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Local Environment and Migration Paths of the Proton Defect in Yttria-Stabilized Zirconia Studied by Ab Initio Calculations and Muon-Spin Spectroscopy

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Abstract: The local binding and migration behavior of the proton defect in cubic yttria-stabilized zirconia (YSZ) is studied by first-principles calculations and muon-spin spectroscopy (μ SR) measurements. The calculations are based on density-functional theory (DFT) supplemented with a hybrid-functional approach with the proton defect embedded in quasi-random supercells of 10.3 mol% yttria content, where the yttrium–zirconium substitutional defects are charge compensated by oxygen vacancies. Representative migration pathways for the proton comprising both transfer and bond reorientation modes are analysed and linked to the underlying microstructure of the YSZ lattice. The μ SR data show the evolution of the diamagnetic fraction corresponding to the muon-isotope analogue with an activation energy of diffusion equal to 0.17 eV. Comparisons between the calculations and the experiment allow an assessment of the character of the short-range migration of the proton particle in cubic YSZ.

Keywords: zirconia; proton; ab initio calculations; muon spectroscopy



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1. Introduction

Yttria-stabilized zirconia (YSZ) in its cubic-fluorite phase is commonly employed in electrochemistry as the electrolyte material in solid-oxide fuel cells [1,2]. Cubic YSZ is a stable ionic conductor for which the electrical conductivity is mediated by the mobility of oxygen ions, although recent studies have also shown that a fraction of the total electrical conductivity at lower temperatures may originate from protons [3–5]. The pioneering studies by Wagner and Stotz were instrumental in giving evidence of the presence of proton defects in zirconia–yttria solid solutions through measurements of water solubility and proton-based conductivity [6,7]. Since then, more recent works have reported high levels of electrical conductivity attributed to protons in bulk nanocrystalline YSZ (nc-YSZ) samples at temperatures below 150 °C [8–12].

Previous calculations of hydrogen species in zirconia phases [13–17] were predominantly static studies based on density-functional theory (DFT) [18,19] that resolved the equilibrium sites, local bonding of monatomic hydrogen impurities and a number of properties, such as the positions of the charge-transition levels inside the fundamental gap and hyperfine constants. Related studies were also carried out for hydrogen states at zirconia grain boundaries [20–23].

Proton diffusion studies in undoped zirconia phases comprise DFT-based molecular-dynamics and molecular-statics calculations in monoclinic zirconia [24,25], DFT-accelerated metadynamics in tetragonal zirconia [26] and static constrained-path calculations in cubic zirconia [27]. Proton-migration pathways and barriers in YSZ have been studied by

DFT calculations [22] that employed the nudged elastic-band (NEB) method [28]. It was shown that the host lattice can sustain proton-migration modes of different character and ranges [22]. One of the conclusions reached was that the rate-limiting paths for long-range macroscopic diffusion are cross-vacancy paths with corresponding barriers in excess of 1 eV. These findings strongly suggest that proton mobility in bulk YSZ should be rather low. Nonetheless, the short-range migration behavior of protons is still not understood, and there is a need for direct experimental verification. Furthermore, the short-range migration of protons can provide crucial information on the local proton environment and its binding and association with common defects within the YSZ host lattice, such as the oxygen vacancies and the yttrium ions.

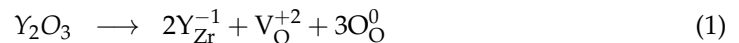
μ SR spectroscopy has grown to be one of the major techniques for studying hydrogen in materials through modelling with muonium [29,30]. This hydrogenic atom is a lighter pseudo-isotope, where the atom consists of a positive muon bound to an electron captured during implantation. Although the muon is much lighter ($\sim 1/9$ of the mass of the proton), the reduced muonium mass is almost equal to that of hydrogen, resulting in nearly identical ground-state properties [29,31]. μ SR also has the additional advantage of being restricted to the high-dilution limit for the muonium impurity which can, thus, generally be regarded as isolated, affected only indirectly by other defects or impurities through the overall Fermi energy. In fact, muon-spin spectroscopy has also been used successfully to investigate the diffusion of the muon: in this case, the lighter mass of the muon implies that quantum effects (in particular, those arising from the zero-point energy) should be more intense. The muon, in this case, provides an extension to lower masses for hydrogen diffusion isotopic studies [30,32]. μ SR-based studies of various cubic zirconia phases stabilized by different transition-metal oxides have led to detailed findings on the electronic and hyperfine properties of monatomic hydrogen and have even provided aspects of the local muon environment [33,34].

