FIRST-PRINCIPLES STUDY OF INTERSTITIAL HYDROGEN IN YTTRIA-STABILIZED ZIRCONIA (YSZ)

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INTRODUCTION

- Hydrogen is a common impurity in materials (semiconductors, oxides, microelectronics devices) sometimes intentionally introduced.

  Passivation of defect and trapping centers (e.g. Si DB's at Si/SiO_2 interface)

- Experimentally it is difficult to obtain a clear signature of isolated hydrogen (mobile/low migration barrier, forms defect associates, e.g. complexing with dopants in Si.)

- Reliability issues in microelectronics, degradation of electrical properties of MOSFETs (under irradiation and electrical stress): increase of interface traps

- A lot about what we know for hydrogen in solids comes from calculations based on density-functional theory (DFT), e.g. defect reactions with participating H

  Electronic behavior of H: source of n-type conductivity

  amphoteric impurity

  Charge-transition levels E(+/0) (donor level) and E(+/-) wrt CBM

  (Van de Walle and Neugebauer 2003, Kiliç and Zunger 2002, J. Robertson's group)

Muonium spectroscopy

$Mu^+ – e^-$: pseudoisotope of hydrogen ($m_\mu \sim \frac{1}{9} m_p$)
Lifetime: 2.2 μsec

Cubic polycrystalline YSZ (9.5 mol% Y_2O_3) (Cox et al., JPCM 2006)

Low T : atomic muonium co-exists with shallow-donor states

(Atomic : high isotropic hyperfine constant, within 20% of free-atom value)

At and above RT: conversion of paramagnetic to diamagnetic fraction(s)

$Mu^0 \rightarrow Mu^-$ Hole ionization: $Mu^0 \rightarrow Mu^- + h$

$Mu^0 \rightarrow Mu^+$ Donor ionization plus site change
(thermal conversion to positive ion)

Density-functional theory GGA-PBE functional for exchange-correlation

VASP code (Vienna Ab-initio Simulation Package) (Kresse, Hafner and Furthmüller, 1993-96)

Projector-augmented-wave method (PAW) / E_{pw} = 470 eV 4**k** points in the IBZ

Semi-core 4s and 4p states as valence for both Zr and Y

Hybrid-functional approach (Heyd, Scuceria, Ernzerhof 2006)

Admix an amount of exact non-local HF exchange to the PBE exchange

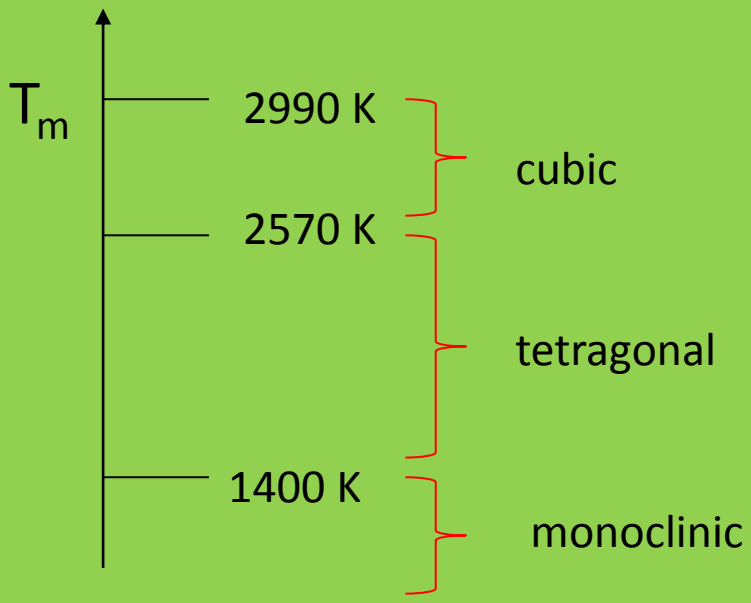
$$E_{xc}^{HSE\,06} = \frac{1}{4}E_{x}^{HF,SR,\mu} + \frac{3}{4}E_{x}^{PBE,SR,\mu} + E_{x}^{PBE,LR,\mu} + E_{c}^{PBE}$$

(μ : spatial decay of HF exchange)

GOALS

- Different minimum-energy configurations of hydrogen in the lattice for a given charge state (H^0, H^+, H^-) .
- Formation energies and charge-transition levels, E(q/q´), in the gap.
- Stability analysis of neutral H^0 in the lattice : site changes of H^0, migration paths, find MEPs, TSTs and corresponding barriers through Nudged-Elastic-Band (NEB) method (DFT-PBE).

