Orientational Defects in Ice Ih: An Interpretation of Electrical Conductivity Measurements

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We present a first-principles study of the structure and energetics of Bjerrum defects in ice Ih and compare the results to experimental electrical conductivity data. While the DFT result for the activation energy is in good agreement with experiment, we find that its two components have quite different values. Aside from providing new insight into the fundamental parameters of the microscopic electrical theory of ice, our results suggest the activity of traps in doped ice in the temperature regime typically assumed to be controlled by the free migration of L defects.

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While the isolated water molecule is one of the simplest in Nature, the condensed phases of H2O reveal many complex features that still elude complete understanding. An example is one of the most abundant crystalline solids on Earth, the proton-disordered hexagonal ice Ih, for which several aspects of structure-properties relationship have yet to be clarified.

An important issue concerns the role of crystal defects in the peculiar electrical properties of ice Ih. When an electric field is applied to an ice specimen, it becomes polarized by the thermally activated reorientation of the molecular dipoles. To explain the molecular origin of this phenomenon, Bjerrum postulated the existence of orientational defects that represent local disruptions of the hydrogen-bond network of ice Ih. While the conceptual picture of these Bjerrum defects is now well established, a quantitative understanding of their structure and energetics is still lacking, rendering a direct interpretation of experimental electrical conductivity data difficult.

Recent atomistic studies based on empirical potentials have provided important qualitative insight into the structure and dynamics of Bjerrum defects, but have not yet attempted to make direct contact with experimental conductivity data. Furthermore, the few ab initio studies in the literature involved clusters that are too small to reliably capture the properties of a defect embedded in bulk crystal. In this Letter, we present an ab initio study of the structure and energetics of Bjerrum defects in ice Ih using a large supercell. Moreover, based on Jaccard’s defect-based microscopic electrical theory of ice, we interpret the results in terms of experimental electrical conductivity data for doped ice Ih.

Fig. 1 provides a schematic picture of the formation of Bjerrum defects in ice Ih. Defect-free ice Ih, in which each molecule is hydrogen-bonded to its four tetrahedrally positioned neighbors, obeys Pauling’s two ice rules: (i) each molecule offers/accepts two hydrogens to/from two neighboring molecules, and (ii) there is precisely one hydrogen between each nearest-neighbor pair of oxygens. The proton-disordered character implies that there is no long-range order in the orientations of the H2O molecules or hydrogen bonds. The Bjerrum defect pair is a violation of ice rule (ii): it is obtained by the indicated rotation of molecule 1, after which there are two hydrogens between molecules 1 and 2 (D defect) and none between molecules 1 and 3 (L defect). After the initial formation, the pair can be further separated by successive molecular rotations, eventually creating a pair of independent, or free, D and L defects. Their motion through the crystal provokes the rotation of the water molecules along their paths, providing a mechanism for electrical polarization.

In both pure as well as doped ice, the conductivity σDL due to Bjerrum defects is essentially controlled by L defects. According to Jaccard’s electrical theory of ice, it takes the form

\[ \sigma_{DL} = q_{DL} n_L \mu_L, \]

where \( q_{DL} \) is the effective charge carried by the Bjerrum defects, \( n_L \) is the concentration of free L defects and \( \mu_L \) is their mobility. Its temperature dependence is described by

\[ \sigma_{DL}(T) \sim \frac{q_{DL}}{T} \exp\left(-\frac{E_{DL}}{k_B T}\right), \tag{1} \]

where \( T \) is the absolute temperature, \( k_B \) is Boltzmann’s constant and \( E \) is a characteristic activation energy. In pure ice, the latter is given by

\[ E = \frac{1}{2} E_{DL} + E_{Lm}, \tag{2} \]

where \( E_{DL} \) is the formation energy of an independent defect pair and \( E_{Lm} \) is the migration energy of a free L defect.

While the activation energy can be determined experimentally by measuring \( \sigma_{DL} \) as a function of \( T \) and adjusting it to Eq. (1), it is not possible to directly isolate the components \( E_{DL} \) and \( E_{Lm} \). To achieve this, additional conductivity measurements need to be carried out on...
doped ice samples, in which an extrinsic concentration of L defects is injected. This indirect procedure, however, is subject to large uncertainties and has revealed incompatibilities between different experiments.

