 50$ . Moreover, since the di-

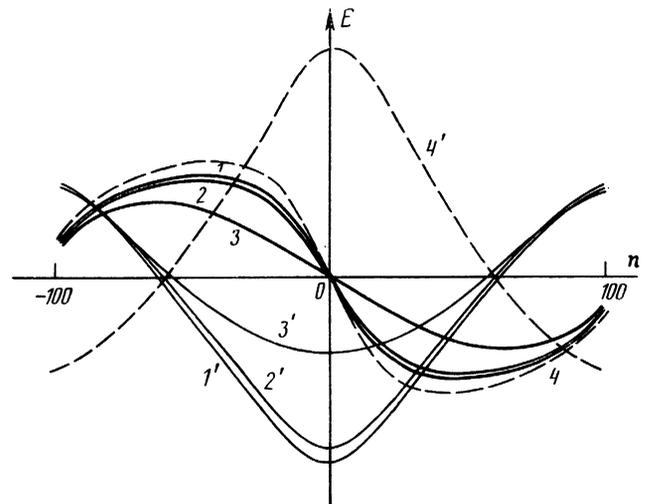


FIG. 4. Longitudinal ( $E_{\parallel}$ , curves labeled by a number without a prime) and transverse ( $E_{\perp}$ , curves labeled by a number with a prime) components of the electric field in a dipole chain at different distances from the chain  $k$  (continuous curves correspond to  $k = 50$  and dashed curves correspond to  $k = -50$ ) and for different localization parameters  $\mu$ : 1), 1') 1.0; 2), 2'), 4), 4') 0.5; 3), 3') 0.1.

poles located in the vicinity of a defect create a field directed in the same way in different parts of the chain, whereas in fact  $E_{\perp}^{\pm}$  has different directions on different sides, the dominant contribution to  $E_{\perp}^{\pm}$  is not made by the region near a defect but by the rest of the chain. It is now clear that an increase in the size of a defect (reduction of its localization) weakens the transverse component  $E_{\perp}^{\pm}$  when  $\mu = 0.1$  (Fig. 4).

It should be pointed out also that the addition of the fields on one side of a chain ( $k = -50$ ) increases also the longitudinal component  $E_{\parallel}^{\pm}$  and the sign of this component is naturally conserved.

The region of the defect can play an important role only when it is located close to the chain, for example, when  $k = 10$  (Fig. 3). In this case the field  $E_{\parallel, \perp}^{\pm}$  along the chain is nonmonotonic and there are sharp peaks at the ends of the chain near the defect. We can see how the configuration of the field changes during the motion of the defect along the chain by examining Fig. 5. Note that the zero of the component  $E_{\parallel}$  and the maximum of the component  $E_{\perp}$  coincide with the center of the defect only at the point  $n = 0$ . However, a defect at any point in a chain attracts a charge of the relevant sign. The question arises whether the motion of the charge and the defect is linked, i.e., whether the defect does indeed carry the charge along the chain.

#### TRANSFER OF CHARGES BY BJERRUM DEFECTS

We consider the motion of a particle of mass  $m$  and charge  $e$  in the presence of a field created by Bjerrum defects of the second kind. In this case  $\mathbf{d}_n$  and  $\mathbf{r}_n$  have the following components:

$$\mathbf{d}_n = \{p \sin \chi_n, (-1)^n q, p \cos \chi_n\}, \quad (18)$$

$$\mathbf{r}_n = \{x, y, z - z_n\}, \quad \chi_n = (-1)^n \varphi_n,$$

where  $q = d \cos \theta_0$ ,  $z_n = an$  is the coordinate of the  $n$ th dipole in the chain, and  $\mathbf{r} = \{x, y, z\}$  is the position of a particle. The system of equations of motion is then of the form

$$m\dot{x}_{it} = e \sum_n \left( -\frac{p}{r_n^3} \sin \chi_n + 3\mathbf{d}_n \mathbf{r}_n \frac{x}{r_n^5} \right),$$

$$m\dot{y}_{it} = e \sum_n \left( -\frac{(-1)^n q}{r_n^3} + 3\mathbf{d}_n \mathbf{r}_n \frac{y}{r_n^5} \right), \quad (19)$$

$$m\dot{z}_{it} = e \sum_n \left( -\frac{p}{r_n^3} \cos \chi_n + 3\mathbf{d}_n \mathbf{r}_n \frac{z - z_n}{r_n^5} \right)$$