Zirconia is an important ceramic commonly used as electrolyte in solid oxide fuel cell (SOFC) technology. High electrical conductivity via oxygen vacancies.



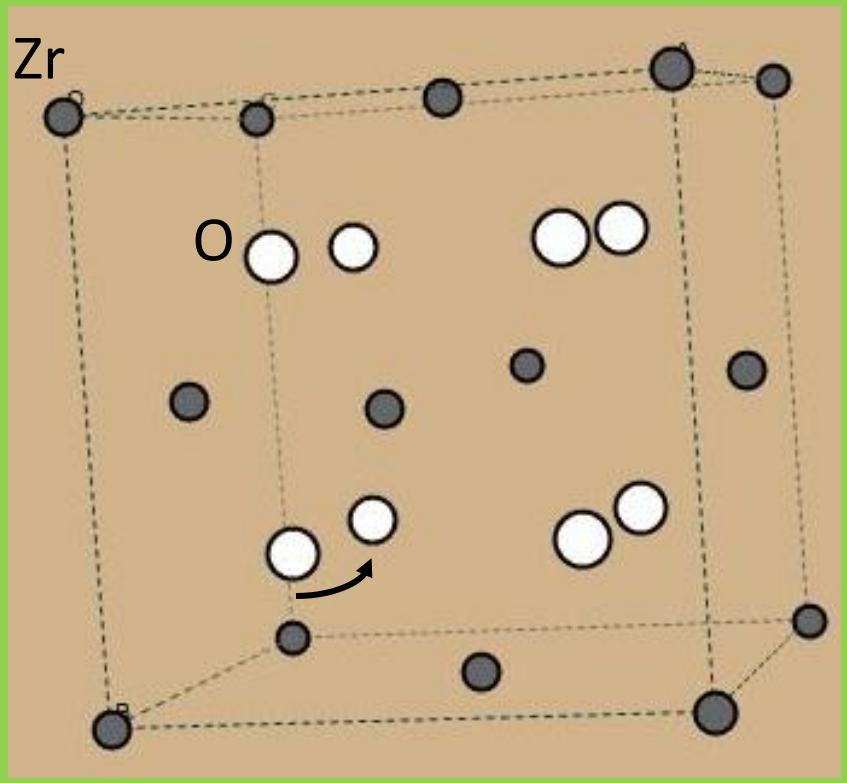
Cubic phase stabilized at lower T by doping with M_2O_3 or MO oxides

Oxygen vacancies compensate the charge of the substitutional defects

IDEAL UN-DOPED CUBIC FLUORITE ZrO_2

$Zr \longrightarrow FCC$

$O \longrightarrow T_h$



Cubic YSZ : ≥ 8 mol % Y_2O_3

Cubic YSZ cell ($2\ a_{latt}$ x $2\ a_{latt}$)

