Supplementary Information.

Hydrogen multicenter bonds

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In Figure 5 we show the density of states (DOS) projected on H and the four nearest-neighbour zinc atoms for the hydrogen substituting an oxygen atom in ZnO. All four zinc atoms contribute to the hydrogen multicenter bond, showing a peak at 6.9 eV below the top of the valence band. In Figure 6 we show charge-density contour plots of the hydrogen multicenter bonds in ZnO and MgO on $(11\bar{2}0)$ and (001) planes, respectively. We note the weak covalent nature of the H-Zn bonds in Figure 6a, and the significant contribution from the next-nearest-neighbour oxygen atoms to the hydrogen multicenter bond in MgO shown in Figure 6b. In Figures 7 and 8 we show the electronic charge density distribution of the lowest-energy unoccupied states related to the hydrogen multicenter bond in ZnO and MgO. These states are about 2 eV and 1 eV above the conduction-band minimum, respectively. Note that the hydrogen site corresponds to a *node* in the wave functions of both nonbonding and antibonding states.

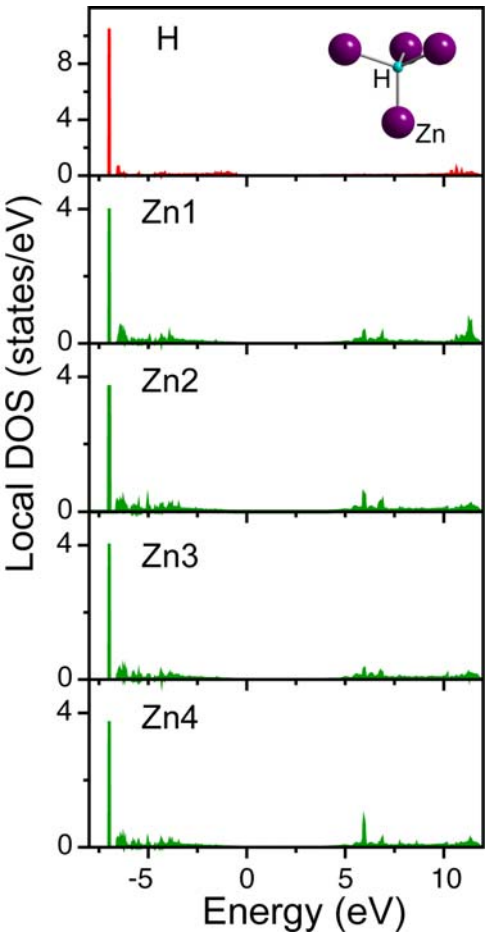

Figure 5 Projected (local) DOS on hydrogen and its four nearest-neighbour zinc atoms in ZnO. In the inset we show the local atomic geometry of hydrogen in the multicenter bond configuration. We can see the equal contribution of the four zinc atoms to the hydrogen multicenter bonding state at -6.9 eV. The zero in energy corresponds to the top of the valence band. We also note small peaks in the local DOS on zinc atoms located in the conduction band. These peaks correspond to antibonding or nonbonding unoccupied states related to the hydrogen multicenter bond, and strongly mix with the host conduction-band states.