Here we use a density-functional theory (DFT) approach to explicitly compute the formation and migration energies $E_{DL}$ and $E_{Lm}$. Our calculations are performed using the 96-molecule supercell labeled $3 \times 2 \times 2$ in Ref. 12. The calculations are executed using the VASP package using the Perdew-Wang 91 generalized-gradient approximation [11] and the projector-augmented-wave [15] approach. Brillouin-zone sampling was limited to the Γ-point and we use a plane wave cut-off of 700 eV. The effects of spurious image dipole interactions were evaluated [16] and found to be negligible for all investigated structures.

First, we relax the defect-free crystal supercell, allowing both the atomic and supercell coordinates to relax at zero stress. The resulting hexagonal lattice parameters $a = 4.383 \AA$ and $c = 7.16 \AA$, are $\sim 2\%$ below the experimental values measured at $T = 10$ K [3]. The average intramolecular oxygen-hydrogen separation of 1.01 Å is in excellent agreement with the experimental value of $\sim 1.006 - 1.008 \AA$. As appears typical of DFT calculations on ice Ih [17] our calculations slightly overestimate the sublimation energy of 0.69 eV compared to the experimental value 0.61 eV [3].

Next, we create an “embryonic” Bjerrum defect pair according to Fig. 1b) and relax it at constant volume. The resulting structure is shown in Fig. 1b) and is qualitatively similar to those observed in a recent molecular dynamics (MD) study [3]. Compared to the initial geometry in Fig. 1b)), one can no longer recognize a D defect in the sense of its description in Fig. 1b) due to the large electrostatic repulsion between the two hydrogen atoms [3, 7, 8]. The total-energy part of the formation energy of this structure is found to be 0.55 eV. To account for zero-point contributions, known to be relevant in ice [3], we also evaluate the change in the local inter- and intramolecular vibrational modes with respect to the defect-free crystal for the molecules in the vicinity of the defect, using the local harmonic approximation [17]. Overall, the zero-point contribution lowers the formation energy by about 10% to 0.50 eV.

To estimate the formation energy $E_{DL}$ of an independent pair of Bjerrum defects, we move the L defect through the crystal by a series of molecular rotations, followed by structural relaxation. Assuming that the zero-point contribution is the same as for the embryonic defect pair, the formation energy as a function of the number of molecular rotations is shown in Fig. 2. It quickly reaches a plateau value around 1.1 eV, subject to small fluctuations due to the disordered character of the hydrogen-bond network. However, a more accurate estimate of $E_{DL}$ requires an analysis of its asymptotic behavior as a function of distance between the defect pair near the plateau value. Because of their effective charges $\pm q_{DL}$, this behavior is expected to be of the form

$$E_{\text{form}}(r) = E_{DL} - \frac{q_{DL}^2}{4 \pi e_0 \epsilon_\infty r},$$

where $r$ is the distance between the point charges $\pm q_{DL}$, and $\epsilon_\infty$ is the high-frequency dielectric constant of ice Ih [3]. For each relaxed Bjerrum defect pair we position a point-charge $+q_{DL}$ on the dangling proton of the D defect and center a charge $-q_{DL}$ midway between the two oxygen atoms of the L defect, after which we adjust the formation energies of the defect pairs separated by more than 3 molecular rotations.

The results, shown in the inset of Fig. 2, are consistent with $1/r$ behavior and the intercept gives an asymptotic value $E_{DL} = (1.153 \pm 0.04) eV$. In addition, the slope of the fit provides an estimate for the effective charge which, using the experimental value $\epsilon_\infty = 3.2$ [3], gives $q_{DL} = (0.34 \pm 0.07)e$, in good agreement with the experimental value $q_{DL} = 0.38e$ [3].

Having determined $E_{DL}$ we now compute the migration energy barrier $E_{Lm}$. Given the disorder in the hydrogen-bond network, this barrier is expected to fluctuate depending on the local environment of the L defect. For this purpose, we computed 6 distinct barriers at different L-defect sites (13, 14 and 17 molecular rotations, cf. Fig. 2) by starting from the relaxed D-L configuration and rotating one of the 2 molecules hosting the L defect as shown in Fig. 3a), constraining only the rotating proton while allowing full relaxation of all other coordinates. This yields transition states of the type shown in Fig. 3a), in which the angle $\angle ABC$ is essentially bisection by the coplanar rotating OH bond. The resulting energy barriers (neglecting zero-point effects) vary in the range $E_{Lm} \simeq 0.10 - 0.14 eV$, indicating the significance of the disorder but an overall high mobility of free L defects. These results are consistent with the recent MD findings obtained at $T = 230$ K [3], for which, assuming an attempt frequency $\nu_0 = 24$ THz typical for librational modes in ice Ih [3], the present barriers give an average migration time ranging between 4 and 35 ps.

