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Phys. Rev. B **110**, L220101 — Published 23 December 2024

DOI: [10.1103/PhysRevB.110.L220101](https://doi.org/10.1103/PhysRevB.110.L220101)

First-Principles Study of Proton Migration in Indium Oxide

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Indium oxide is widely used as a transparent conducting oxide. Interstitial hydrogen (H_i) acts as a shallow donor, but is expected to be quite mobile, thus enabling potential applications in electrochemical synapses or electrochemical random-access memory. Understanding the diffusion of interstitial hydrogen is essential for controlling its incorporation and stability. Using first-principles calculations based on hybrid density functional theory we find that the proton is the most stable charge state for Fermi levels up to 0.77 eV above the conduction-band minimum. Based on the nudged elastic band method we find that local hopping of the H atom, corresponding to a realignment of the O-H bond, can occur with an activation energy of 0.24 eV; this process can thus occur at low temperatures but does not lead to long-range diffusion. The long-range migration path of H_i^+ can be decomposed into rotations of the hydrogen atom around oxygen atoms and jumps between two oxygen atoms, with an overall activation energy of 0.94 eV. We compare our results with recent experiments, finding excellent agreement in both the low-temperature and high-temperature regimes, but leading to a re-evaluation of the measured activation energy. Our results provide insight into the different physical mechanisms that govern hydrogen motion in the different temperature regimes, and highlight the necessity of including the quantum-mechanical behavior of protons at low temperature.

Indium oxide (In_2O_3) is commonly doped with tin for applications as a transparent conductive oxide. Its high transparency and low resistivity [1–3] render it useful as a front contact in optoelectronic devices. Dopants other than Sn have also been explored; in particular, hydrogen leads to high carrier concentrations while retaining high carrier mobility and low absorbance [4].

Using density functional theory within the semi-empirical Hubbard-corrected local density approximation (LDA+ U) Limpijumng *et al.* [5] showed that both interstitial (H_i) and substitutional (H_O) can act as a shallow donor in In_2O_3 .

Subsequent calculations using hybrid functionals confirmed the shallow-donor nature [6–8].

Interstitial hydrogen is typically highly mobile in the lattice [9]. In most device applications, one has to ensure that the dopant remains fixed in the lattice and does not diffuse at operating temperatures. On the other hand, some devices are based on facile migration of dopants. Recent work has utilized electrically controlled proton intercalation in WO_3 to fabricate resistive switches for analog computing [10]. The change in electronic conductivity induced by proton insertion thus enables electrochemical random-access memory (ECRAM) [11] or solid-state electrochemical synapses [12] for physical neural networks. Given the shallow donor nature of hydrogen interstitials, In_2O_3 could serve as a potential host material, but has been unexplored from this perspective. Studying the migration of hydrogen in In_2O_3 is thus relevant for a variety of device architectures.

Yin *et al.* [7] experimentally investigated in-diffusion of H into In_2O_3 . They assigned an O-H vibrational line at 3306 cm^{-1} to interstitial H, and found that H was diffusing in the form of H_i^+ , with a diffusivity $5 \times 10^{-9}\text{ cm}^2\text{s}^{-1}$ at $450\text{ }^\circ\text{C}$ (723 K). Weiser *et al.* [13] studied stress-induced alignment of O-H bonds with vibrational spectroscopy. Qin *et al.* [14] later combined these low-temperature (153 K to 165 K) data with high-temperature (573 K to 723 K) measurements of in-diffusion and out-diffusion of H_i^+ . By combining the low-temperature and high-temperature data, they obtained a diffusion activation energy of 0.48 eV.

In this work, we investigate the incorporation and migration of hydrogen in In_2O_3 using hybrid density functional theory (DFT). We calculate the formation energy of the three charge states of H_i and find that H_i is stable in the +1 charge state (i.e., acts as a shallow donor) for Fermi levels up to 0.77 eV above the conduction-band minimum (CBM), and is bonded to a neighboring oxygen atom in an antibonding position.