We can show that at a distance  $r \gg 4a$  the influence of the charge on the defect can be ignored. In fact, for  $\mu = 0.5$ , the defect spreads over  $N = \pi/\mu \approx 6$  molecules. Therefore, the action of the charge at a distance  $r > 2a$  should destroy the defect by smearing it out over the chain, since the dipoles then tend to rotate relative to the charge. In the opposite case the forces of the dipole-dipole interaction and of the hydrogen bonds will tend to confine the defect. Let us compare the energy binding the first unperturbed dipole lying along the axis ( $n = 4$ ) with its neighbors, and the energy of its interaction with a charge. The relevant expressions are

$$\mathcal{E}_{ab} = -\left( \frac{2d^2}{a^3} + \varepsilon \right),$$

$$\mathcal{E}_e = -\frac{edn}{a^2(n^2 + k^2)^{3/2}}.$$

Substituting  $d = 1.85D$ ,  $a = 3 \text{ \AA}$ ,  $\varepsilon = 0.23 \times 10^{-12} \text{ erg}$ , and  $e = 4.8 \times 10^{-10} \text{ cgs esu}$ , we can show that already at a distance of  $r = 4a$  ( $k = 4$ ) from the defect the influence of the charge is an order of magnitude less than that of the bonds to the neighboring molecules, whereas for  $k = 10$  it is two orders of magnitude less. Consequently, for  $k > 4$  we can consider the motion of a charge in the field of a Bjerrum defect ignoring the influence of the charge on the defect. Then, Bjerrum defects of the first type are described by the function (5), whereas those of the second type are described by the following expression, which is deduced from Eqs. (5a) and (8):

$$\chi_n^{\text{II}}(t) = (-1)^n \arccos \{ \pm \text{th} [\mu(n - n_0 - vt)] \}, \quad (5b)$$

where the plus and minus signs correspond to the  $L$  defects. Since the Bjerrum defect creates a field equivalent to the field of the point charge, it is natural to assume that an electron or a proton travels around the defect in a circular orbit with its plane perpendicular to the chain and they also move simultaneously with the defect along the chain at the velocity of the defect. We therefore solve the system of equations of motion subject to the conditions

$$x^2 + y^2 = \rho^2, \quad z = vt \quad (20)$$

and then adopt a coordinate system moving at the velocity  $v$  of the defect; this can be done by substituting  $n - n_0 - vt \rightarrow n$  and  $z = vt \rightarrow 0$ . Moreover, only consider defects of the second type, because this allows us to find simply the solution of the problem (as demonstrated below).

In this case the system of equations becomes

$$x_{it} = \frac{e}{m} \sum_n \left\{ \mp \frac{(-1)^n p \text{sech}(\mu n)}{(\rho^2 + z_n^2)^{3/2}} + \frac{3\mathbf{d}_n \mathbf{r}_n}{(\rho^2 + z_n^2)^{5/2}} x \right\}, \quad (21a)$$

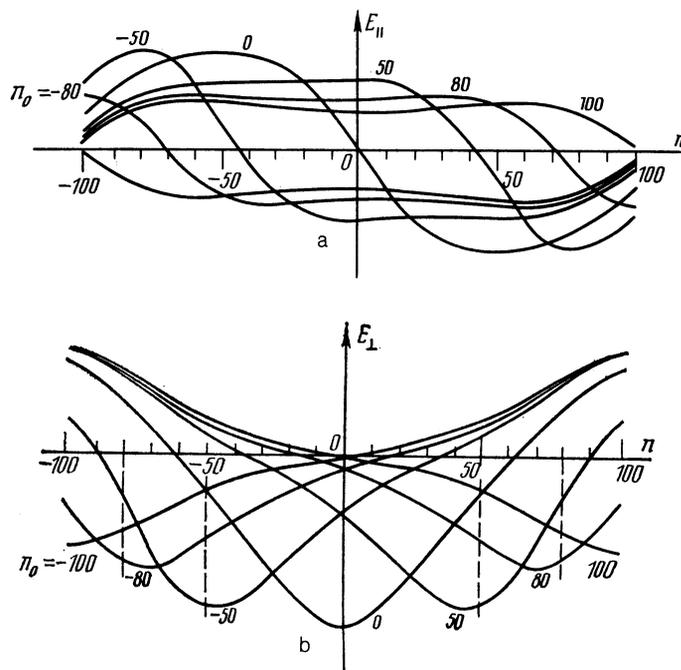


FIG. 5. Changes in the field configuration as a defect moves along the chain showing longitudinal (a) and transverse (b) components;  $n_0$  is the coordinate of the defect center,  $k = 50$ , and  $\mu = 0.5$ .