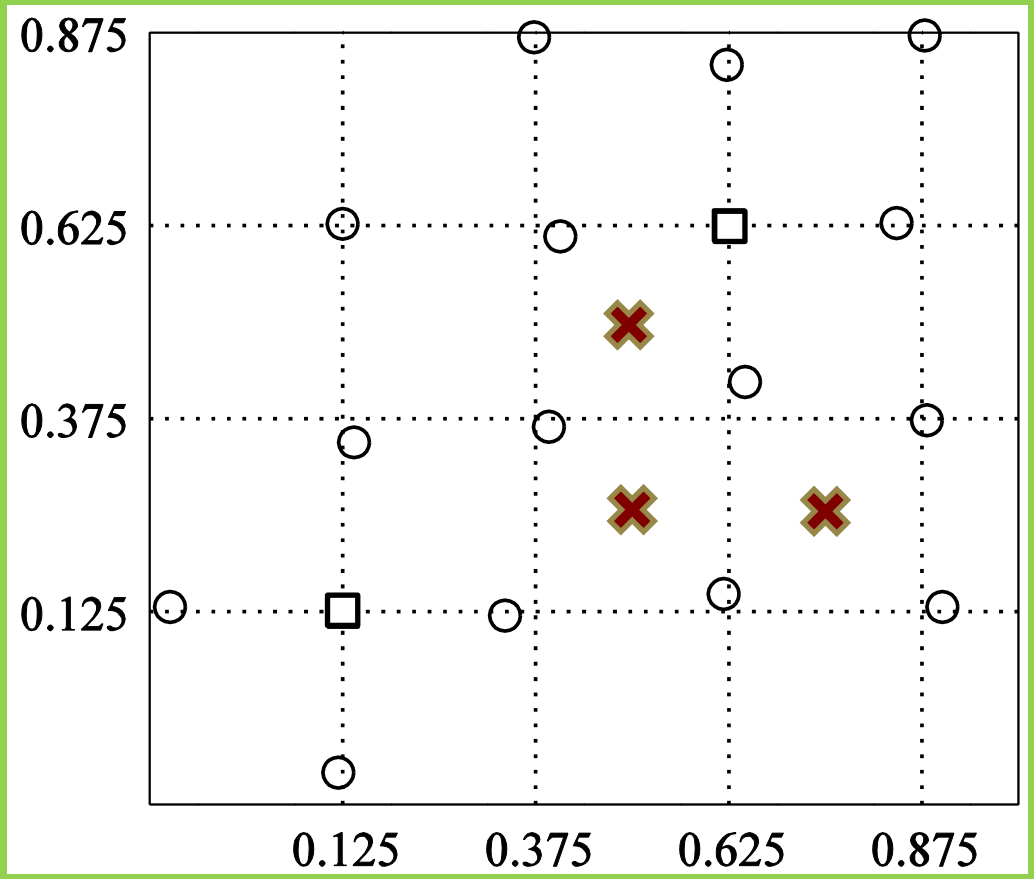
10.3 mol% Y_2O_3

Corners: ideal O sites in fluorite lattice

□ Oxygen vacancies

(at least 5th nn)

Oxygen sublattice



✖ Y

O_{NN}'s predominantly displace along [001] directions

V_O – O_{NN} attraction

$\Delta s(O_{NN})$: 0.22 – 0.56 Å

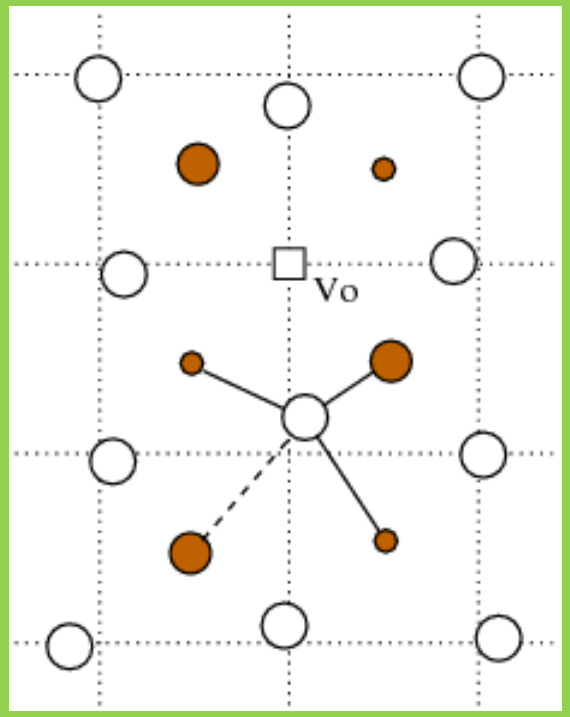
$\Delta s(O_{NNN})$: 0.12 – 0.30 Å

$\Delta s(Zr_{NN})$: 0.13 – 0.25 Å

$\Delta s(Zr_{NNN})$: 0.02 – 0.17 Å

Bulk crystal YSZ (10.3 mol%)

□ : Oxygen vacancies (Vo)