We employ the climbing-image nudged elastic band (NEB) [15] method to calculate migration barriers and find that local hopping between $\text{AB}_{\text{O}1}$ sites with different O-H orientations can occur with a barrier of 0.24 eV. Long-range migration requires rotation of the H around an O atom into a higher-energy local minimum ($\text{AB}_{\text{O}2}$), followed by a jump to an $\text{AB}_{\text{O}1}$ site on a different O atom, with an overall activation energy of 0.94 eV. These results allow us to re-interpret the experimental results of Refs. 13 and 14 and assign the 0.24 eV barrier to the low-temperature reorientation, and the 0.94 eV to the long-range migration. Our results elucidate the qualitative differences in hydrogen motion in the high- and low-temperature regimes, and point to the need to in-

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clude quantum-mechanical aspects of proton motion at low temperatures.

We perform first-principles calculations using DFT as implemented in the VASP code [16]. The electron wave functions are described using projector augmented-wave potentials [17], with a cutoff for the plane-wave basis set of 400 eV. The d states from the indium atoms are treated as valence electrons. The incorporation of interstitial hydrogen is modeled using the supercell approach [18, 19]. Spin polarization is explicitly taken into account when unpaired electrons are present. In_2O_3 has a bixbyite crystal structure ($Ia\bar{3}$ space group) with 40 atoms in the primitive unit cell. Here we employ the cubic 80-atom conventional cell as a supercell and sample the Brillouin zone with a $2 \times 2 \times 2$ k-point mesh centered on the Γ point leading to 4 irreducible k-points. Atomic relaxations are performed with a force convergence criterion of 0.005 eV/Å (0.01 eV/Å in the NEB calculations). Initial structures always include displacements of neighboring atoms to allow for symmetry breaking.

To obtain an accurate description of the fundamental bandgap and of localized impurity levels we employ the screened hybrid exchange-correlation functional of Heyd, Scuzeria, and Ernzerhof (HSE) [20]. The HSE mixing parameter is chosen to reproduce the experimental bandgap, while the screening parameter was kept at the default value of $0.2 \text{ \AA}^{-1}$. Experimental work has reported the gap to be between 2.67 eV and 2.93 eV [21, 22]. Here we utilize a mixing parameter $\alpha=0.28$, as in recent calculations [23], which produces a bandgap of 2.89 eV. The calculated lattice parameter for the 80-atom cubic conventional cell is 10.14 Å, in agreement with an experimental value of 10.117 Å [24]. The calculated lattice vectors of the pristine cell are then fixed for the subsequent impurity calculations.

To address the thermodynamic stability we calculate the formation energy [18] $E^f[\text{H}_i^q]$ of H_i in charge state q :

$$E^f[\text{H}_i^q] = E_{\text{tot}}[\text{H}_i^q] - E_{\text{tot}}[\text{In}_2\text{O}_3] + \mu(\text{H}) + qE_F + \Delta^q, \quad (1)$$

where $E_{\text{tot}}[\text{H}_i^q]$ is the total energy of the supercell containing the impurity in charge state q in its relaxed geometry. $E_{\text{tot}}[\text{In}_2\text{O}_3]$ is the total energy of the pristine supercell, E_F is the Fermi level referenced to the valence-band maximum, and $\mu(\text{H})$ is the chemical potential of hydrogen.

Within periodic boundary conditions, charged impurities have a spurious interaction with their periodic images as well as the implicitly assumed neutralizing background charge in the supercell. Δ^q is the correction term that accounts for this effect; we calculate its value by applying the correction scheme of Refs. 25 and 26. We find a value of 0.26 eV in the +1 charge state and 0.20 eV in the -1 charge state.

The chemical potential $\mu(\text{H})$ represents the abundance of atomic species during growth or processing. We reference the hydrogen chemical potential to the energy of a hydrogen atom in an H_2 molecule:

$$\mu(\text{H}) = E_{\text{tot}}(\text{H}) + \Delta\mu_{\text{H}}. \quad (2)$$

The possible range of $\Delta\mu_{\text{H}}$ is determined by the limiting phases during growth or processing. In this case, water (H_2O) is the limiting phase, thus making the chemical potential of H dependent on that of O. We explicitly derive $\Delta\mu_{\text{H}}$ for O-rich and In-rich conditions in the Supplemental Material [27] (see also Ref. 28 therein). Values for intermediate conditions can be obtained from the provided information.

