

Oriental 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 [1,2]. An example is one of the most abundant crystalline solids on Earth, the proton-disordered hexagonal ice Ih, for which several aspects of the structure-properties relationship have yet to be clarified [3].

A particularly important issue concerns the role of crystal defects in the peculiar electrical properties of ice Ih. When an electric field is applied, the ice becomes polarized by the thermally activated reorientation of the molecular dipoles. To explain the molecular origin of this phenomenon, Bjerrum [4] 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, [3] a quantitative understanding of its molecular structure and energetics is still lacking.

Recent atomistic studies [5–7] 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 [8,9] involve clusters that are too small to reliably capture the properties of a defect embedded in bulk crystal. In this Letter, we present a first-principles 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 [3,10], we interpret the results in terms of experimental electrical conductivity data for doped ice Ih.

Figure 1(a) provides a schematic picture of the formation of Bjerrum defects in ice Ih. Defect-free ice Ih, in which each molecule is linked to its four tetrahedrally positioned neighbors by hydrogen bonds, obeys Pauling's two ice rules [3]: (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 of the structure implies that there is no long-range order in

the orientations of the H₂O molecules or hydrogen bonds. The Bjerrum defect pair constitutes 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 *D* and *L* defects can be further separated by successive thermally activated 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 molecular mechanism for electrical polarization.

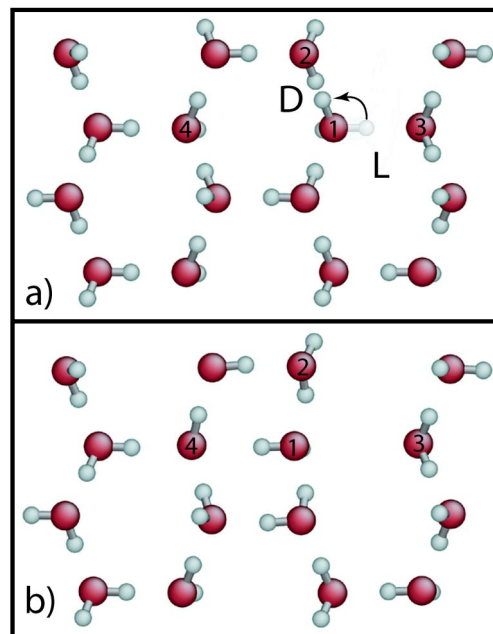


FIG. 1 (color online). (a) Schematic picture of the formation of a Bjerrum defect pair from the defect-free ice Ih structure. The defect pair is created by the indicated rotation of molecule 1. (b) Relaxed DFT structure obtained from the configuration in panel (a).

In both pure as well as doped ice, the conductivity σ_{DL} due to Bjerrum defects is essentially controlled by L defects [3]. According to Jaccard's electrical theory of ice [10] it takes the form

$$\sigma_{DL} = q_{DL} n_L \mu_L, \quad (1)$$

where q_{DL} is the effective charge carried by the Bjerrum defects, n_L is the concentration of free L defects, and μ_L is their mobility. Its temperature dependence is described by [3]

$$\sigma_{DL}(T) \sim \frac{q_{DL}}{T} \exp(-E/k_B T), \quad (2)$$

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 [3]

$$E = \frac{1}{2} E_{DL} + E_{Lm}, \quad (3)$$

where E_{DL} is the formation energy of a pair of free D and L defects which controls the thermal equilibrium concentration n_L , and E_{Lm} is the migration energy characterizing the free mobility μ_L .

While the activation energy can be determined experimentally by measuring σ_{DL} as a function of T and fitting it to Eq. (2), it is not possible to independently measure the components E_{DL} and E_{Lm} . To achieve this, additional measurements need to be carried out on *doped* ice samples, [3] 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 [3].

Here we use a density-functional theory (DFT) [11] approach to explicitly compute the formation and migration energies E_{DL} and E_{Lm} . Our calculations were performed using the 96-molecule proton-disordered ice Ih cell labeled $3 \times 2 \times 2$ in Ref. [12]. The DFT calculations were executed using the state-of-the-art VASP package [13,14] using the Perdew-Wang 1991 generalized-gradient approximation [11] and the projector-augmented-wave [15] approach. Brillouin zone sampling was limited to the Γ point and we used a plane wave cutoff of $E_{\text{cut}} = 700$ eV. The effects of spurious image dipole interactions due to the periodic boundary conditions were found to be negligible for all investigated structures [16].