The present work presents a combined theoretical and experimental study of the proton defect in YSZ, with an emphasis on understanding proton binding in the YSZ lattice and the character of proton migration. The main aim of the calculations was to focus on a local network of paths and assess the relative relevance of proton transfer versus bond re-orientation diffusion modes, with the addition of zero-point energy effects that were not included before. The calculations are based on density-functional theory under two different approximations for exchange and correlation effects. Proton diffusion paths and associated energy profiles were determined by the nudged elastic-band method (NEB). Experimentally, we report new results of μ SR spectroscopy experiments in yttria-stabilized zirconia above room temperature and in a zero-field configuration (no externally applied magnetic field). The results allow us to follow muon motion above room temperature, thus providing information on the diffusion of the diamagnetic (positively charged) fraction.

2. Theoretical and Experimental Preliminaries

First-principles calculations based on density-functional theory were performed with the VASP computational code [35–37]. A plane-wave basis limited by a cut-off energy of 420 eV was taken for the expansion of the crystalline valence-electron wavefunctions. Pseudopotentials based on the projector-augmented wave method [38] were used to represent the valence–core interaction. Exchange and correlation effects between the electrons were described by two different approaches: first, within the generalised-gradient approximation and the PBE (Perdew, Burke and Ernzerhof) semilocal functional [39]; additionally, by the HSE06 hybrid-functional approach [40,41], which includes exact (non-local) screened exchange: a fraction of 0.25 of the exact exchange led to an energy band gap of 5.52 eV, in excellent agreement with experimental data [42]. Structurally, the YSZ lattice was represented by means of bulk cubic-zirconia supercells doped with a certain number of yttria units. Three yttria formula units (Y_2O_3) were added to a 96-atom $2 \times 2 \times 2$ fluorite lattice to achieve a stoichiometry of 10.3 mol% for the yttria–zirconia solid solution, which is within

the stability limits of the cubic phase [43]. The incorporation of yttria can be described by the following reaction:



which fulfils charge and site conservation. The yttrium atoms were introduced substitutionally in the cation sublattice of zirconia. The resulting negatively charged Y_{Zr} defects are charge compensated by the creation of doubly positively charged oxygen vacancies, V_{O}^{+2} , in order to achieve overall charge neutrality. These vacancies, therefore, are intrinsic atomic defects and should be considered as part of the equilibrium structure of YSZ. The symbol O_{O}^0 denotes the oxygen atoms at their normal lattice sites with zero effective charge. Several structural models were created by sampling various arrangements of vacancy–vacancy and yttrium–vacancy associations. Subsequent energy minimization showed that in the lowest-energy YSZ supercell, the oxygen vacancies were at least fifth-nearest neighbours, and yttrium ions displayed a strong tendency to occupy second-nearest-neighbour sites with respect to the vacancies, in agreement with previous DFT calculations of cubic YSZ lattices [44–46]. More details can be found in refs. [16,22]. The final lowest-energy YSZ supercell employed for the defect calculations is shown in Figure 1a.

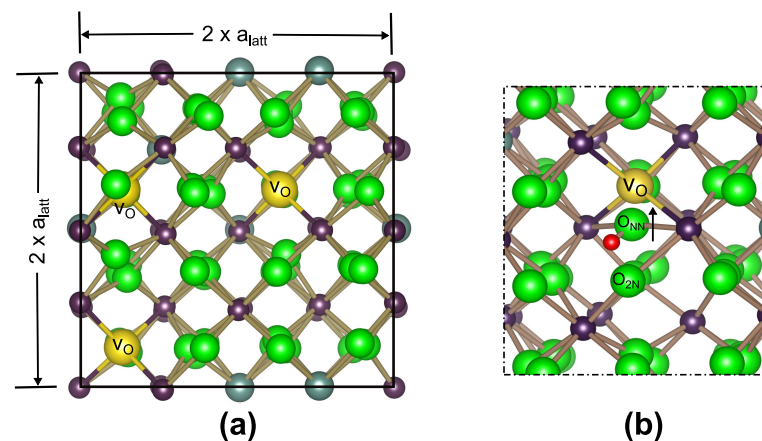


Figure 1. (a) YSZ supercell after structural relaxation. The bulk lattice parameter a_{latt} equals 5.18 Å and is obtained from optimisation with the HSE06 functional [16]. (b) Atomistic structure of a proton configuration in the YSZ lattice, showing the formation of a dative O-H bond and strong displacement of the nearest-neighbour oxygen atom, O_{NN} , towards the closest oxygen vacancy. The oxygen vacancies (V_{O}) are depicted as the yellow spheres. Zr and O are small purple and large green spheres, respectively. Y ions are large grey spheres. The proton is the small red sphere.