O

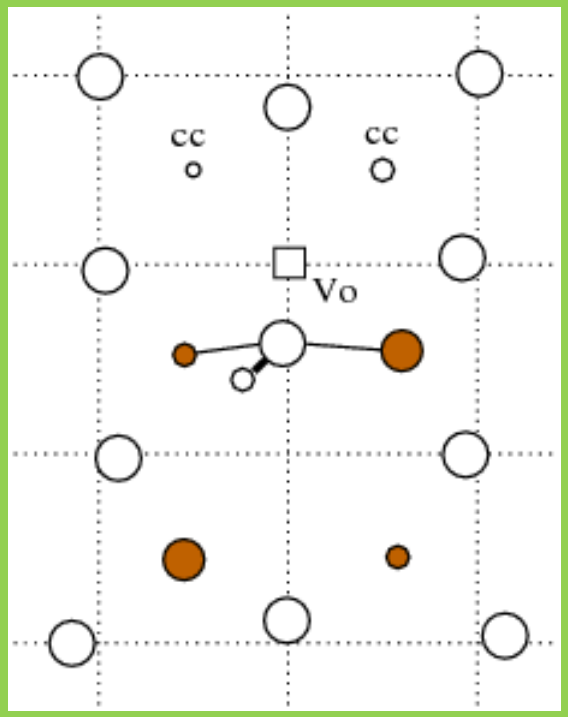
Zr

Largest distortions near oxygen vacancies

O ions attracted to NN vacancies

CN_O becomes 3 near Vo's

Minimum-energy hydrogen configurations



H

OH- bond-type configurations
O-H: 0.98Å (large lattice relaxation)

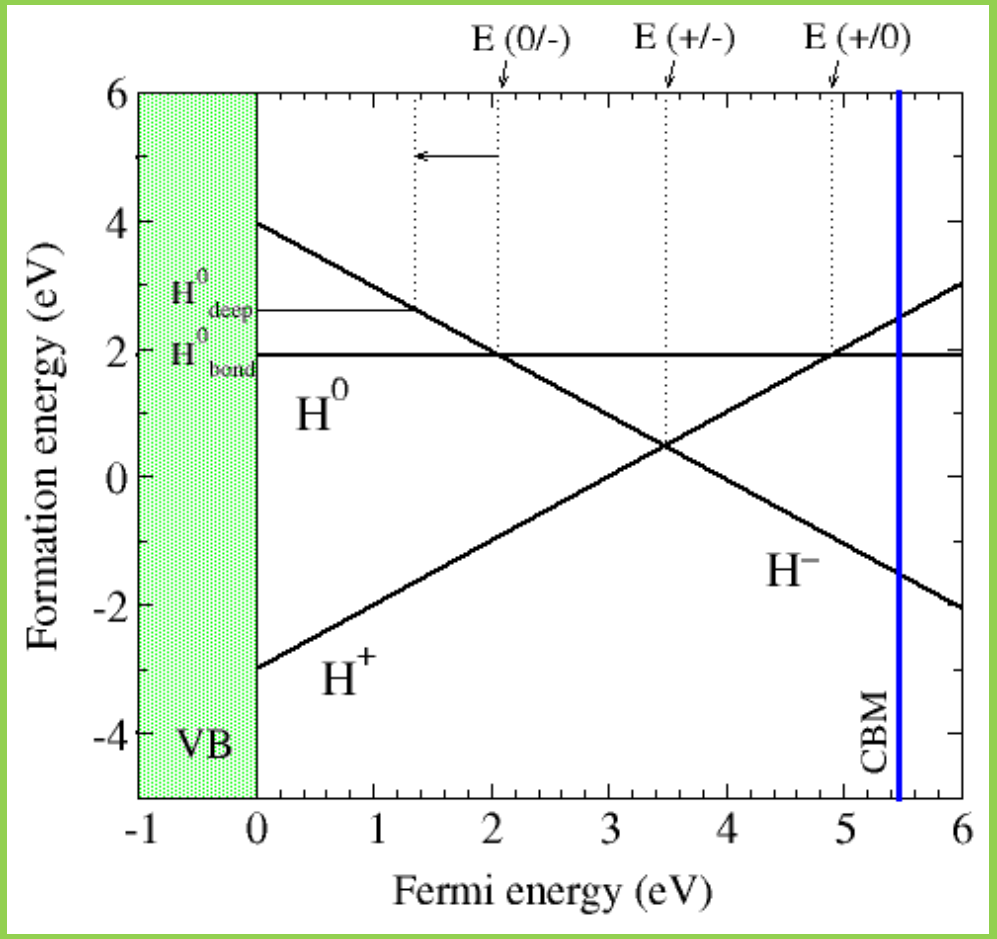
} All H charge states

CN_O : 2 + 1 (Zr–O : 2.10 – 2.30 Å)