Calculated migration barrier energies are related to experimentally measurable diffusion coefficients through the following relation:

$$D = D_0 e^{-\frac{E_b}{kT}}, \quad (3)$$

where E_b is the activation energy, k is the Boltzmann constant, and T is the temperature. The prefactor D_0 can be estimated based on a typical interatomic hopping distance and an attempt frequency (for which we take the O-H stretch frequency) [29], leading to a D_0 value on the order of $10^{-3} \text{ cm}^2\text{s}^{-1}$.

The stability of the different charge states of H_i in In_2O_3 can be examined by plotting the formation energy [Eq. (1)] of each charge state in the lowest-energy configuration as a function of the Fermi level. Figure 1(a) shows formation energies for O-rich conditions; additional results for In-rich conditions are in the Supplemental Material [27]. The formation energy of H_i^+ is lower than that of the other charge states for Fermi levels below 3.66 eV (0.77 eV above the CBM). Based on a parabolic approximation for the conduction band and an effective mass of $0.30 m_e$ [30], we find that this Fermi level position corresponds to an electron concentration of $\sim 5 \times 10^{20} \text{ cm}^{-3}$. Up to that carrier concentration, interstitial hydrogen acts as a shallow donor in In_2O_3 . H_i behaves as a negative- U center [9], i.e., the neutral charge state is always higher in energy than the positive or negative charge states [see Fig. 1(a)]. We find the value of U to be -2.68 eV.

While the neutral and negative charge states are not thermodynamically stable for Fermi levels within the bandgap, we explicitly confirmed that they correspond to the occupation of localized defect states (rather than occupying the conduction-band states). In Fig. 1(a), we show the Kohn-Sham states corresponding to the different charge states. The distinction between Kohn-Sham states and charge-state transition levels, which correspond to the crossing points of the formation energies [see Fig. 1(a)], is discussed in Sec. I B 3 of Ref. [18]. In the positive charge state, there are no defect states within the gap. Adding an electron to the positive charge state results in the neutral charge state, with the added electron occupying a defect orbital that has moved into the gap. Finally, in the negative charge state, both of the added electrons occupy a now spin-degenerate defect orbital.

We now discuss the atomic structure of hydrogen interstitials for the various charge states. By symmetry, all the oxygen sites in In_2O_3 are equivalent. The crystal possesses two inequivalent sixfold coordinated In sites, 8b

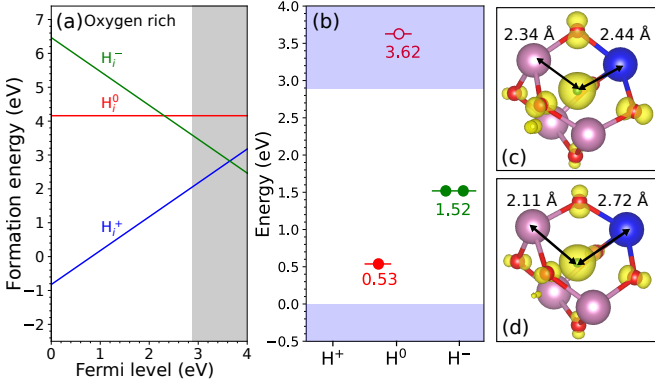


FIG. 1. (a) Calculated formation energies of hydrogen interstitial impurities in In_2O_3 as a function of Fermi energy in oxygen-rich conditions. The shaded region indicates Fermi-level positions above the CBM. (b) Kohn-Sham states at the Γ point for the different charge states of interstitial hydrogen in In_2O_3 . The shading indicates the valence band and conduction band in the pristine In_2O_3 system. The inset depicts the atomic structure of the negative charge state, with In_1 atoms shown in blue, In_2 in pink, O in red, and H in green; O-H and In-H interatomic distances are indicated in Å. (c) and (d) Charge density isosurfaces (yellow) of the occupied impurity states are shown for the (b) neutral and (c) negative charge states. The isosurface corresponds to a charge density of $0.01 a_0^{-3}$, which is 10% of the maximum density.

and 24d in Wyckoff notation [24]. We use the notation from Ref. 5 and refer to the 8b and 24d indium atoms as In_1 and In_2 , respectively, with the In_1 atoms shown in blue and In_2 in pink in the figures. For each In_1 site, there are three In_2 sites in the lattice.

