FIRST-PRINCIPLES COMPUTATIONAL AND NEUTRON SCATTERING STUDY OF PROTONIC CONDUCTORS

Fuel cells, which produce electricity via hydrogen oxidation to water, have emerged in the last decade as one of the key technologies for meeting the world's energy needs well into the 21st century. Solid-oxide fuel cells (SOFCs) are the most promising among the many different types of fuel cells being developed. However, the required high operating temperature of an SOFC places stringent requirements on its component materials. Potential candidates to replace the oxygen-conducting electrolyte used in current SOFCs include the perovskite-based high-temperature protonic conductors (HTPCs), since switching from anionic to protonic conduction can lower the practical operating temperature from 1300 K to around 1000 K.

We undertook neutron vibrational spectroscopy (NVS) measurements of various HTPCs (namely, $SrCeO_3$ and $SrZrO_3$ aliovalently doped with different rare earth cations) in order to probe the bonding potentials experienced by the residual protons incorporated as OH$^-$ species via steaming. At high temperatures, these protons migrate from site to site, giving rise to protonic conduction. The NVS measurements revealed the existence of dopant-related perturbations to the bending-mode energies of OH$^-$ in $SrCe_{0.95}M_{0.05}H_xO_{3-\delta}$ (M = Sc, Ho, and Nd), confirming the trapping effects of the

dopants. The bending-mode energy could be correlated with the size of the dopant cation, generally increasing for smaller cations. NVS measurements of $SrZr_{0.95}M_{0.05}H_xO_{3-\delta}$ (M = Sc, Y, and Nd) indicated differences in the OH$^-$ bending-mode energies between the cerates and zirconates. These differences reflect changes in the lattice potential experienced by the protons, which ultimately effects the proton jump rates and therefore the performance of these materials for use in fuel cells.

An understanding of the dynamics of the undoped perovskites is the first step towards a comprehensive picture of the protonated doped materials. To explore this in more detail, we performed *ab initio* total-energy calculations using the CAmbridge Serial Total Energy Package (CASTEP). We calculated the Q = 0 phonons in the primitive unit cell (i.e., $Zr_4Sr_4O_{12}$) of undoped strontium zirconate and compared with the experimental density of states (DOS) at room temperature, as shown in Fig. 1. While at low energies, the calculated modes are almost at the same energies as observed modes, at high energies, we overestimate the energies of the modes by about 10 %. However there is still a one-to-one correspondence between the main experimental and calculated spectral
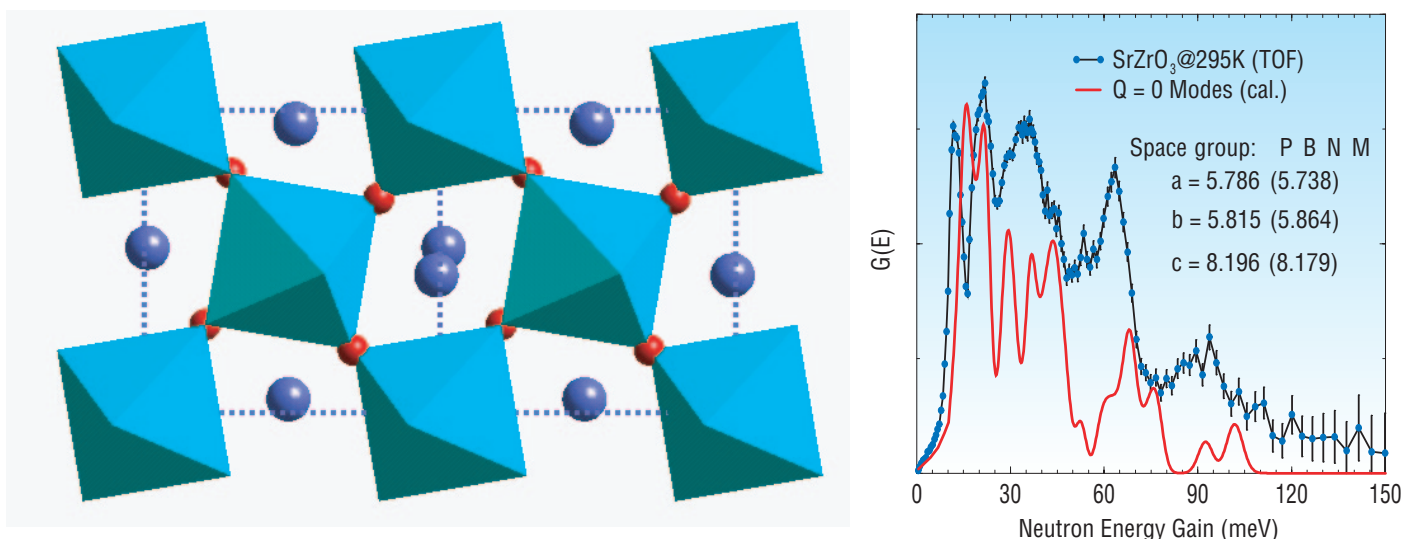

FIGURE 1. LEFT: A view of the structure of undoped SrZrO$_3$ in the [001] direction. RIGHT: Vibrational spectra for SrZrO$_3$ measured by neutron time-of-flight spectroscopy. The space group and the lattice parameters (in Å) are also shown. Numbers in parentheses are the theoretical values. The lower solid line is the DOS of the Q = 0 phonons calculated from first principles.

T. Yildirim, T. J. Udovic, C. Karmonik, and
D. A. Neumann
NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, MD 20899-8562

features, allowing us to identify the modes observed by our NVS measurements.

