

Anomalous Proton Dynamics in Ice at Low Temperatures

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We present incoherent quasielastic neutron scattering measurements on ice *Ih* (ordinary ice) and *Ic* (cubic ice) which show the existence of nonharmonic motion of hydrogen at low temperatures, down to 5 K. We show that this dynamics is localized, nonvibrational, and related to the hydrogen disorder since it is absent in ordered ice VIII. A main jump distance of 0.75 Å is identified, hence close to the distance between the two possible proton sites along the oxygen-oxygen bond. The dynamics is non-Arrhenius, has a large time rate of $2.7 \times 10^{11} \text{ s}^{-1}$, and affects only a few percent of the total number of hydrogen atoms in the crystal. These results give evidence for the existence of concerted proton tunneling in these ice phases.

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Ordinary ice is the best known and most fundamental example of a hydrogen-bonded solid [1]. The ice *Ih* structure constitutes a nearly perfect tetrahedral network of hydrogen bonds. The principal building units are buckled hexagons with the oxygen at corners and one single hydrogen in between. There are six possible orientations for a water molecule in its tetrahedral bonding environment, each corresponding to a different arrangement of protons in the four H bonds. In ice *Ih* all possible orientations of the water molecule at each lattice site are equally realized; hence, the phase is proton disordered [2]. This implies that there exist two hydrogen sites between two oxygen atoms, both being randomly occupied with equal probability. The disordered arrangement of deuterium atoms has been demonstrated by neutron diffraction measurements in heavy ice [3], while indirect evidence for the disordered arrangement of the protons in ordinary ice [4] is derived from the nonzero value of the zero-temperature entropy (0.82 cal/mol K). In 1935, Pauling showed, using a classical counting argument [5], that the disordered nature of hydrogen atoms in ice *Ih* can account for most of the entropy measured in low temperature experiments. Better quantitative agreement is obtained by taking the possibility for proton correlations in oxygen rings into account [6].

The H disorder in ice presents, in principle, a degree of freedom for hydrogen to move between different sites induced by whatever mechanism. In this Letter, we report neutron scattering data which probe the stochastic motion of hydrogen in ice *Ih* and ice *Ic* (cubic ice). These indicate that the hydrogen dynamics does not freeze out at low temperatures but persists, for a small fraction of atoms, down to 5 K with jump lengths of typically 0.75 Å.

Neutron scattering experiments are very well suited to observe the motion of the proton due to its exceptionally large incoherent cross section [7] ($\sigma_{\text{inc}} \approx 81$ barn). In particular, quasielastic neutron scattering (QENS) is associated with the energy transfer resulting from the inelastic

interaction of a neutron with a particle in movement. It produces a zero-frequency-centered Doppler-broadened signal whose width is proportional to the time rate of the particle motion and whose integrated intensity is proportional to the number of particles involved in the process [8].

The incoherent dynamic structure factors of ice *Ih* and ice *Ic* were measured in comparison to that of the ordered phase ice VIII on the time-of-flight spectrometer IRIS at the U.K. spallation source ISIS (Chilton, Didcot). Whereas ice phases *Ih* and *Ic* are proton disordered with identical O-O and O-H distances, ice VIII is fully proton ordered. In ice VIII, only one proton site in a well-defined position is available per O-O bond. Ice VIII is hence an ideal phase to investigate the effect of disorder on the hydrogen dynamics compared to ices *Ih* and *Ic*.

The samples have been produced from 500 mm³ of Sigma-Aldrich deionized water at 99.9% purity. The sample of ice VIII was prepared following a procedure described in Ref. [9], produced in a Paris-Edinburgh press at 2.5 GPa and recovered at liquid nitrogen temperature. We first measured the ice VIII sample in the temperature range between 5 and 120 K, where ice VIII is (meta-) stable. Subsequently, the sample was warmed up to $T = 145$ K, where it transformed to ice *Ic*. The ice *Ic* sample was measured at 160 K and down to 5 K. Finally, the ice *Ic* sample was warmed again up to $T = 240$ K, where it converted to ordinary hexagonal ice and was measured at several temperatures between 5 and 260 K. Following this procedure, we minimized all of the possible spurious differences between the measurements in the two phases, which are ultimately obtained by transitions of the same sample from the proton-ordered to the proton-disordered solid phase. The IRIS spectrometer is provided with a high intensity diffraction detector bank which has been used, during the QENS measurements, to check the effective phase of the sample. We verified that the recovered sample of ice VIII had no detectable contamination from other ice

phases and that the phase transformation to ice *Ic* and to ice *Ih* was complete before performing the relative QENS measurements.