$$y_{it} = \frac{e}{m} \sum_n \left\{ -\frac{(-1)^n q}{(\rho^2 + z_n^2)^{3/2}} + \frac{3\mathbf{d}_n \mathbf{r}_n}{(\rho^2 + z_n^2)^{5/2}} y \right\}, \quad (21b)$$

$$0 = \frac{e}{m} \sum_n \left\{ \mp \frac{p \operatorname{th}(\mu n)}{(\rho^2 + z_n^2)^{3/2}} + \frac{3\mathbf{d}_n \mathbf{r}_n}{(\rho^2 + z_n^2)^{5/2}} z_n \right\}. \quad (21c)$$

The sum in Eq. (21c) contains a function which is odd in  $n$ , so that this sum vanishes. Consequently, Eq. (21c) is satisfied.

We now consider two equations; (21a) and (21b). These equations contain the scalar product  $\mathbf{d}_n \mathbf{r}_n$ . We can calculate this product conveniently by representing  $\mathbf{d}_n$  as a sum of three vectors:

$$\mathbf{d}_n = \mathbf{p}_n^z + \mathbf{p}_n^x + \mathbf{q}_n, \quad (22)$$

where  $\mathbf{p}_n^z + \mathbf{p}_n^x = \mathbf{p}_n$  is the projection of  $\mathbf{d}_n$  on the  $xz$  plane. We then have

$$\mathbf{d}_n \mathbf{r}_n = p_n^z r_n \cos \alpha_n + p_n^x r_n \cos \beta_n + q_n r_n \cos \gamma_n, \quad (23)$$

where  $\alpha_n$ ,  $\beta_n$ , and  $\gamma_n$  are the angles between the relevant vectors and  $\mathbf{r}_n$ . When the charge moves in a circle, the angle  $\alpha_n$  between  $\mathbf{p}_n^z$ , lying along the chain axis and  $\mathbf{r}_n$  remains constant and, consequently, is independent of  $x$  and  $y$ . If we consider Bjerrum defects of the second type [Eq. (5b)], then  $\mathbf{p}_n^x$  and  $\mathbf{p}_{-n}^x$  are directed to different sides perpendicular to the axis and we also have  $\cos \beta_n = -\cos \beta_{-n}$ , so that

$$\sum_n p_n^x r_n \cos \beta_n = 0.$$

Similarly, because of the structure of the chain (Fig. 6), the vectors  $\mathbf{q}_n$  and  $\mathbf{q}_{-n}$  are also directed oppositely and we have

$$\sum_n q_n r_n \cos \gamma_n = 0.$$

It therefore follows that Eq. (23) can be written in the form

$$\mathbf{d}_n \mathbf{r}_n = p_n^z r_n \cos \alpha_n = \text{const} \quad (24)$$

and that we can introduce instead the quantities

$$\Omega = \frac{3e}{m} \sum_n \frac{\mathbf{d}_n \mathbf{r}_n}{(\rho^2 + z_n^2)^{3/2}}, \quad (25)$$

$$\alpha_{L,D} = \mp \frac{ep}{m} \sum_n \frac{(-1)^n \operatorname{sech}(\mu n)}{(\rho^2 + z_n^2)^{3/2}}, \quad (26)$$

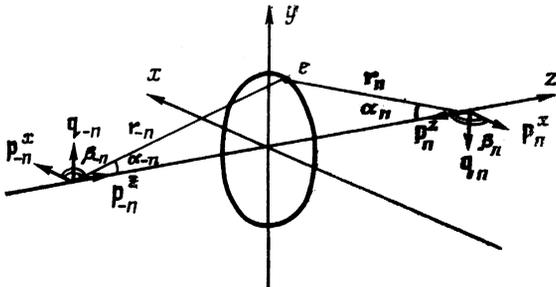


FIG. 6. Interactions of the  $\mathbf{d}_n$  and  $\mathbf{d}_{-n}$  dipoles with a charge in the case of a  $D$  defect of the second type.