In order to model the dynamics of protons trapped in Sc-doped $SrZrO_3$, we replaced one of the Zr atoms in the $\sqrt{2} \times \sqrt{2} \times 1$ supercell by (Sc + H), which yields a cell formula $Sr_8Zr_7ScHO_{24}$ (See Fig. 2). We performed calculations for protons at either the "undoped" (U) or "doped" (D) sites. Even though the MO_6 octahedra are quite rigid, the distortions due to the presence of the proton at these sites are quite large.

These distortions are also reflected by the vibrational spectrum of the proton. The two tangential OH- bending modes depend strongly on the proton siting. At the Sc site, the lowest tangential mode is found at 122.9 meV. However at the Zr site, the mode is much softer at 88.5 meV. Interestingly, we observe new features in our NVS spectra at these energies upon proton addition. To further investigate this effect, we performed "embedded cluster" calculations in which the vibrational spectrum of the $H-MO_6$ cluster is calculated while all other atoms are kept at their equilibrium positions. The similarity between experiment and the calculated spectrum from $H-ZrO_6 + H-ScO_6$ clusters suggests that the mode observed near 120 meV is due to protons trapped at the Sc sites

while some portion of the peak near 80 meV is due to protons at the undoped sites. Thus NVS can be used to determine the hydrogen occupancy of the various sites.

For a better understanding of the protonic conduction in these materials, we calculated the total energy of the system as the proton migrates from Zr to Sc sites. We found that the doped site has a much lower energy (-1.13 eV) than the undoped site. The two sites are separated by an energy barrier of 1.5 eV. Hence, we expect that most of the protons are trapped at the dopant site. This is primarily because the proton prefers to be closer to the Sc cation, which has a charge of +3 compared to +4 for Zr. Yet, one also has to consider steric effects; i.e., if the dopant cation has a larger radius, then the proton may prefer to occupy the Zr site, despite the larger Coulomb interaction. Thus these calculations indicate that the protonic transport is sensitive to the competition between short-range repulsive and Coulomb interactions, and suggest that the use of a large dopant cation is one important step in developing a HTPC with increased protonic conductivity. We are currently testing the usefulness of the calculated proton potentials for predicting the protonic diffusional motions observed experimentally via quasielastic scattering measurements.
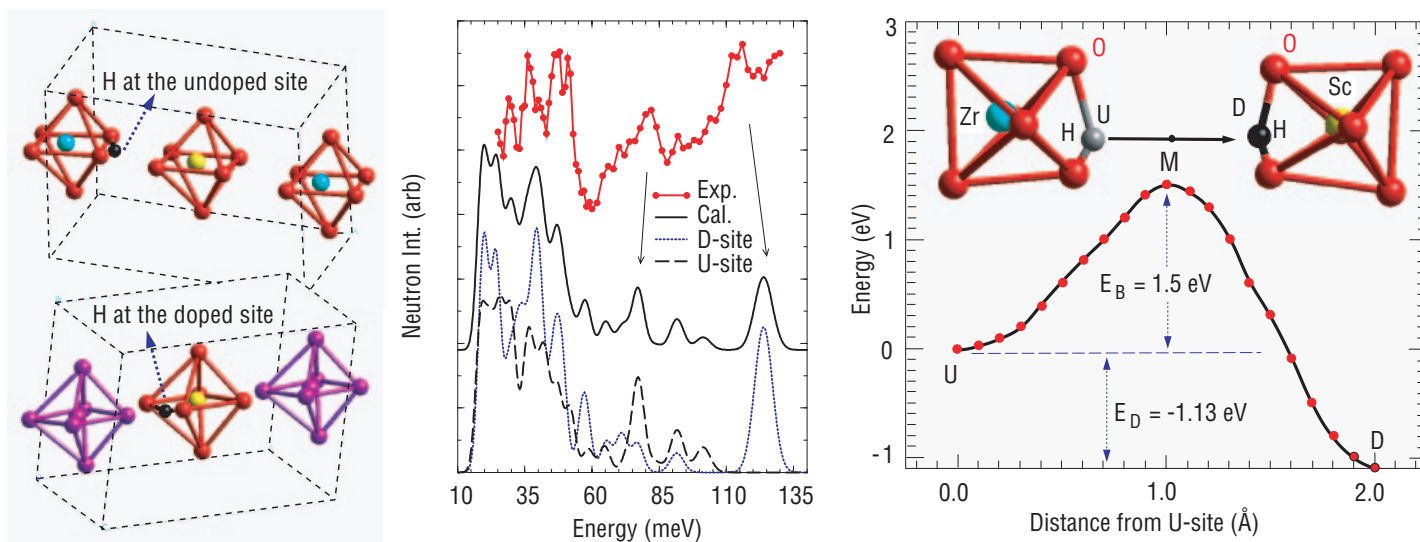

FIGURE 2. LEFT: Optimized structures when the proton is trapped at the undoped site (top) and at the doped site (bottom). **MIDDLE:** Comparison of the neutron vibrational spectrum of $SrCe_{1-x}Sc_xH_xO_3$ (top) and $SrZr_{1-x}Sc_xH_xO_3$ (calculated). Dashed and dotted lines shown at the bottom are the contributions from the $H-MO_6$ clusters, where M = Zr (undoped site) and Sc (doped site), respectively. **RIGHT:** Potential energy of the crystal as the proton migrates from the undoped site (U) to the doped site (D).