The experimental estimates for the formation and migration energies are obtained from conductivity measurements on ice doped with a substitutional concentration of HF [10, 19] or HCl [20] molecules. Since each molecule has only one proton, they introduce an extrinsic, temperature-independent concentration of L defects. Measurements of the conductivity $\sigma_{DL}$ as a function of $T$ then typically yield an Arrhenius-type plot with 3 distinct activation energies, as shown in Fig. 1b) [3].

The high-temperature regime $I$ is believed to be controlled by intrinsic behavior, characterized by the activation energy Eq. 2. The lower-temperature regimes II and III are assumed to be dominated by the extrinsic L defects. In the former, the temperature dependence of the conductivity has been attributed to the free motion...
of extrinsic L defects [3] so that \( E_{\text{II}} = E_{\text{diss}} + E_{\text{Lm}} \). In regime III the temperature is so low that the extrinsic L defects are not completely dissociated from their dopant molecules so that the activation energy involves an additional dissociation energy, giving \( E_{\text{III}} = \frac{1}{2}E_{\text{diss}} + E_{\text{Lm}} \). [3]

Considering the experimental results reproduced in Table I, the activation energy for regime I is quite well established, even for different dopant species, showing a dispersion of less than 0.05 eV among the different experiments. The values for the individual components \( E_{\text{DL}} \) and \( E_{\text{Lm}} \), however, show considerably larger deviations. The migration barrier values vary between 0.19 eV and 0.315 eV, leading to formation energies \( E_{\text{DL}} \) ranging from 0.66 eV to 0.79 eV.

Comparing these to our DFT calculations (cf. Table I), we notice that both components of the activation energy deviate significantly from the experimental values. The DFT result for \( E_{\text{DL}} \) is more than 46 % larger than the largest experimental value, whereas \( E_{\text{Lm}} \) is about 37 % lower than the lowest experimental estimate. In this light, it is quite striking that, despite the discrepancies for the individual components, the DFT estimate for the net activation energy in Eq. (2) agrees quite well with the experimental results, deviating about 10 % from the highest experimental estimate. This seems to demonstrate the difficulty involved in the interpretation of conductivity experiments in doped ice samples under conditions not controlled by intrinsic properties. Specifically, the fact that the DFT estimate for the migration barrier is systematically and significantly lower than all experimental estimates indicates that, as suggested in Ref. [3], the regime interpreted as being controlled by free extrinsic L defects, may in fact involve the activity of traps that obstruct their motion, leading to the higher effective migration barriers deduced experimentally.

In summary, we have conducted a first-principles study of the energetics of Bjerrum defects in ice Ih and compared the results to experimental electrical conductivity for doped ice samples. The results provide new insight into the parameters in Jaccard’s microscopic electrical theory of ice. While the DFT value for the net activation energy is in good agreement with experiment, we find that its two components have quite different values from those inferred from experiment. In particular, our results predict a migration barrier for L-defect motion that is significantly lower than the lowest experimental estimate, hinting at the presence of traps in the regime usually interpreted as being controlled by the free migration of extrinsic L defects.

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TABLE I: Activation energies and their components $E_{DL}$ and $E_{Lm}$ determined from doped ice experiments and the present DFT calculations.

| Ref.    | $E$   | $E_{Lm}$ | $E_{DL}$ |
|---------|-------|----------|----------|
| Ref. 10 (HF) | 0.575 | 0.235    | 0.68     |
| Ref. 19 (HF) | 0.625 | 0.315    | 0.664    |
| Ref. 20 (HCl) | 0.585 | 0.190    | 0.79     |
| This work | 0.696 ± 0.04 | 0.120 ± 0.02 | 1.153 ± 0.04 |

FIG. 1: a) Schematic picture of the formation of a Bjerrum defect pair from the defect-free ice Ih structure. The defect pair is created by the indicated rotation of molecule 1. b) Relaxed DFT structure obtained from the configuration in panel a).
FIG. 2: Formation energy of the Bjerrum defect pair as a function of the number of molecular rotations separating them. Dashed line is to guide the eye. Inset shows least-squares fit of the formation energies of the defect pairs separated by more than 3 molecular rotations to Eq. 3.

FIG. 3: Identification of transition state for the migration of an independent L defect. a) Equilibrium structure of the independent L defect. b) Typical transition state.

FIG. 4: Schematic representation of a characteristic experimental Arrhenius plot of the conductivity $\sigma_{DL}$ as a function of temperature in a doped ice Ih sample.