As a first step, we relax the defect-free crystal supercell, allowing both the atomic and the supercell degrees of freedom to relax at zero stress. The resulting hexagonal lattice parameters are in good agreement with experimental values, with $a = 4.383$ Å and $c = 7.16$ Å, about 2% below the 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 ~ 1.006 – 1.008 Å. As appears typical of DFT calculations on ice Ih [17] our calculations slightly overbind the solid,

giving a 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. 1(a) and relax it at constant volume. The resulting structure is shown in Fig. 1(b) and is qualitatively similar to those observed in a recent molecular dynamics (MD) study [7]. Compared to the initial geometry in Fig. 1(b), one can no longer recognize a D defect in the schematic sense of Fig. 1(a) due to the large electrostatic repulsion between the two hydrogen atoms [3,6,7]. The total-energy part of the formation energy of this structure was found to be 0.55 eV. To account for quantum-mechanical zero-point contributions, known to be relevant in ice [3], we also evaluated the change in the local inter and intramolecular vibrational modes of the molecules in the immediate vicinity of the defect structure compared to those in the defect-free crystal using the local harmonic approximation [18]. Overall, the zero-point contribution lowers the formation energy by about 10% to 0.50 eV. The corresponding formation entropy at the melting point is $S_f = 2.2k_B$.

To estimate the formation energy E_{DL} of an independent defect pair, 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 configuration, the formation energy as a function of the number of molecular rotations is shown in Fig. 2. An estimate of E_{DL} requires an asymptotic analysis of the formation energy for large separations, which, because of their effective charges $\pm q_{DL}$, is expected to be of the form

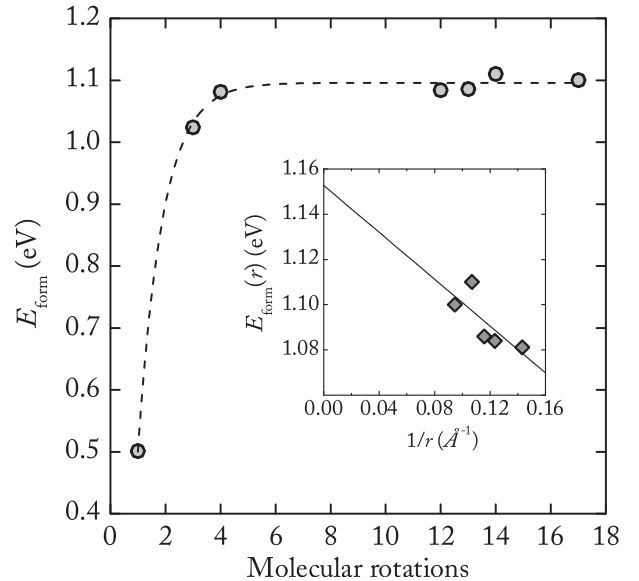


FIG. 2. Formation energy of the Bjerrum defect pair as a function of the number of molecular rotations separating them. Dashed line is to guide the eye. Inset shows least-squares fit of the formation energies of the defect pairs separated by more than 3 molecular rotations to Eq. (4).

$$E_{\text{form}}(r) = E_{DL} - \frac{q_{DL}^2}{4\pi\epsilon_0\epsilon_\infty r}, \quad (4)$$

where r is the distance between the point charges $\pm q_{DL}$, and ϵ_∞ is the high-frequency dielectric constant of ice Ih [3]. We define the centers of charge such that the charge $+q_{DL}$ is positioned on the dangling proton of the D defect, while the charge $-q_{DL}$ is centered midway between the two oxygen atoms of the L defect. By fitting the formation energies of the relaxed defect pairs separated by more than 3 rotations to Eq. (4), we obtain the straight line in the inset of Fig. 2. The results are clearly consistent with $1/r$ behavior, subject to fluctuations ~ 0.01 eV due to the disorder. The intercept gives $E_{DL} = (1.153 \pm 0.04)$ eV, whereas the slope, assuming the experimental value $\epsilon_\infty = 3.2$ [3], yields $q_{DL} = (0.34 \pm 0.07)e$. The latter is in excellent agreement with the experimental value $q_{DL} = 0.38e$ [3] and provides further confidence in the used *ab initio* approach.

Having estimated the formation energy E_{DL} we now compute the migration energy barrier E_{Lm} . Because of the disorder, this barrier is also expected to fluctuate depending on the local environment of the L defect. For this purpose, we computed 6 distinct barriers at 3 different L -defect sites (13, 14, and 17 molecular rotations cf. Figure 2) by starting from the relaxed D - L configuration and rigidly rotating one of the 2 molecules hosting the L defect as shown in Fig. 3(a), followed by a constrained relaxation in which the rotating proton is allowed to move only in the plane of the molecule, while allowing full relaxation of all other degrees of freedom. Using 5° angular increments, the maxima of the relaxed energy as a function of rotation angle give transition states in which the angle $\angle ABC$ is essentially bisected by the coplanar rotating OH bond, as shown in Fig. 3(b). The resulting energy barriers (neglecting zero-point effects) vary in the range $E_{Lm} \approx 0.10$ – 0.14 eV, indicating an overall high mobility of free L defects and revealing the role of disorder.