A hollow cylinder sample cell was used to minimize the sample self-shielding and multiple scattering (which was found, through a Monte Carlo simulation, to contribute for less than 18% to the total scattering intensity). A thin aluminum cell was used in order to minimize the scattering due to the cell itself. A careful comparison to a vanadium standard sample inserted into the cell allowed an absolute calibration of the intensity.

Figure 1 illustrates the measured intensity of ice *Ih* at 5 K for a selected Q value. Its ordered phase VIII and the instrument resolution are also displayed for comparison. The selected energy resolution of 15 μeV allows dynamics faster than 100 ps to be probed, with all of the slower processes contributing to the resolution-broadened elastic line. The presence of a quasielastic contribution in ice *Ih* beyond the experimental resolution is evident, even at the lowest measured temperature. Furthermore, the QENS contribution is absent in the H-ordered phase ice VIII, whose spectrum coincides with the measured resolution, while it is present in ice *Ic* with an intensity a factor 3 lower

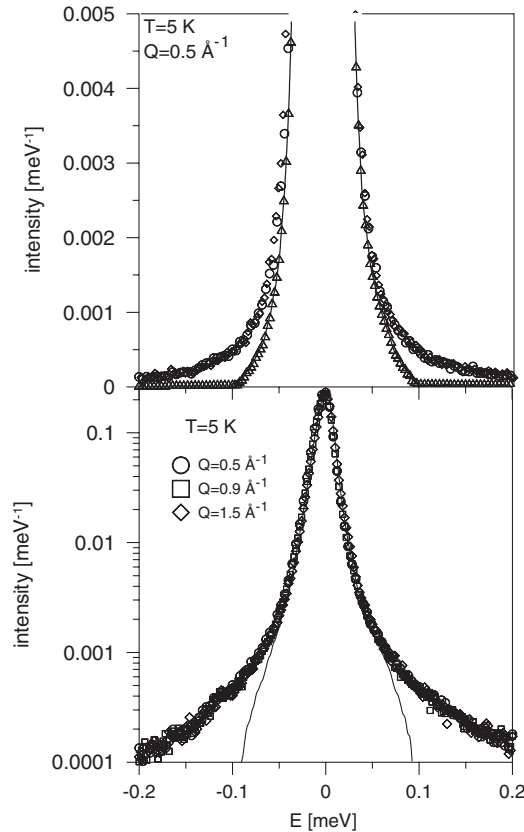


FIG. 1. Upper panel: quasielastic contribution in ice *Ih* at 5 K (\circ) compared with ice VIII spectrum (\triangle) at the same temperature. Lower panel: quasielastic contribution in ice *Ih* at 5 K as a function of the wave vector. In both panels, the solid line curve represents the instrument energy resolution.

than in ice *Ih*. This straight comparison indicates that the quasielastic contribution has its origin in the disorder-related motion of protons, which is prevented in the proton-ordered phase. As shown in Fig. 1, the QENS contribution has a Q -independent width, which indicates that the observed motion is localized.

We modeled the spectra of ice *Ih* at various temperatures in the range from -0.2 to $+0.2$ meV by the sum of an elastic line $\delta(\omega)$ with intensity $1 - C(Q, T)$ and a quasielastic Lorentzian line $L(\omega, \tau_c)$ with intensity $C(Q, T)$, along with a half width at half maximum intensity equal to $1/\tau_c$, with τ_c being the time scale associated with the dynamical process:

$$S(Q, \omega)_{\text{mod}} = \exp[-A(T)Q^2] \left[[1 - C(Q, T)]\delta(\omega) + C(Q, T) \frac{1}{\pi} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \right]. \quad (1)$$

Here, $\exp[-A(T)Q^2]$ is the Debye-Waller factor, with $A(T) = 2/3\langle u^2 \rangle$ proportional to the mean square displacements of protons [2]. As anticipated, the quasielastic component exhibits a Q -independent full width at half maximum of approximately 350 μeV in hexagonal ice and of 460 μeV in cubic ice (see Fig. 2), corresponding to a jump time of approximately 3.7 and 2.9 ps. The T dependence of τ_c is non-Arrhenius in the observed temperature range which excludes a classical hopping or a cage-confined motion of the proton as a driving mechanism. The large jump rate ($k_0 = 2.7 \times 10^{11} \text{ s}^{-1}$) implies an activation energy barrier [10] for the observed dynamics of the order of a few meV. This appears incompatible with a stepwise rearrangement of the proton in the bond or with