H at deep interstitial sites
(minimal relaxation) : cc, Vo

} H^0 and H^-

Formation energies and charge-transition levels E(q/q´)



Amphoteric behavior for H

Transition level E(+/-) deep in the gap: E_{VBM} + 3.50 eV

Hydrogen not source of n-type conductivity

Deep acceptor and donor levels

Not consistent with shallow-donor behavior observed by muSR (inferred muonium ionization energies E_D ~ 10 - 30 meV)

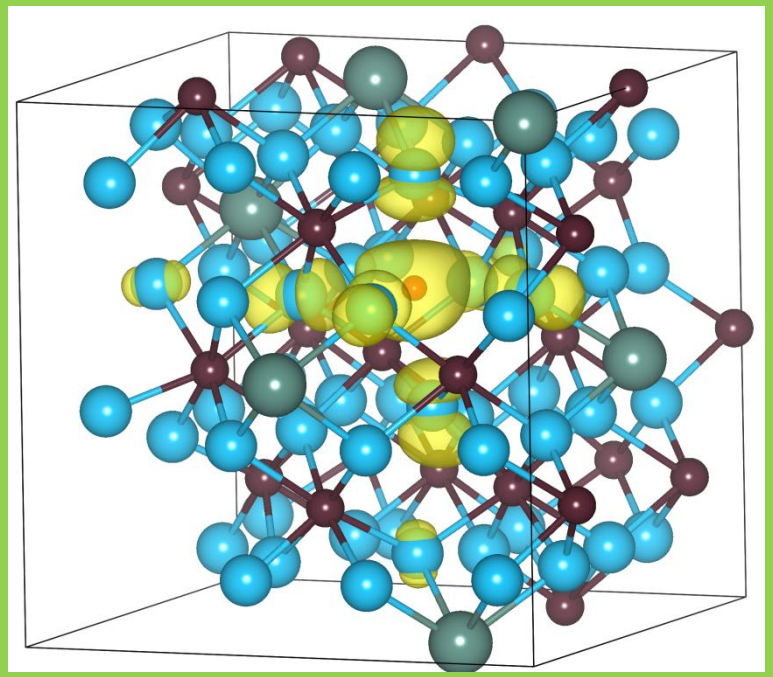
Delocalized solution unstable

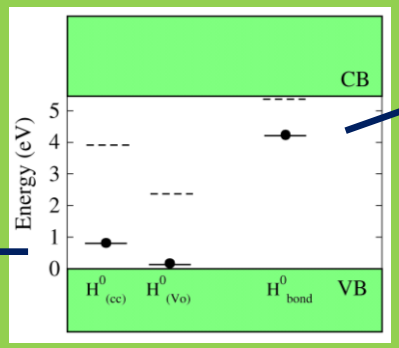
$$E_{form}^{(q)} = E_{tot}^{(q)} - E_{tot}^{bulk} - \mu_H + q(E_F + E_{VBM})$$