$$\beta_{L,D} = \mp \frac{eq}{m} \sum_n \frac{(-1)^n}{(\rho^2 + z_n^2)^{3/2}}, \quad (27)$$

which are independent of  $x$  and  $y$ . Then, the system (21a)–(21b) becomes

$$x_{it} = \alpha_{L,D} + \Omega x, \quad (28a)$$

$$y_{it} = \beta_{L,D} + \Omega y, \quad (28b)$$

but it has a solution which describes finite rotational motion of the charge around the defect only in the case  $\Omega < 0$ :

$$x = \frac{\alpha_{L,D}}{\omega_0^2} + \rho \sin \omega_0 t, \quad y = \frac{\beta_{L,D}}{\omega_0^2} + \rho \cos \omega_0 t, \quad (29)$$

where  $\omega_0 = (-\Omega)^{1/2}$ ;  $\rho = [(\alpha/\omega_0^2)^2 + C/\omega_0^2]^{1/2}$  is the radius of the charge orbit;  $C$  is the constant of integration governing the value of  $\rho$ . The sign of  $\Omega$  is governed by the sign of the particle charge  $e$  and by the sign of  $\mathbf{d}_n \mathbf{r}_n$  of Eq. (24), which depends on the nature of the defect. For a  $D$  defect it follows from Eq. (24) that

$$\mathbf{d}_n \mathbf{r}_n = p_n^z r_n \cos \alpha_n > 0,$$

since  $|\alpha_n| < \pi/2$  (see Fig. 6), so that in order to satisfy the condition  $\Omega < 0$ , we have to assume  $e < 0$  and, as expected, the field of a  $D$  defect is equivalent to the field of a positive charge which can capture a negative charge. On the other hand, an  $L$  defect characterized by  $\cos \alpha_n < 0$  ( $\pi/2 < |\alpha_n| < \pi$ ) captures a positive ( $e > 0$ ) charge. Bearing this point in mind, we find that  $\alpha_{L,D}$  has the same sign in both cases:

$$\alpha_{L,D} = -\frac{|e|p}{m} \sum_n \frac{(-1)^n \operatorname{sech}(\mu n)}{(\rho^2 + z_n^2)^{3/2}} = \alpha, \quad (30)$$

which is true also of the quantity

$$\omega_0^2 = \frac{3|e|}{m} \sum_n \frac{|\mathbf{d}_n \mathbf{r}_n|}{(\rho^2 + z_n^2)^{3/2}}, \quad (31)$$

which positive and governs the frequency of rotation of a charge around a defect.

We can show that the series described by Eqs. (27), (30), and (31) and governing the quantities  $\alpha$ ,  $\beta$ , and  $\omega_0^2$  converge. Let us estimate the values of these series. Adopting the discrete representation characterized by  $\rho = ak$  and  $z_n = an$ , we obtain from Eq. (30)

$$\begin{aligned} \alpha &= \frac{|e|p}{ma^3} \sum_{n=-\infty}^{\infty} \frac{(-1)^n \operatorname{sech}(\mu n)}{(k^2 + n^2)^{3/2}} \\ &\leq \frac{|e|p}{ma^3} \left[ \frac{1}{k^3} + 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{(k^2 + n^2)^{3/2}} \right] = \frac{|e|p}{ma^3} \left[ \frac{1}{k^3} - 2\eta(3/2, k^2) \right], \end{aligned} \quad (30a)$$

where  $\eta(3/2, k^2)$  is the generalized Riemann  $\eta$  function.<sup>19</sup> Similarly, it follows from Eq. (27) that

$$\begin{aligned} \beta &= \mp \frac{|e|q}{ma^3} \sum_{n=-\infty}^{\infty} \frac{(-1)^n}{(k^2 + n^2)^{3/2}} \\ &\leq \mp \frac{|e|q}{ma^3} \left[ \frac{1}{k^3} + 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{(k^2 + n^2)^{3/2}} \right] \\ &= \mp \frac{|e|q}{ma^3} \left[ \frac{1}{k^3} - 2\eta(3/2, k^2) \right]. \end{aligned} \quad (27a)$$