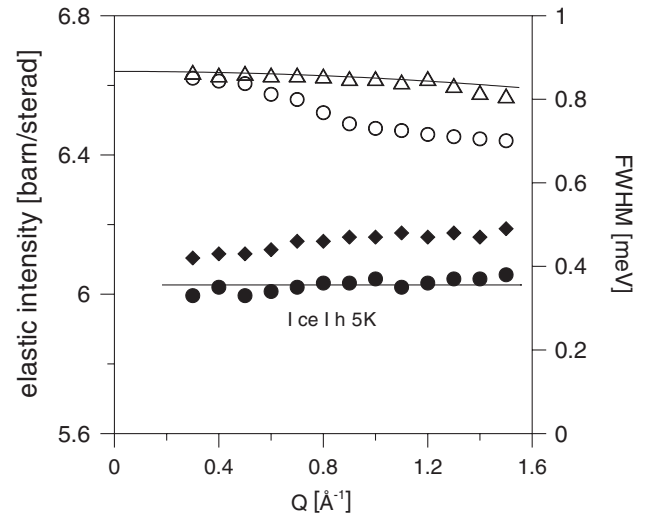


FIG. 2. Right axis: wave vector dependence of the time rate $1/\tau_c$ for hexagonal ice (\bullet) and cubic ice (\blacksquare). Left axis: wave vector dependence of the energy integrated elastic contribution (EISF) of ice *Ih* (\circ) compared with ice VIII (\triangle) and with behavior expected for a harmonic crystal (solid line) [2].

a simple rotation of the water molecule around the oxygen site, which would produce an ionic defect or a Bjerrum defect, respectively, whose energy barrier is much higher.

The presence of nonharmonic dynamics can also be revealed by the Q behavior of the elastic incoherent structure factor (EISF), corresponding here to $1 - C(Q, T)$ times the Debye-Waller factor if the elastic intensity is integrated over a broad energy domain. Deviations of the EISF from the expected exponential behavior are displayed in Fig. 2 where the Q trend expected for a harmonic crystal (where dynamics is purely vibrational) is reported for comparison. The Q -intensity trend confirms the hypothesis that the protons in ice *Ih* do not sit in a harmonic well. A fit of the EISF with an anharmonic Debye-Waller factor of the form $\exp\{-[A(T)Q^2 + B(T)Q^4]\}$ has been tempted as an alternative to the usual harmonic form $\exp[-A(T)Q^2]$. Although such a model provides a rather good fit of the data, we consider it unreliable since the coefficient $B(T)$ of the anharmonic (Q^4) term is almost temperature independent, contrary to all possible expectations. Therefore, the usual harmonic form for the Debye-Waller factor deduced by diffraction data [2] is assumed, and the decrease of the elastic intensity with increasing Q is ascribed to the presence of nonvibrational motion.

The Q dependence of the EISF, or alternatively of the quasielastic incoherent structure factor (QISF), accounts, via Fourier transform, for the average positions of the proton, i.e., provides information about the geometry of the motion. The small momentum transfer range accessible (up to $\sim 1.8 \text{ \AA}^{-1}$) prevents a reliable full Fourier transform, but we can derive insights on the distance involved by modeling the integrated fraction of quasielastic contribution, reported in Fig. 3, by a double well model for a powder sample [11–14]:

$$C(Q, T) = 2C(T)[1 - \sin(qd)/qd]. \quad (2)$$

Here $C(T)$ is the product of the occupation numbers of the two sites separated by a distance d . The fit of the integrated intensities in the overall temperature range indicates a main distance of $d = 0.75 \text{ \AA}$. This distance is of the order of the distance between the two possible proton sites along the oxygen-oxygen bond. This result strongly supports the identification of the localized dynamics with a proton jump between the two allowed sites in the bond. However, the temperature dependence of the population factor, $C(T)$, reported in the inset of Fig. 3, along with the aforementioned T independence of the jump time up to 100 K, indicates that the jump between the two sites is active down to the lowest temperatures and it is non-Arrhenius. These results suggest that the observed motion could be a quantum proton tunneling process, which is phonon assisted at the higher temperature. It is well known [15] that simple proton tunneling between the two proton sites is hindered at low temperature by the strong constraints imposed by the Bernard-Fowler rules. However, these ice