The minimum-energy paths (MEPs) and classical migration barriers of proton/muon diffusion were determined by the NEB method [28], which offers a practical implementation of transition-state theory [47] for calculating the reaction coordinates of diffusion processes in solids. NEB calculations provided both the MEP and barriers through optimisation of the intermediate system replicas connecting initial and final proton/muon configurations. The total migration barrier, E_{barr} , for a specific path can be obtained as the sum of the classical activation barrier (the NEB results) and a zero-point energy (ZPE) correction term:

$$E_{\text{barr}} = E_{\text{cl}} + \delta E_{\text{ZPE}}. \quad (2)$$

The classical barrier is obtained as the DFT total-energy difference between the initial (*ini*) lower-energy and the higher-energy saddle-point (SP) configurations for each individual path, namely:

$$E_{\text{cl}} = E_{\text{tot}}^{(\text{SP})} - E_{\text{tot}}^{(\text{ini})} \quad (3)$$

The zero-point correction term is quantum mechanical in origin and is given as follows [48]:

$$\delta E_{\text{ZPE}} = \sum_i \frac{h\nu_i^{\text{SP}}}{2} - \sum_i \frac{h\nu_i^{\text{ini}}}{2} \quad (4)$$

The vibrational frequencies ν_i^{ini} and ν_i^{SP} in Equation (4) correspond to normal modes of vibration i and were determined from the diagonalization of the local dynamical matrices of the respective systems with the proton occupying the *ini* and SP positions, respectively. The ZPE correction for the muon was obtained within a harmonic approximation for the zero-point motion [49] by scaling the ZPE-correction for the proton by the isotopic mass factor, $\sqrt{m_p/m_\mu}$. This equals 2.98, since $m_\mu = 0.113 m_p$.

The muon-spin spectroscopy experiments were conducted using the EMU instrument of the ISIS Facility, Rutherford Appleton Laboratory, UK. A nanocrystalline YSZ ($\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$) sample with grain size 17 nm, kindly provided by Innovnano, was investigated. In the experiments, 4 MeV positive muons were implanted into the sample, and muon-spin spectroscopy measurements were undertaken without applying any external magnetic field (zero-field configuration) and in the temperature interval 8.6 K to 700 K. Calibration measurements using an externally applied magnetic field with $B = 10$ mT were also undertaken. Data analysis was done using the WiMDA program [50].

3. Results

3.1. Local Proton Binding and Energetics

The proton defects, H^+ , are the ionized states of monatomic hydrogen. They were introduced interstitially at various locations in the cubic YSZ supercell, and the final equilibrium sites were determined by treating the structural relaxation effects through energy minimisation using the semilocal PBE functional. Subsequently, the HSE06 functional was employed to obtain the formation energies [16] of all final relaxed non-equivalent proton configurations. Structurally, it was observed during structural relaxation that H^+ binds to oxygen ions, forming hydroxyl-type O-H bonds with bond lengths spanning a very narrow range: from 0.98 to 1.00 Å. A second oxygen ion is also found near the proton at distances ranging from 1.60 to 2.00 Å. Owing to the disordered structure of the YSZ lattice, the O-H configurations are not iso-energetic. The final proton energies are depicted in Figure 2a, where a sizeable energy scatter of ~ 1.3 eV is observed. Inspection of these energies, however, reveals an important trend: the lower formation energies were recorded for O-H configurations formed very near the intrinsic oxygen vacancies. More specifically, protons bind preferably with the oxygen ions that are the nearest neighbours of these vacancies.

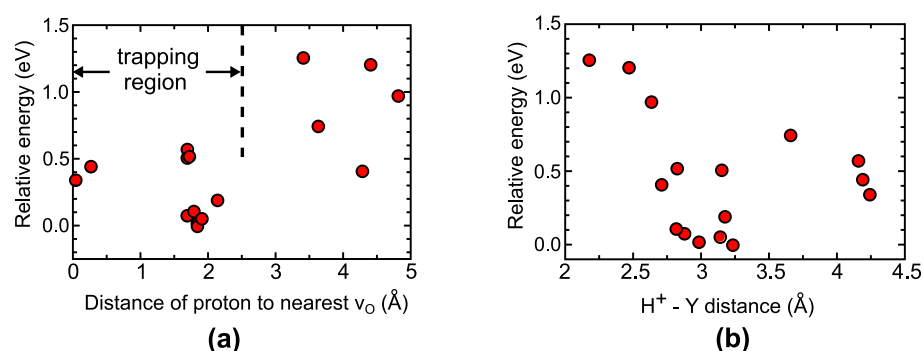


Figure 2. (a) HSE06 formation energies of proton configurations versus distance from the nearest oxygen vacancy. (b) HSE06 formation energies of proton configurations versus distance from the nearest yttrium ion. The energies are given with respect to the lowest-energy configuration.