We estimate  $\omega_0^2$  bearing in mind  $p_n^z = p \cos \chi_n = \pm p \tanh(\mu n)$ , where the plus and minus signs correspond to the  $L$  and  $D$  defects, respectively, and also  $r_n = a(k^2 + n^2)^{1/2}$  and  $\cos \alpha_n = n/(k^2 + n^2)^{1/2}$ , so that Eq. (24) implies

$$\mathbf{d}_n \mathbf{r}_n = p_n^z r_n \cos \alpha_n = \pm n p a \operatorname{th}(\mu n)$$

and Eq. (31) becomes

$$\omega_0^2 = \frac{3(\pm e)p}{ma^4} \sum_{n=-\infty}^{\infty} \frac{\pm n \operatorname{th}(\mu n)}{(k^2 + n^2)^{3/2}}. \quad (31a)$$

Here the sign of the charge is allowed for explicitly; it corresponds to the case of attraction between charge and the defect. The sum in the above expression is easily calculated for given values of  $k$  and  $N$ , which is the number of particles in a chain. If we introduce

$$\tilde{\omega}_0^2(k, N) = \sum_{n=-N/2}^{N/2} \frac{n \operatorname{th}(\mu n)}{(k^2 + n^2)^{3/2}}, \quad (31b)$$

we can see that the values of  $\tilde{\omega}_0^2$  for  $N = 100$  are practically the same as  $\tilde{\omega}_0^2$  for  $N = 200$ . We can therefore limit our analysis to finite chains. For example, if  $k = 5$ , we have  $\tilde{\omega}_0^2 = 1.36 \times 10^{-5}$  and for  $k = 10$  we obtain  $\tilde{\omega}_0^2 = 1.06 \times 10^{-4}$ . Having calculated  $\omega_0 = (3pe/ma^4)^{1/2} \tilde{\omega}_0$  for  $e = 4.8 \times 10^{-8}$  cgs esu,  $d = 2.5D$ ,  $a = 3 \text{ \AA}$ , and  $m$  equal to the mass of an electron or a proton, we find that for  $k = 5$  ( $\rho = 5a = 15 \text{ \AA}$ ) the frequency of revolution of an electron around a defect is  $\omega_e \approx 7.2 \times 10^{14} \text{ s}^{-1}$ , the frequency of a proton is  $\omega_p \approx 1.7 \times 10^{13} \text{ s}^{-1}$  if  $k = 10$ , the corresponding values are  $\omega_e = 2 \times 10^{14} \text{ s}^{-1}$  and  $\omega_p = 4.7 \times 10^{12} \text{ s}^{-1}$ .

We can calculate similarly the quantity defined by Eq. (30). If we represent Eq. (27) in the form  $\beta = \tilde{\beta}(k)eq/ma^3$ , where

$$\tilde{\beta}(k) = \frac{1}{k^2} + 2 \sum_{n=1}^{N \rightarrow \infty} \frac{(-1)^n}{(k^2 + n^2)^{3/2}}, \quad (27b)$$

we can show by direct calculations that  $\tilde{\beta}(k) \rightarrow 0$  in the limit  $N \rightarrow \infty$ .

We now find the values of the parameters of the solution which ensure that the condition (20) is satisfied. Substituting Eq. (29) for  $x$  and  $y$  and averaging over one charge revolution around the defect, we can show that this condition is satisfied if  $\alpha/\omega_0^2$ . In fact, the smallness of  $\rho^2 \gg \alpha^2/\omega_0^4$  compared with  $\rho$  means that the shift of the center of the charge orbit from the origin of the coordinate system along the  $x$  axis is small compared with the orbit radius. (It should be pointed out that the shift along the  $y$  axis is altogether absent because  $\beta = 0$ .) We now estimate numerically the shift along  $x$ ; in doing this we bear in mind that

$$\frac{\alpha}{\omega_0^2} = \frac{a}{3} \frac{\tilde{\alpha}}{\tilde{\omega}_0^2} \quad \tilde{\alpha} = \sum_n \frac{(-1)^n \operatorname{sech}(\mu n)}{(k^2 + n^2)^{3/2}}.$$

Calculation of the value of  $\tilde{\alpha}$  and comparison with  $\tilde{\omega}_0^2$  shows that  $\alpha/\omega_0^2 \sim 10^{-2}a$ . This is true both for  $\rho = 5a$  ( $k = 5$ ) and for  $\rho = 10a$  ( $k = 10$ ), i.e., the shift can be ignored compared with the orbit radius and, consequently, the condition of Eq. (20) is satisfied.