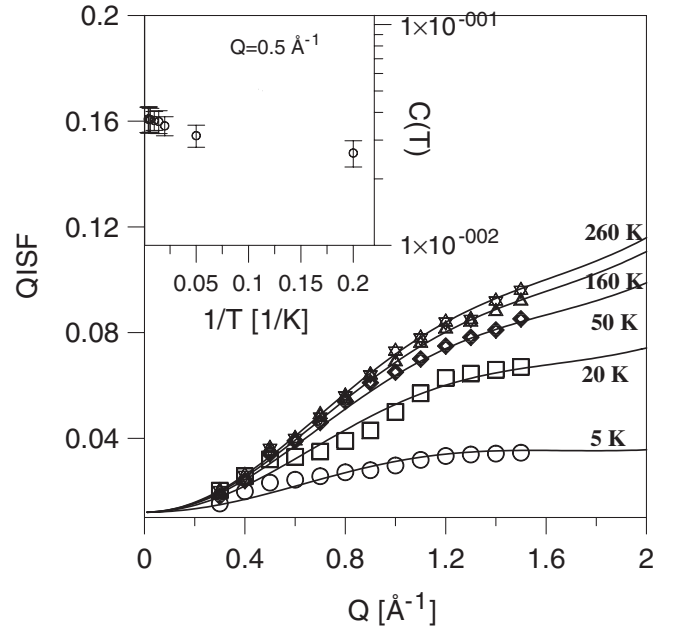


FIG. 3. Wave vector dependence of the energy integrated QISF for four selected temperatures compared with the best fit results of the model described in the text. Inset: product of the occupation populations of the two sites as a function of temperature.

rules are not violated if the motion we observe involves several hydrogen atoms simultaneously [5].

From the integrated intensity of the quasielastic contribution, we estimate the fraction of protons involved in the motion to 4% in ice *Ih* and 2% in ice *Ic* at 5 K, i.e., approximately the fraction of H atoms in ordered hexagonal loops. By *ordered loops*, we mean hexagonal loops, both in the hexagonal plane and perpendicular to it, where the protons occupy the same site in all six bonds. The statistical occurrence of such loops is $1/32$, and they might be involved in the observed proton dynamics as they would allow to move all six H atoms from one allowed position to the other along each bond without disturbing the rest of the crystal structure. As a consequence, the six protons can be moved with no change of the total energy of the crystal and no change of its entropy [16]. It remains to be shown by theory if the energy barrier for such a process is sufficiently low under realistic conditions or if a more complex mechanism has to be considered. Unfortunately, neither classical molecular dynamics simulations of the lattice nor quantum calculations on the isolated ring would allow us to provide a realistic estimation of the energy barrier involved in the process. A full *ab initio* quantum calculation of a lattice containing at least one ordered loop could instead yield useful information on the observed phenomenon, thus providing the wave function of the six hydrogens in the *ordered ring* and the corresponding electronics states. However, this is a nontrivial and, due to the high number of atoms to be considered, numerical time-consuming task, which is beyond the aim of our experimental study. The

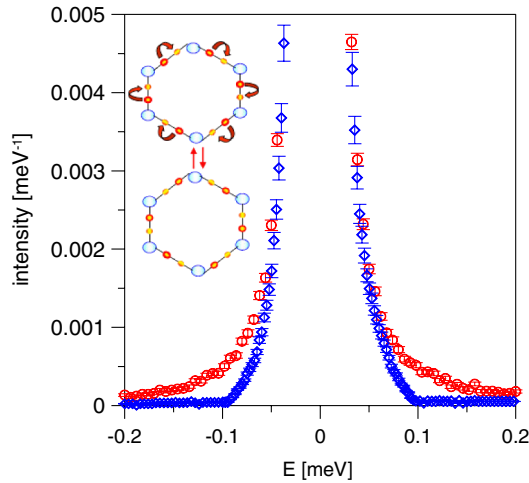


FIG. 4 (color online). Quasielastic contribution in hydrogenated ice *Ih* (○) compared with partially deuterated (◇), both at 5 K. Inset: a sketch of the proposed concerted tunneling of the hydrogen atoms in the ordered loops.

possibility of nonvibrational motions across the bond, generating short-lived dangling bonds on the time scale observed [17], has also been considered as an alternative mechanism. However, on one hand, the amount of surface to bulk ratio in the sample is too low to produce such a quantitative effect in the intensity; on the other hand, the same measurement performed on an ice *Ih* sample produced directly from the liquid gives the same amount of QENS signal.

Furthermore, to establish the effective role of ordered hexagonal rings, we performed the same quasielastic study on a partially deuterated ice *Ih* sample where the symmetric cyclic networks are broken. The substitution of 20% of deuterium in the sample assures that statistically 74% of all ordered rings contain at least one deuterium, i.e., a breaking of the symmetry of these rings. As shown in Fig. 4, where the two samples are compared at 5 K, deuterating hinders the observed dynamics. We believe that this additional experiment corroborates the assignation of the observed dynamics to a concerted proton tunneling process.

To conclude, in this Letter we provide experimental evidence of proton jumps in ice *Ih* and ice *Ic* at low temperatures. We observe a localized non-Arrhenius proton motion which occurs in the H-disordered phases of ice

only. The distance ($d = 0.75 \text{ \AA}$) involved, the high time rate ($2.7 \times 10^{11} \text{ s}^{-1}$), and the temperature dependence of the population factor suggest that the dynamics observed could be associated to quantum tunneling along the O-O bond, possibly in a concerted movement involving several H atoms simultaneously.

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