Nature of defect levels of neutral H^0 configurations

Deep interstitial H^0 configurations

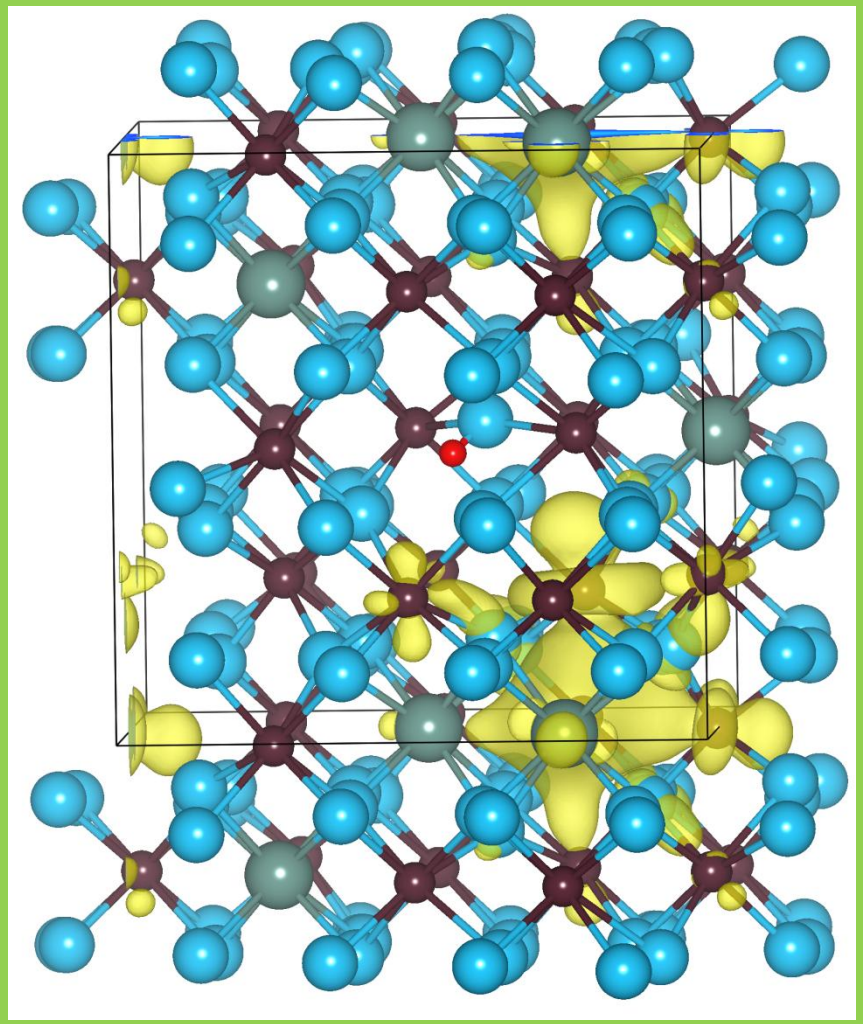
Higher energy





E_{CBM}
- 1.2 eV

Bond-type configurations

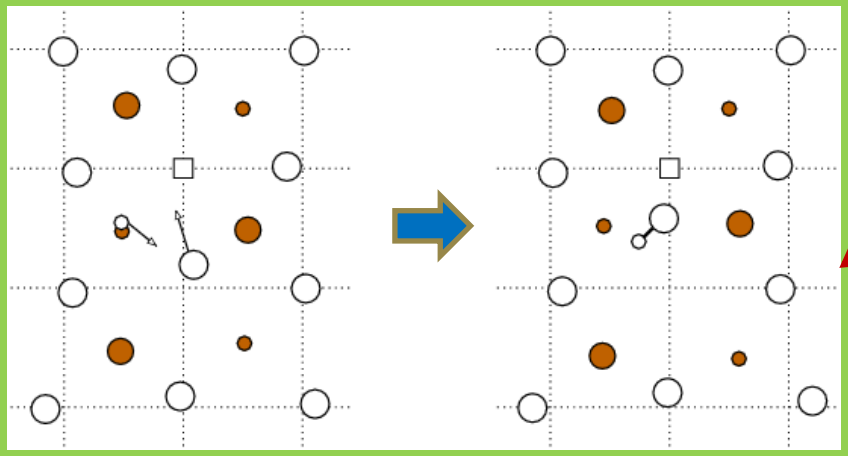


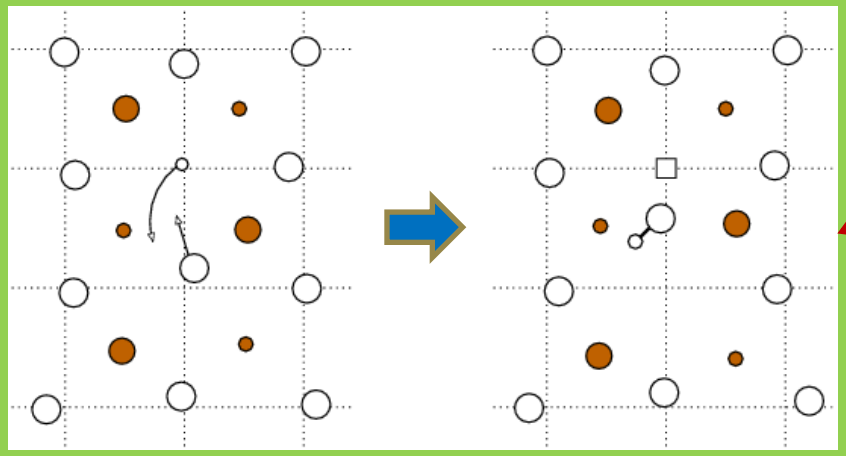
Excess e^- on neighboring Zr ions and empty cube centers of O subllatice