This suggests that the intrinsic vacancies of the lattice act indirectly as trapping regions for protons. Due to the considerable scatter of the energies, a binding-energy magnitude cannot be uniquely obtained; nonetheless, from a consideration of the median energies

for these two distinct groups, a trapping energy of ~ 0.6 eV can be inferred for protons residing near the vacancies. Figure 1b displays the atomistic structure of one of the lower-energy proton defects located very close to one of the intrinsic oxygen vacancies of the host lattice. The defect is actually a hydroxide ion whereby the hydrogen binds to an oxygen atom (O_{NN}) with the formation of a short dative-type bond with a bond length equal to 0.98 Å. The second-nearest-neighbour oxygen ion (O_{2N}) resides at a distance of 1.86 Å from the proton. The structural relaxation pattern shows that the formation of the O-H hydroxyl bond is accompanied by a strong displacement of the O_{NN} ion towards the nearest oxygen vacancy. A consequence of the defect-induced relaxation also entails the breaking of two (out of the four) Zr-O host bonds. This renders the participating O_{NN} ion under-coordinated, with a coordination number of two (see Figure 1b).

Defect association of the inserted protons with the negatively charged acceptor dopants, Y_{Zr} , was also examined. Existing studies of proton incorporation in acceptor-doped perovskites [51] show an attractive proton-dopant interaction that eventually limits proton mobility in these materials. The corresponding energies of all proton configurations versus the proton distance from their nearest yttrium ion are shown in Figure 2b. The final results display higher energies for smaller proton-yttrium distances. Thus, any anticipated electrostatic attraction of the protons with the negatively charged Y_{Zr} defects is not reflected in the energetics. The disordered YSZ structure, owing to the high doping and the presence of vacancies, appears to eliminate any favourable short-range association of the protons with the yttrium ions. Overall, the present results suggest that proton-vacancy association is the dominant factor in cubic YSZ with this yttria content.

Examination of the density of electronic states (DOS) of the bulk and protonated supercells was also performed in order to assess the effects of the proton defect. The DOS calculations were carried out by considering eight k points in the irreducible wedge of the supercell Brillouin zones and Gaussian smearing with a width of 0.1 eV for the electron levels. The DOS plots are displayed in Figure 3. Overall, the bulk DOS agrees well with the experimental measurements by X-ray photoemission spectroscopy performed for YSZ crystals with 9.5 mol% yttria doping [52]. It can be seen that the incorporation of the proton defect does not introduce any defect levels in the fundamental gap of the oxide. Also, protonation does not affect the occupied valence bands. The latter comprise the oxygen-dominated upper valence band, which is mainly composed of O-2p states, and two narrower subbands at deeper (more negative) energies: the O-2s subband and the Y-4p subband. Nonetheless, the proton defect is responsible for the appearance of two localised defect levels in the valence-band region: these are the O-H bonding levels, and they appear at approximately -6.7 eV and at approximately -20.1 eV with respect to the VB edge, inside the VB heteropolar gaps. The former level originates from the 2p-1s O-H bonding, whereas the latter from the 2s-1s O-H bonding.

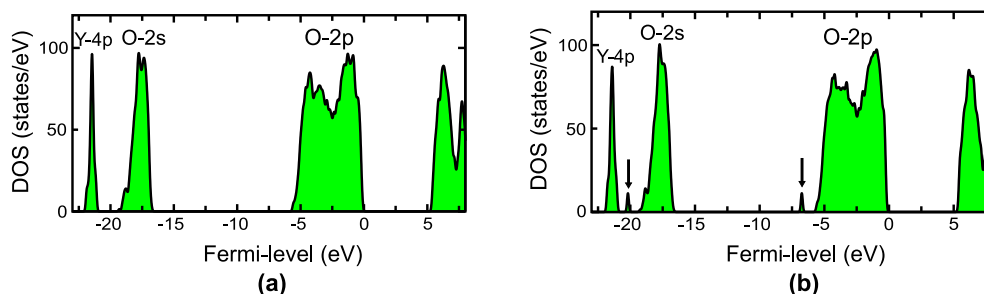


Figure 3. (a) Density of electronic states (DOS) for the bulk YSZ supercell. (b) Density of electronic states (DOS) for the YSZ supercell with the proton. The zero-energy for the Fermi levels corresponds to the valence-band (VB) edge. Negative energies indicate occupied valence bands. The arrows denote the position of the defect-induced levels (see text).