## ANALYSIS AND CONCLUSIONS

Our analysis thus shows that one of the possible states of a charge-defect system is that in which the charged particle follows along a circular orbit of constant radius around the center of the defect and the plane of the orbit is perpendicular to the chain axis, i.e., the charge is captured by a Bjerrum defect. The charge may be a free proton or an electron, always present in ice and similar systems. The question arises how far classical ideas are applicable to the motion of such charges. Let us estimate the de Broglie wavelength of these particles in the case when they are captured by a Bjerrum defect.

On the one hand, the energy of a particle is

$$E = \frac{\hbar^2 k^2}{2m} = \frac{1}{2m} \left( \frac{2\pi\hbar}{\lambda} \right)^2,$$

where  $\lambda$  is the de Broglie wavelength. On the other, the energy of a particle following an orbit of radius  $\rho$  at an angular velocity  $\omega$  is

$$E = m\omega^2 \rho^2/2.$$

These two relationships give

$$\lambda = 2\pi\hbar/m\omega\rho. \quad (32)$$

For the values  $\omega_e = 7.2 \times 10^{14} \text{ s}^{-1}$  for an electron and  $\omega_p = 1.7 \times 10^{13} \text{ s}^{-1}$  for a proton when the orbit diameter is  $2\rho = 30 \text{ \AA}$ , we find  $\lambda_e = 6 \text{ \AA}$  and  $\lambda_p = 0.15 \text{ \AA}$ , i.e., the quantum size of a proton is two orders of magnitude less than the orbit diameter and therefore in this situation we can regard it as a classical particle. However, the size of an electron is only one-fifth of the orbit diameter so that in this case the above treatment is fairly rough. Estimates of the dimensions of an electron and a proton for  $2\rho = 60 \text{ \AA}$  give the same ratios of these quantities to the orbit radius as for  $2\rho = 30 \text{ \AA}$ .

The influence of thermal fluctuations on the motion of a charge captured by a Bjerrum defect is unimportant. In fact, the energy of gyrations of an electron or a proton at the angular velocities given above is  $\approx 3 \text{ eV}$ , whereas the thermal energy  $kT = 0.025 \text{ eV}$  is two orders of magnitude less.

We shall now consider the problem of the direction in which a charge-defect complex moves in an external electric field. A free  $D$  defect moves in a field as a positively charged particle, whereas an  $L$  defect moves as a negative particle. This is because after the passage of a proton or a hole in a field of a given direction the molecular dipole moments are in an energetically unfavorable position because they are oriented against the field (Fig. 1c),<sup>16</sup> and there is only direction of motion in a chain with a given configuration. However, if the defect captures the charge, then generally over distances of the order of one segment of the chain we cannot exclude the influence of the charge on the defect and we must regard them as a single complex. Once we do this, the influence of an external field on this complex is determined not only by the action of the field on the defect but also that of the field on the charge, which is opposite in sign (!) and different in value. If this interaction is stronger than that with the defect, the complex moves in the direction governed by the sign of the charge and not that of the defect. This allows us to explain why there hydrogen is not evolved at the electrodes in a system of this kind and the current through a sample of ice can flow as long as we please in spite of the limited number of

the elementary charges ( $H^+$ ,  $OH^-$ ,  $D$ , and  $L$ ) in a given volume of ice:<sup>17,18</sup> electrons are transferred by the  $D$  defects from the negative to the positive electrodes, where they remain, whereas the  $D$  defects return to the negative electrode and the process is repeated.

The field influences the charge and defect in different ways: the interaction with the charge is linear and that with the defect is nonlinear (tending to saturation),<sup>16</sup> so that in general we can have cases in which (for other values of the field) its influence on the defect is stronger than on the charge. In other words, the effective charge of the same complex may depend on the field and for different complexes  $D + e$  and  $L + p$  the dependence may be different. It is quite likely that this accounts for the broken nature of the current-voltage characteristic of ice.<sup>20</sup>

We must mention one other important feature. In the model of transport of ionic defects (a proton  $H^+$  or a hole  $OH^-$ ) developed in Ref. 9 the molecules of a chain to the left and right of these defects are also oriented in different ways. The configuration of the chain in the course of the transport of, for example,  $H^+$  is similar to the configuration of the chain with an  $L$  defect, and, therefore, a field of the negative charge is created, but it does not capture any other positive charges; instead it stabilizes the already implanted proton  $H^+$  and the resultant field of the proton in the chain (or at least its transverse component) should be close to zero. This is why ionic defects should not capture and transfer other charges apart from their own intrinsic charges.