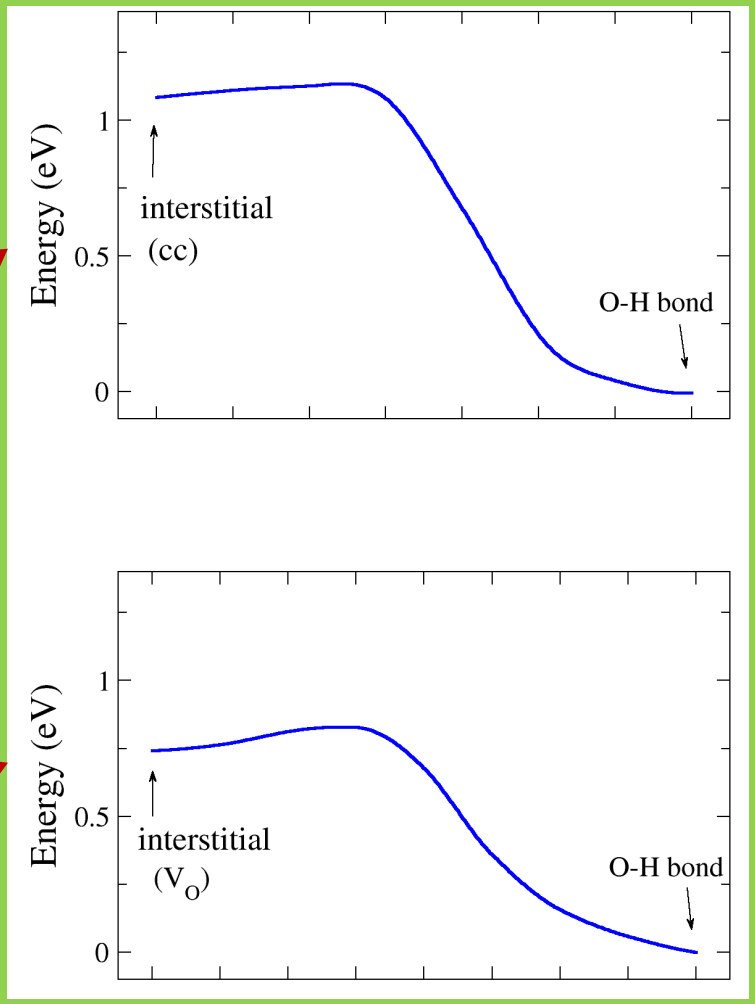
Neutral H^0 : interstitial – to – bond site changes

Local transformation between two nearby configurations: requires simultaneous displacements of H^0 and O's of the host

Energy for minimum-energy paths (MEPs) (NEB method)