3.2. Migration Pathways and Barriers

The static calculations presented in Section 3.1 allowed us to identify a large number of minimum-energy proton sites. Furthermore, from the calculated energetics, it can be inferred that protons migrating in cubic YSZ will have a longer average residence time within the regions surrounding the oxygen vacancies. Thus, focusing on a specific vacancy, a number of proton sites were taken as the end points (initial and final) of several representative proton pathways. These are schematically shown in Figure 4, which displays, for simplicity, only the oxygen sublattice (with an average O-O distance of 2.59 Å) close to an oxygen vacancy. It can be seen that the proton-site degeneracy around the oxygen ions varies: the O_B ion, for instance, can form three non-equivalent O-H configurations of different orientation with a nearby proton. The pathways encompass both proton-transfer and bond-reorientation modes [53]. In the former, the protons migrate (hop) between neighbouring oxygen ions through a bond-breaking and bond-reforming process. In the latter, the protons stay bound to a single oxygen ion and perform rotational diffusion. The various pathway segments in Figure 4 are designated by their character: *t* for transfer and *r* for reorientation. All pathways are short-ranged, with proton displacements less than 3 Å per single hopping event.

Subsequent PBE calculations led to the migration-energy profiles and barriers for these pathways by NEB optimisation of the sequence of system replicas connecting the initial and final proton sites of the pathways. The final results of the NEB minimum-energy paths and total-energy profiles are shown in Figure 4. The magnitudes of the classical (NEB) barriers are given for each path below the NEB energy curves for both forward (right arrow) and backward (left arrow) motion. The ZPE corrections were subsequently calculated after locating the corresponding saddle points (SPs) along each path. For most of the paths, the SPs were identified as the system replicas that are energy maxima and were found to be associated with at least one imaginary vibrational mode. For all other cases, the SPs were obtained by interpolation between the two higher-energy system replicas bounding the NEB-curve maxima, again verifying the existence of an imaginary frequency. The magnitude of the ZPE-corrected total barriers for the muons (and for protons inside the parentheses) are given for each path above the corresponding NEB curves in Figure 4.

Examining the obtained magnitudes of the migration barriers shown in Figure 4, we can draw the following conclusions: (a) The magnitudes of the barriers cluster within a broad energy range from zero to about 1.2 eV, with pronounced asymmetries in forward versus backward motion for most of the paths. The scatter of the magnitudes and the observed asymmetries are rather substantial, and their origin should be traced to the structural disorder of the YSZ lattice and, also, to the related fact that the equilibrium proton configurations are not iso-energetic. (b) The bond re-orientation migration modes are associated with smaller barriers compared to the proton-transfer modes. (c) As expected, the ZPE corrections for both the proton and the muons tend to decrease the total barriers and are, in most cases, smaller compared to the classical (NEB) barriers. The ZPE corrections also exhibit sizeable variations depending upon the path. For the muon, the obtained ZPE-correction values range from 0.03 eV reaching even up to ~0.40 eV (t_{CD} path). ZPE corrections of similar magnitude were also determined in calculations of muon diffusion in perovskite oxides [54].

Figure 4 also shows two cross-vacancy pathways (t_{cr}) where the protons leave the vacancy region towards the surrounding lattice. These pathways have a longer range (exceeding 3 Å) and are uniquely of the proton-transfer type. Previous calculations [22] showed that these pathways are linked to long-range macroscopic diffusion in YSZ and are associated with large migration barriers (larger than 1 eV).