Finally, we need to assess the extent to which the previous results might depend on the particular disordered hydrogen-bond configuration of the supercell. The fact that the electrostatic $1/r$ behavior in Fig. 2 sets in for

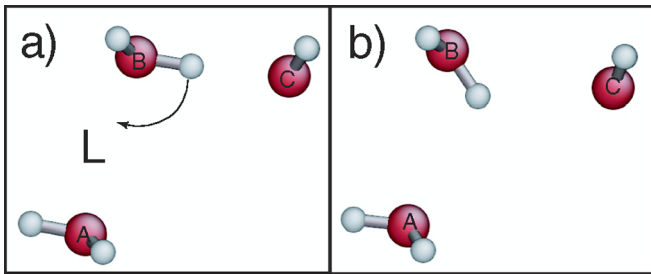


FIG. 3 (color online). Identification of transition state for the migration of an independent L defect. (a) Equilibrium structure of the independent L defect. (b) Typical transition state.

distances as short as $r \approx 6$ Å indicates that the disorder effect operates on a length scale that is significantly smaller than the dimensions of the cell. This implies that the influence of disorder is local in nature, rather than a property of the cell as a whole. Furthermore, our results for E_{Lm} are consistent with recent MD findings [6] based on cells with different sizes and hydrogen-bond arrangements. If we compute the average migration times corresponding to our E_{Lm} data using an attempt frequency of 24 THz, which is typical for the librational modes in ice Ih [3], we obtain values between 4 and 35 ps at $T = 230$ K. This is consistent with the MD values for the same temperature, which were reported to range between a few ps to several tens of ps [6]. In light of these facts, it appears unlikely that our results would be significantly different if a cell with a different disordered hydrogen-bond arrangement were used.

The experimental estimates for the formation and migration energies are obtained from conductivity measurements on doped ice [3], in which a substitutional concentration of HF [10,19] or HCl [20] molecules is introduced into the crystal. Since each molecule has only one proton, they introduce an extrinsic, temperature-independent concentration of L defects. Measurements of the conductivity σ_{DL} as a function of T then typically yield an Arrhenius-type plot with 3 distinct activation energies, as shown in Fig. 4 [3].

The high-temperature regime I is attributed to intrinsic behavior, characterized by the activation energy Eq. (3). The lower-temperature regimes II and III are believed to be dominated by the extrinsic L defects, where the former has been attributed to the *free* motion of extrinsic L defects [3]

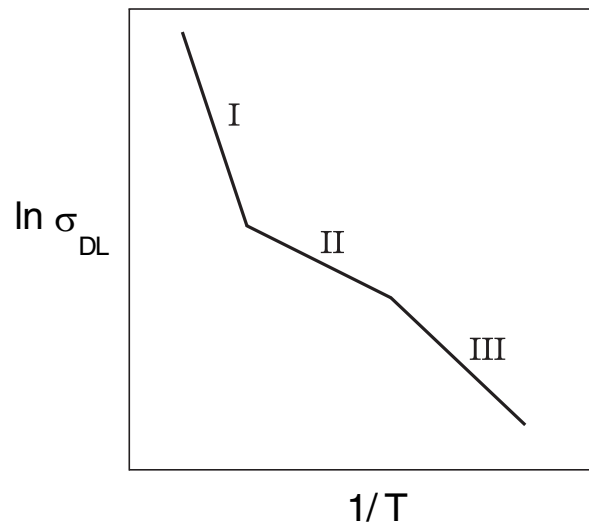


FIG. 4. Schematic representation of a characteristic experimental Arrhenius plot of the conductivity σ_{DL} as a function of temperature in a doped ice Ih sample [3]. Transitions between regimes I and II, and between II and III typically occur around temperatures of -50°C and -120°C , respectively, (e.g., Ref. [20]).

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

	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

with $E_{II} = E_{Lm}$. 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 $E_{III} = \frac{1}{2}E_{diss} + E_{Lm}$ [3].

Considering the experimental results [10,19,20] 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 individual components E_{DL} and E_{Lm} , however, show considerably larger deviations. The migration barrier values vary between 0.19 and 0.315 eV, leading to formation energies E_{DL} ranging between 0.66 and 0.79 eV.

Comparing our DFT calculations to these experimental results, we notice that both components of the activation energy deviate significantly from the experimental values. The DFT result for E_{DL} is more than 46% larger than the largest experimental value, whereas E_{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 of Eq. (3) agrees quite well with the experiments, deviating about 10% from the highest experimental estimate. This seems to be a direct demonstration of the difficulties involved in the interpretation of conductivity experiments in doped ice samples under conditions not controlled by intrinsic ice properties. Specifically, the fact that the DFT estimate for the migration barrier in pure ice is systematically and significantly lower than all experimental estimates indicates that, as suggested earlier [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 data 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 an L -defect migration barrier 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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