In the neutral charge state, hydrogen stabilizes at a highly symmetric site where it is equidistant from three In_2 sites, at a distance of 2.34 Å, and 2.44 Å from an In_1 site, as shown in the inset of Fig. 1(b). The structure is similar in the negative charge state, but with a higher asymmetry: 2.11 Å from three In_2 sites and 2.72 Å from the In_1 site [Fig. 1(c)].

In the positive charge state, H_i^+ bonds to an oxygen atom, as expected for a proton. All oxygen atoms in the lattice are equivalent; they are bonded to one In_1 and three In_2 atoms. The four O-In bond lengths show some variation (which we will see to be related to the energetics of the various possible sites for the proton). In the pristine lattice, the three O- In_2 bond lengths are 2.22, 2.19, and 2.14 Å, whereas the O- In_1 bond length is 2.18 Å.

We considered eight possible sites: four bond-center sites, where H is positioned close to the center of an O-In bond, and four antibonding sites, where H is (approximately) located on the extension of an In-O bond. Similar to what was reported in Ref. 5 we find the bond-center sites to be either unstable (with the proton relaxing towards one of the antibonding positions), or to be very high in energy (more than 1.4 eV above the global minimum discussed next). The antibonding sites, which we

label $\text{AB}_{\text{O}1}$ – $\text{AB}_{\text{O}4}$ (as in Ref. 5), are shown in Fig. 2. The most stable position [$\text{AB}_{\text{O}1}$, Fig. 2(a)] is situated on the extension of the O-In bond that is the longest (in the pristine system). The next-higher-energy position [0.48 eV above the global minimum, $\text{AB}_{\text{O}2}$, Fig. 2(b)] is on the extension of the second-longest O-In bond. $\text{AB}_{\text{O}3}$ [Fig. 2(c)] and $\text{AB}_{\text{O}4}$ [Fig. 2(d)] are higher in energy by 0.83 eV and 1.18 eV. These results are in qualitative agreement with Ref. 13. In both the global minimum and the next-higher local minimum, the O-H bond length is equal to 0.99 Å.

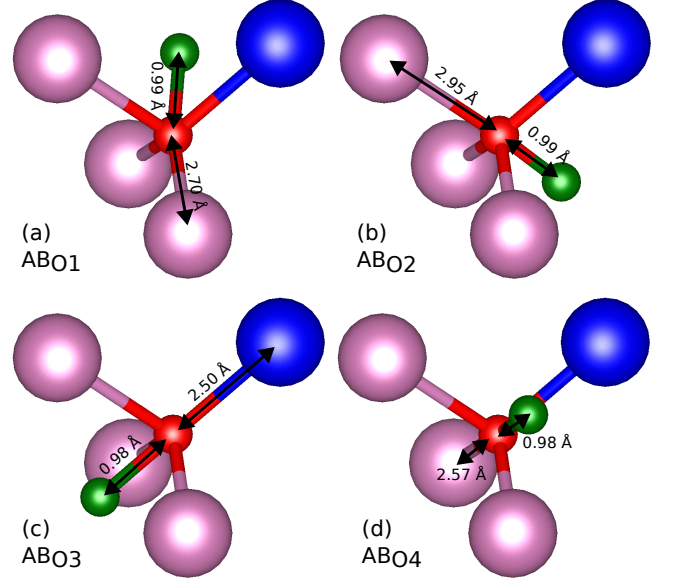


FIG. 2. Schematic illustration of the atomic geometry of interstitial H_i in the positive charge state in In_2O_3 . (a) Depicts the global minimum at $\text{AB}_{\text{O}1}$, (b)-(d) show higher-energy local minima $\text{AB}_{\text{O}2}$, $\text{AB}_{\text{O}3}$, and $\text{AB}_{\text{O}4}$ in order of increasing energy. In_1 atoms are shown in blue, In_2 in pink, O in red, and H in green; O-H and In-H interatomic distances are indicated in Å.