The proposed model applies to an isolated chain. How do neighboring chains affect the motion of a charge associated with a defect? First of all, we note that the Bjerrum defect concentration is fairly low ( $10^{-5}$  mol/liter),<sup>21</sup> so that chains with defects in ice are surrounded by many ordered defect-free chains. The latter create only longitudinal electric fields and the field transverse to the chain axis is created only by the chain with a defect, which is why the charge is trapped.

It therefore follows that Bjerrum defects may act as traps and as charge carriers: an  $L$  defect can carry a proton and a  $D$  defect can carry an electron. These defects can play the main role in proton and electron transport, because in ice the concentrations of orientational  $D$  and  $L$  defects are five

orders of magnitude higher than ionic  $H_3O^+$  and  $OH^-$  defects.<sup>21</sup> It is also possible that the main contribution to the current comes from the transport of electrons by  $D$  defects, because electrons are 2000 times lighter than protons and, consequently, they should be captured more easily.

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- <sup>1</sup>J. D. Bernal and R. W. Fowler, *J. Chem. Phys.* **1**, 515 (1933).  
<sup>2</sup>V. F. Petrenko and I. A. Ryzhkin, *Zh. Eksp. Teor. Fiz.* **87**, 558 (1984) [*Sov. Phys. JETP* **60**, 320 (1984)].  
<sup>3</sup>V. N. Pak and N. G. Ventov, *Fiz. Khim. Stekla* **6**, 317 (1980).  
<sup>4</sup>J. Vanderkooy, J. D. Cuthbert, and H. E. Petch, *Can. J. Phys.* **42**, 1871 (1964).  
<sup>5</sup>N. Bjerrum, *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **27**, No. 1 (1951); *Science* **115**, 385 (1952).  
<sup>6</sup>N. D. Sokolov, *Usp. Fiz. Nauk* **57**, 205 (1955).  
<sup>7</sup>M. Eigen and L. de Maeyer, *Proc. R. Soc. London Ser. A* **247**, 505 (1958).  
<sup>8</sup>S. Yomosa, *J. Phys. Soc. Jpn.* **51**, 3318 (1982).  
<sup>9</sup>V. Ya. Antonchenko, A. S. Davydov, and A. V. Zolotariuk, *Phys. Status Solidi B* **115**, 631 (1983).  
<sup>10</sup>L. N. Kristoforov and A. V. Zolotaryuk, *Phys. Status Solidi B* **146**, 487 (1988).  
<sup>11</sup>St. Pnevmatikos, N. Flytzanis, and A. R. Bishop, *J. Phys. C* **20**, 2829 (1987).  
<sup>12</sup>P. Misiak and H. Chojnacki, *THEOCHEM* **44**, 339 (1988).  
<sup>13</sup>S. Pnevmatikos, *Phys. Rev. Lett.* **60**, 1534 (1988).  
<sup>14</sup>Y. Kashimori, T. Kikuchi, and K. Nishimoto, *J. Chem. Phys.* **77**, 1904 (1982).  
<sup>15</sup>A. I. Sergienko, *Ukr. Fiz. Zh.* **31**, 1637 (1986); *Fiz. Tverd. Tela (Leningrad)* **30**, 860 (1988) [*Sov. Phys. Solid State* **30**, 496 (1988)].  
<sup>16</sup>A. I. Sergienko, *Phys. Status Solidi B* **144**, 471 (1987).  
<sup>17</sup>V. F. Petrenko, T. Ebinuma, and N. Maeno, *Phys. Status Solidi A* **93**, 695 (1986).  
<sup>18</sup>V. A. Chesnakov, V. F. Petrenko, I. A. Ryzhkin, and A. V. Zaretskiĭ, *J. Phys. (Paris)* **48**, Colloq. 1, C1-99 (1987).  
<sup>19</sup>M. Abramowitz and I. A. Stegun (eds.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, Dover, New York (1964).  
<sup>20</sup>H. Engelhardt and N. Riehl, *Phys. Lett.* **141**, 20 (1965).  
<sup>21</sup>T. N. Zatsepina, *Physical Properties and Structure of Water* [in Russian], Moscow State University (1987).

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