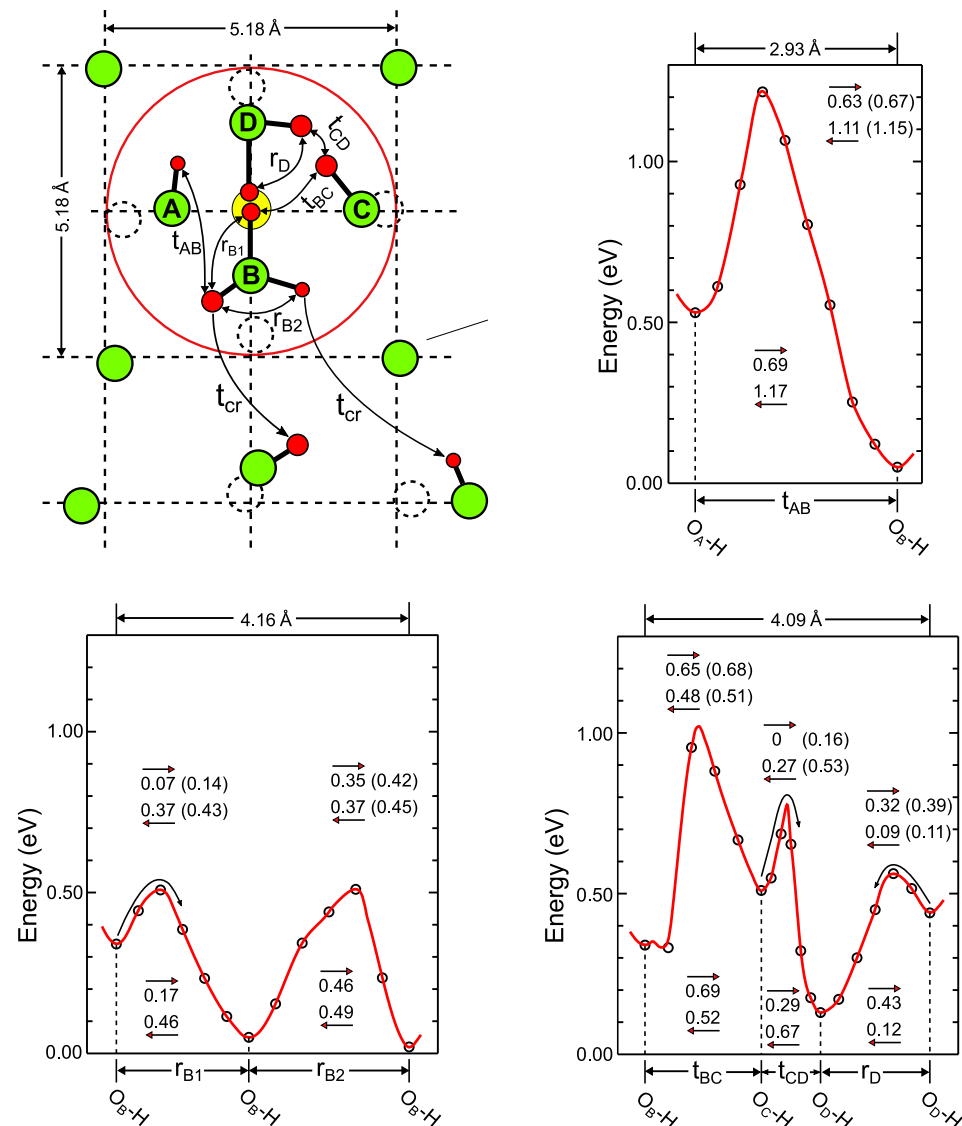


Figure 4. Migration paths of protons (small, filled red circles) in the YSZ lattice within an oxygen-vacancy region, denoted by the arrows connecting initial and final proton sites. The vacancy site is depicted as a yellow circle. The dashed circles denote the initial oxygen-ion positions before the introduction of the protons. Proton-transfer and bond-reorientation modes are designated by t and r , respectively. The energy profiles of proton-migration paths were obtained by NEB-PBE calculations. The NEB energy barriers (in eV) for forward/backward motion (arrows pointing towards the left and right, respectively) are shown below the curves for all migration paths. The total energy barriers (NEB plus the ZPE correction) are depicted above the corresponding curves and provide the values for both the muons and the protons (the latter values inside the parentheses). The curved arrows mark the paths with the lower-energy barriers.

3.3. Muon Spin Spectroscopy Measurements

As discussed in ref. [34], below room temperature, the visible muon-spin polarization signal is composed of at least two distinct contributions that correspond to a donor-like configuration at an oxygen-bound position: a neutral configuration with an electron trapped close to the muon and a positive configuration without the nearby electron. These two contributions imply distinct relaxation of the muon-spin polarization. In ref. [34], the neutral configuration was assigned to a fast-relaxing component with relaxation with an exponential (Lorentzian) shape of about $0.27 \mu\text{s}^{-1}$ at $T = 8.6 \text{ K}$, attributed to unresolved muonium hyperfine lines. The positively charged configuration was assigned to a slowly relaxing

component with a relaxation one order of magnitude lower due to the distribution of nuclear magnetic fields arising from the nuclei with spin (here, essentially from the ^{91}Zr isotope, which has an 11% abundance). Albeit difficult, the separation of these two components is still possible at temperatures below 100 K, but it becomes nearly impossible as room temperature is approached as the value of fast relaxation decreases (with an activation energy determined to be 0.012(1) eV in ref. [34]) and becomes closer to that of slow relaxation. In this work, we focus on the behavior above room temperature, where it is no longer possible to separate these contributions.