In our studies of migration we focus on migration of the proton, since H_i^+ is by far the most stable charge state. Long-range migration of H_i^+ requires moving the proton between two identical sites in neighboring unit cells. Due to the complex crystal structure, the unit cells are large; however, the cells consist of a repetition of the type of structural motifs as depicted in Fig. 2, and therefore the long-range migration can be broken up in a series of repeating segments.

Barriers are calculated using the climbing-image NEB method [15], in which the force and energy between each pair of adjacent images are interpolated using cubic polynomials. We divide the possible migration pathways into fundamental trajectories corresponding to H_i^+ jumps or rotations between two neighboring local minima. We use 5 images in the NEB calculations, not including the endpoints of the trajectories. One segment we examined is depicted in Fig. 3; it moves the proton between two global minima ($\text{AB}_{\text{O}1}$) within an interstitial void. Based on our

NEB calculations we find a barrier height of 0.24 eV. As shown in Fig. 3(b), the distance over which the proton moves is quite short; the energy barrier is mainly due to the need to significantly change the relaxation of the different O atoms to which the H is bonded in the initial and final states. This path does not allow for long-range migration, since the proton remains trapped within the interstitial void. In order to escape from this local configuration, the proton needs to follow a path that involves bonding in higher-energy antibonding sites. However, the path examined in Fig. 3 involves a reorientation of the proton, which has been experimentally observed at low temperatures and will be discussed below.

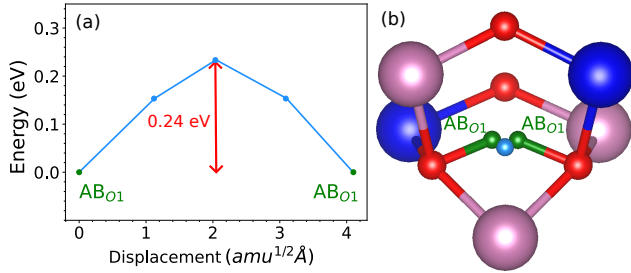


FIG. 3. (a) Potential energy along a short-range migration path for H_i^+ between two AB_{O1} sites in an interstitial void In_2O_3 as a function of displacement, defined as the square root of the sum over mass-weighted squares of atomic displacements. (b) Corresponding path shown within the pristine crystal structure. For clarity, only the end points and saddle point are depicted

A path that allows for long-range migration is shown in Fig. 4; it is composed of rotations and jumps involving AB_{O1} and AB_{O2} sites (the global minimum and the next-higher local minimum, at 0.48 eV). Starting in an AB_{O1} site, a proton can either *rotate* to the AB_{O2} position on the same O atom (as shown in orange), or *jump* to an AB_{O2} site on a different O atom (shown in blue). The rotation requires overcoming a barrier with a height of 0.68 eV, while the jump requires 0.94 eV. One may wonder whether the metastable minimum at AB_{O2} could serve as an intermediate site that lowers the overall activation energy to 0.68 eV (since the barrier to jump from AB_{O2} to AB_{O1} is only 0.46 eV). However, the depth of the well at AB_{O2} (0.2 eV) is insufficient to keep the proton on this site for a long enough time to make a material difference in the migration process. The overall activation energy for long-range migration is thus 0.94 eV.

We checked whether higher-energy AB_O sites could be involved in the migration process. Since AB_{O4} is 1.18 eV higher than the global minimum, it would lead to a barrier that is higher than the one for the path we already identified. AB_{O3} is only 0.83 eV higher, but a jump or rotation from AB_{O1} to AB_{O3} requires overcoming a barrier that is again higher than the one we already identified. We thus find that the AB_{O3} and AB_{O4} local minima do not contribute to the migration mechanism.