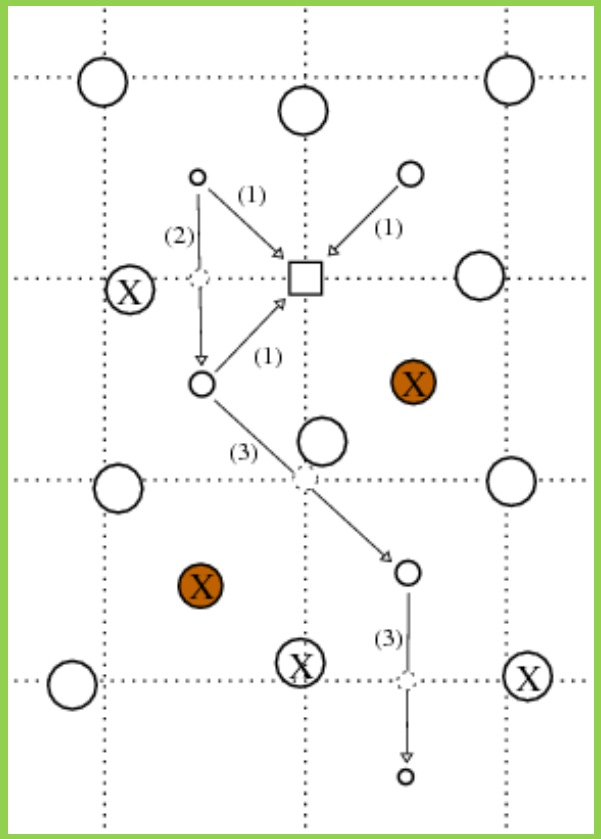




REACTION COORDINATE

Explore the global character of the migration behavior of H^0

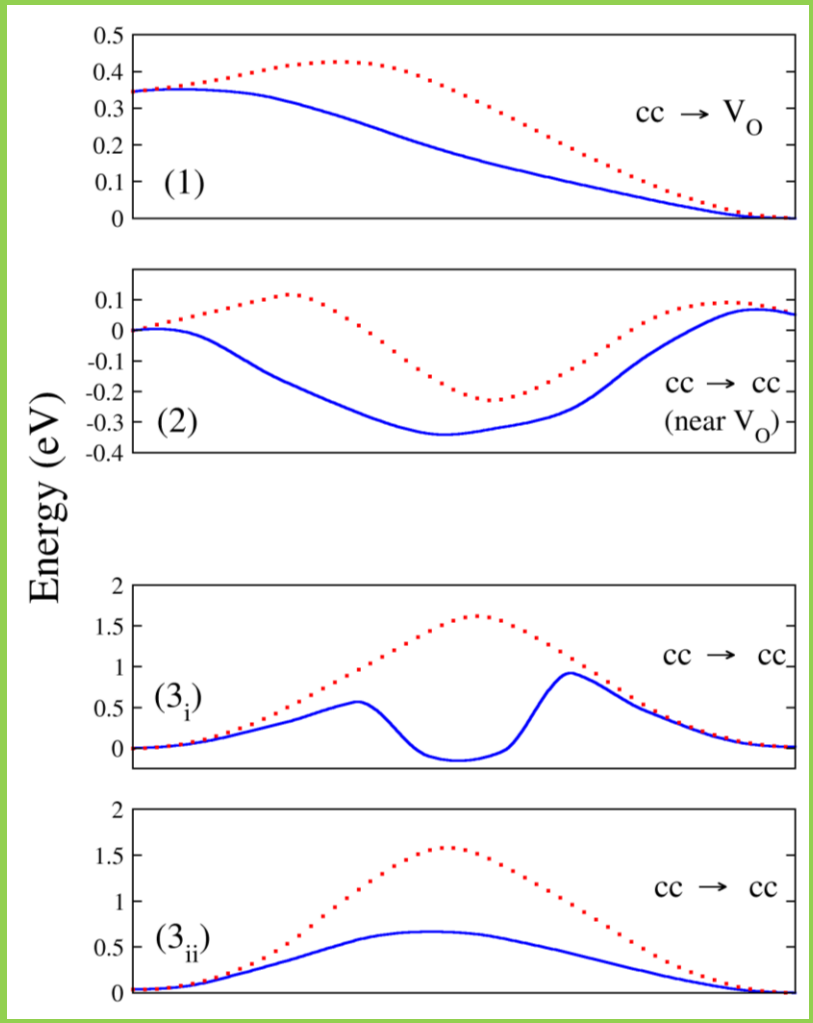
Migration paths connecting interstitial sites in the lattice



MEPs and barriers

rigid-lattice condition

full relaxation



at / near Vo's

Away from Vo's

SUMMARY

- H incorporates in cYSZ (10.3 mol%) in two distinct configurations

  Interstitial configurations H_{int} (cc and Vo sites) (acceptor sites)

  Bond-type configurations H_{bond} (donor sites)

- Amphoteric behavior of hydrogen : E(+/-) level deep in the gap

  Donor level of H^0: deep in the gap centered on neighboring Zr atoms

- NEB calculations of MEPs and barriers for neutral H:

  Transformation of interstitial to bond configuration: $H_{int} \rightarrow H_{bond}$

  Small barrier but requires rearrangement of host lattice (attain equilibrium)

- Vo's play important role in migration behavior of neutral H

  Reduce barriers in their vicinity : facilitate instability towards H_{bond}

  Away from Vo's : higher E_{act} are needed for H_{int} to migrate