Figure 5 shows a representative μSR time spectrum at $T = 300\text{ K}$ in a zero-field configuration (no external magnetic field is applied). As usual, the normalized asymmetry $A(t)$ (in %) in the number of decay positrons detected in the forward direction, N_F , and in the backward direction, N_B , (with respect to the muon beam) is represented as a function of time: $A(t) = (N_F - N_B) / (N_F + N_B)$ [29,30]. Clear decay of the muon-spin asymmetry with time is observed, indicating the presence of one (or more) depolarizing mechanism(s). The signal is composed of at least two distinct contributions that were described above.

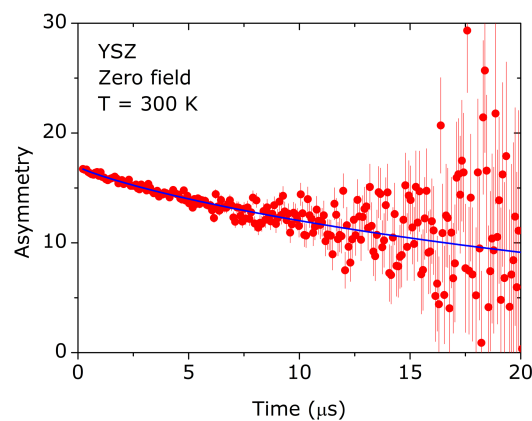


Figure 5. Representative μSR time spectrum in the zero-field configuration (where no external magnetic field is applied) at $T = 300\text{ K}$. The line is fit with a stretched exponential function (see text).

In order to obtain a coherent description at all temperatures, we have chosen to describe the time spectra by a single component with stretched exponential relaxation, which is adequate to describe situations where a distribution of relaxing components are present [55]. The time spectra at all temperatures were, therefore, fitted with the following phenomenological expression:

$$A(t) = A_0 \exp[-(\lambda t)^\beta] \quad (5)$$

where A_0 is the initial asymmetry, λ is the *effective* relaxation parameter and β is the stretched-relaxation parameter that describes the *effective shape* of the relaxation ($\beta = 1$ for purely exponential behavior and $\beta = 2$ for purely Gaussian behavior). As mentioned above, this description is not expected to provide a complete description of the data at low temperatures, but it is particularly adequate for describing the temperature dependence above room temperature. In Figure 6a, we present the temperature dependence of the relevant relaxation parameter, λ , and in Figure 6b, we present the corresponding temperature dependence of the β parameter. The initial asymmetry is reasonably constant with temperature and is consistent with the previous results in ref. [34]. The β parameter is also observed to be centred around the expected $\beta = 1$, although it has a large variation that is associated with the change of the *effective shape* of the relaxation. We attribute no further special significance to this and will not discuss it further.

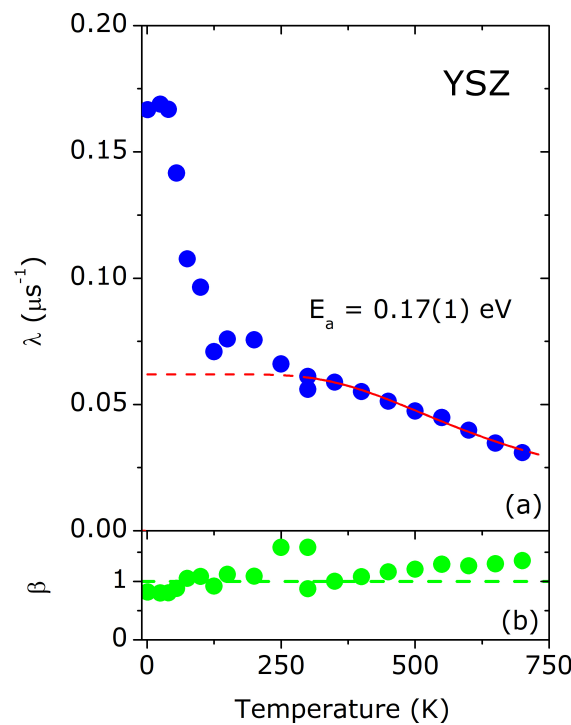


Figure 6. Temperature dependence of the (a) relaxation λ and (b) β parameters of the stretched exponential function used to fit the time spectra. The red line in (a) is a fit with a Boltzmann-like function to the high-temperature ($T \geq 300$ K) data, as discussed in the text. The red dashed line is the extrapolation of the fitted curve to low temperatures. The green dashed line in (b) corresponds to the $\beta = 1$ value associated with the pure exponential shape.

The most relevant information in Figure 6 is, therefore, the temperature dependence of the *effective* relaxation parameter in Figure 6a. Below room temperature, this effective relaxation is observed to decrease from about $\lambda = 0.17 \mu\text{s}^{-1}$ at $T = 8.6$ K to about $\lambda = 0.06 \mu\text{s}^{-1}$ at $T = 300$ K. This corresponds to the low-temperature dynamics described in ref. [34], which are associated with an activation energy $0.012(1)$ eV. Our data are consistent with the more detailed picture obtained in this earlier work.