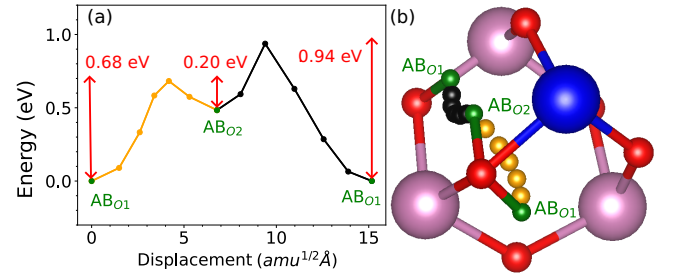


FIG. 4. (a) Potential energy along sections of a long-range migration path for H_i^+ migration in In_2O_3 as a function of the mass-weighted position. The rotation around a single O atom (from AB_{O1} to AB_{O2}) is shown in orange, and the jump from AB_{O2} to AB_{O1} on a different O atom is shown in blue. (b) Corresponding paths shown within the pristine crystal structure.

We now discuss how our results relate to experimental observations. Yin *et al.* [7] introduced H into In_2O_3 by placing bulk samples in sealed quartz ampoules filled with H_2 and annealing at elevated temperature. They performed detailed vibrational spectroscopy and absorption measurements and assigned an O-H vibrational line at 3306 cm^{-1} to interstitial H. They concluded that hydrogen was indiffusing in the form of H_i^+ , with a diffusivity $5 \times 10^{-9}\text{ cm}^2\text{s}^{-1}$ at 450°C (723 K). This value is consistent with our calculated activation energy of 0.94 eV if we assume a prefactor of $0.016\text{ cm}^2\text{s}^{-1}$.

Weiser *et al.* [13] built on the work of Ref. 7; upon applying [001] stress at 165 K they observed a realignment of the center with the characteristic vibrational frequency of 3306 cm^{-1} , which had been previously assigned to interstitial H. Weiser *et al.* [13] interpreted the observed realignment as related to a hydrogen diffusion jump, which would involve moving H_i^+ from an AB_{O1} to an AB_{O2} site. Our calculated barriers for this process indicate that they are much too high to account for the observed low-temperature motion of H_i . Instead, we suggest that the realignment is purely due to the hopping process between AB_{O1} sites with a barrier of 0.24 eV. This process does not lead to long-range diffusion, but that is not necessary to explain the experiments of Ref. 13. Our calculated barrier of 0.24 eV is significantly lower than the barrier of 0.48 eV extracted by Weiser *et al.* [13]; however, the latter result was obtained by combining the low-temperature results with the diffusivity data obtained in Ref. 7 at 723 K.

Additional temperature-dependent measurements were performed by Qin *et al.* [14]. They produced more detailed low-temperature (153 K to 165 K) measurements of the realignment process, and studied both in-diffusion and out-diffusion of H_i^+ at high temperature (573 K to 723 K). Again, the assumption was made that the low-temperature and high-temperature are governed by the same process, leading to an expression for the diffusivity: $D = 1.9 \times 10^{-7} \exp(-0.42/kT)\text{ cm}^2\text{s}^{-1}$. As explained above, we feel the assumption that the

same process governs both low- and high-temperature hydrogen motion is unjustified; in fact, inspection of Fig. 7 in Ref. 13 indicates that the slope of the Arrhenius line provides a good fit neither in the high-temperature range nor in the low-temperature range. In addition, the prefactor ($1.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is unphysically low for a migration process.

We performed independent Arrhenius fits of the data in Ref. 13 (see Fig. 5 for the details of the fitting). In the high-temperature regime, our Arrhenius fit leads to $D_H = 9.0 \times 10^{-3} \exp(-0.99/kT) \text{ cm}^2 \text{ s}^{-1}$. This activation energy is in good agreement with our value of 0.94 eV, and the prefactor is in line with the expected value for a thermally activated diffusion process. All of this confirms that long-range diffusion of protons in In_2O_3 proceeds with an activation energy of $\sim 0.94 \text{ eV}$.