However, above room temperature, this first process is over, and a second step is now observed in the *effective* relaxation, which is observed to decrease significantly up to $\lambda = 0.03 \mu\text{s}^{-1}$ at $T = 700$ K. We describe this temperature dependence with a Boltzmann-like function:

$$\lambda(T) = \frac{\lambda_0}{1 + N \exp(-E_a/k_B T)} \quad (6)$$

where $\lambda_0 = 0.062(1) \mu\text{s}^{-1}$ is the value of the relaxation at the lowest temperature (here, around $T = 300$ K), k_B is the Boltzmann constant, $N = 16(4)$ is a parameter associated with the shape of the binding potential, and $E_a = 0.17(1)$ eV is the activation energy of the process. The fitted curve is shown in Figure 6a together with the obtained fitted value for the activation energy.

We recall that in ref. [34], the $0.012(1)$ eV process observed below 100 K was considered to be likely arising, essentially, from the binding energy of the electron to the muon in the neutral configuration, although muon motion between equivalent hydrogen/muon sites could not be excluded. The present calculations seem to support this interpretation since hydrogen/muon motion seems to require energies higher than 12 meV.

The new process observed above room temperature most likely arises from a motional narrowing effect, as the distribution of nuclear magnetic fields at the muon site are averaged out due to muon motion, either short-range or long-range. The observed activation energy

of 0.17(1) eV can be compared with the DFT calculations, which are compiled in Figure 7. It can be inferred that the experimental activation energy is consistent with the lower energies obtained for the muon barriers, upon considering zero-point effects, and supports either reorientation motion from a muon/proton bound to an oxygen (paths r_{B1} and r_D) or transfer between neighbouring oxygens (path t_{CD}). It is also noteworthy that the experimental value agrees very well with obtained DFT barriers (equal to 0.14 eV and 0.15 eV) reported for a pair of proton-transfer paths at the core of an YSZ grain boundary (GB) [22]. This finding suggests that the measured activation energy from the μ SR data may also originate from muon diffusion within these internal interfaces of the nanocrystalline samples.

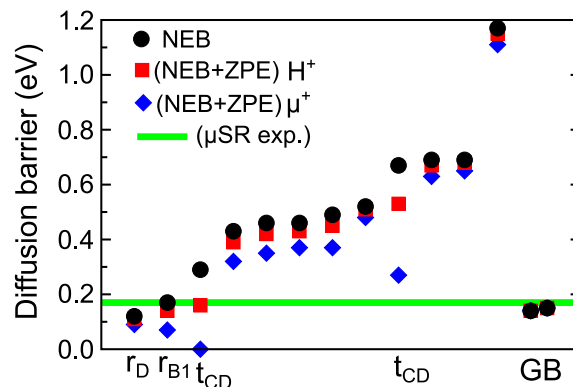


Figure 7. Compilation of the DFT-based diffusion barriers for all proton paths shown in Figure 4, together with a pair of barriers obtained in ref. [22] for proton migration at the core of an YSZ grain boundary (GB). The displayed barriers comprise the NEB results, as well as the total barriers after applying the ZPE corrections, for both muons (μ^+) and protons (H^+). The experimental value obtained by the μ SR analysis is depicted by the horizontal (green) line.

It is noteworthy to mention that existing analyses and interpretations of experimental data propose that proton conduction in nanocrystalline and porous YSZ is interfacially controlled and takes place either by proton hopping or vehicular transport (via more complex ions) confined to the hydrated internal surfaces and pore walls of these materials [10–12]. The present findings do not necessarily contradict these interpretations. Rather, they focus instead on the character of proton conduction that originates from the bulk-like regions of the internal microstructure of YSZ materials.

4. Summary

The local binding and diffusion behavior of the proton defect in cubic YSZ was studied by a combination of first-principles DFT calculations and muon-spin spectroscopy measurements. The calculations showed that proton defects preferably reside near the intrinsic oxygen vacancies of the YSZ host lattice, with no evident association with the yttrium defects. For a detailed network of paths, the obtained NEB results supplemented with zero-point energy corrections displayed a sizeable variation of barriers owing to the disordered lattice. Comparison of the migration calculations with the activation energy of diffusion derived from the μ SR data suggests that protons migrate by a combination of low-energy barrier bond-reorientation and proton-transfer modes confined either within the vacancy regions of the bulk YSZ lattice or at the core of grain boundaries.

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