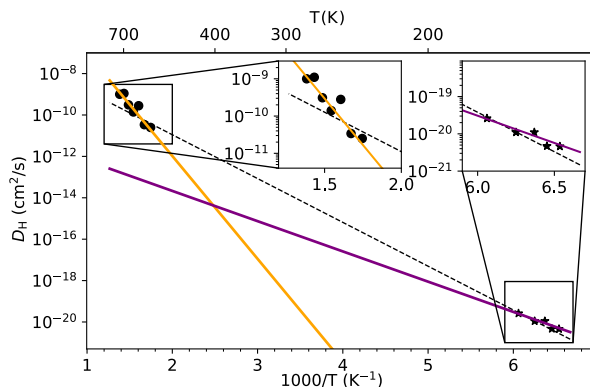


FIG. 5. Diffusivity D_H plotted as a function of inverse temperature for H_i^+ in In_2O_3 . Black symbols are experimental data from Ref. 13. The filled circles near 700 K show the diffusivity measured by in-diffusion and out-diffusion. The filled stars near 160 K show values determined from stress alignment. The black dotted line shows the fit including both datasets as reported in Ref. 13. The orange and purple lines show separate fits to the high-temperature and low-temperature data, respectively.

At low temperature, the physics is quite distinct. Fitting to the data in Ref. 13 in the range between 153 K and 165 K, we find $D_H = 1.8 \times 10^{-11} \exp(-0.29/kT) \text{ cm}^2 \text{ s}^{-1}$; or, from a fit to the rates $1/\tau^*$ (where τ^* are the time constants extracted from the stress-alignment experiment): $1/\tau^* = 5.3 \times 10^5 \exp(-0.28/kT) \text{ s}^{-1}$. The fitted activation energy of 0.29 eV is in very good agreement with the barrier of 0.24 eV obtained from our first-principles calculations, but the prefactor $1/\tau_0^*$ is more than eight orders of magnitude smaller than would be expected for thermally activated hopping. We attribute this to the fact that at low temperatures there is a quantum-mechanical aspect to the hydrogen motion; indeed, experiments on muonium, a pseudo-isotope of hydrogen, produced a

temperature-independent hop rate of $\sim 2 \times 10^3 \text{ s}^{-1}$ at temperatures below room temperature [31], consistent with the fact that the much lighter muon ($1/9^{\text{th}}$ of the proton mass) would move entirely by quantum-mechanical tunneling. In the case of the proton, the motion is definitely thermally assisted and could potentially be described by Flynn-Stoneham theory [32]; a Flynn-Stoneham analysis in Ref. 33 for proton motion in BaSnO_3 , where similar migration barriers were found (0.2–0.3 eV), indeed produced a prefactor $\sim 2 \times 10^4 \text{ s}^{-1}$, consistent with what we find for the proton in In_2O_3 .

In summary, we have systematically studied the incorporation and migration mechanism of interstitial hydrogen in In_2O_3 using hybrid density functional theory. Based on our calculations of formation energies, we find that H_i^+ is stable (and acts as a shallow donor) for Fermi levels up to 0.77 eV above the CBM. H_i is bonded to an oxygen atom in an antibonding position, with four possible orientations of the O-H bond. We find that H_i^+ can locally hop between sites with different O-H orientation with a barrier of 0.24 eV. Long-range migration requires rotation of the H around an O atom into a higher-energy local minimum, followed by a jump to a different O atom, with an overall activation energy of 0.94 eV. These findings allow a re-examination of experimental results [13, 14]: our results are in very good agreement with data obtained at low temperature from stress alignment and at high temperature from mass transport, but highlight that these processes are physically distinct and are described by very different activation energies.

Our findings impact applications in two ways. First, the experimentally observed reorientation at low temperatures does not impact proton conduction, since it does not lead to long-range diffusion. Second, our results indicate the diffusion activation energy is significantly higher than previously reported, resulting in much lower proton conductivity (by five orders of magnitude) at room temperature, and thus limiting the application of In_2O_3 in ECRAM.

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

This work was supported by Superior Energy-efficient Materials and Devices (SUPREME), one of seven centers in JUMP 2.0, a Semiconductor Research Corporation program sponsored by the Defense Advanced Research Projects Agency. Computational resources were provided by Bridges-2 at Pittsburgh Supercomputing Center through allocation DMR070069 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation grants #2138259, #2138286, #2138307, #2137603, and #2138296.

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