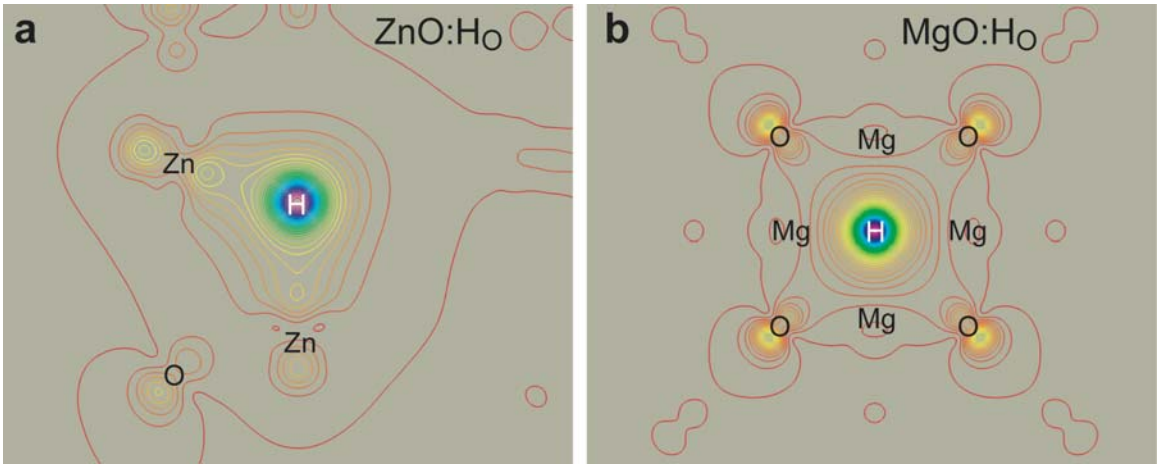

Figure 6 Contour plots of the electronic charge density of the lowest-energy hydrogen multicenter bond in (**a**) ZnO and (**b**) MgO. In the case of ZnO, we show the contour plot on the $(11\bar{2}0)$ plane passing through hydrogen and two nearest-neighbour zinc atoms, and the difference between the isolines is 0.015 electrons/Å^3. In the case of MgO, we show the contour plot on the (001) plane passing through hydrogen, four nearest-neighbour magnesium atoms, and four next-nearest-neighbour oxygen atoms. The difference between the isolines is 0.010 electrons/Å^3.

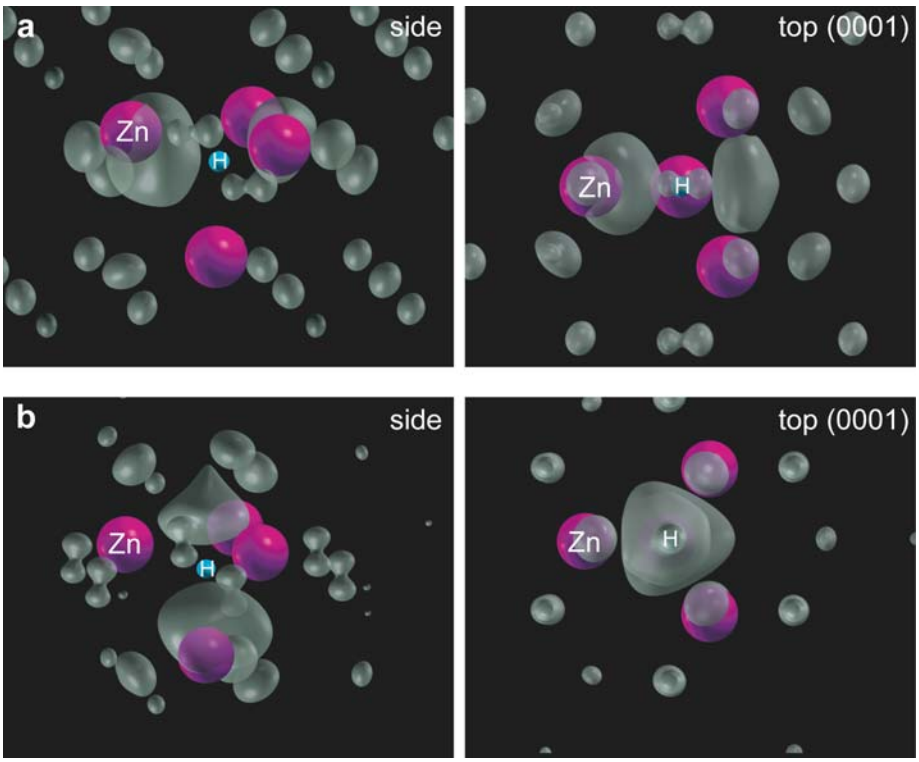

Figure 7 Electronic charge density distribution of the lowest-energy unoccupied states related to the hydrogen multicenter bond in ZnO. These states are at 2.1 eV (top) and 2.3 eV (bottom) above the conduction-band minimum. We note the nodes on hydrogen site, characteristic of antibonding or nonbonding states. The isosurfaces correspond to 0.02 electrons/Å^3. We also note a significant mixing with the host conduction-band states.

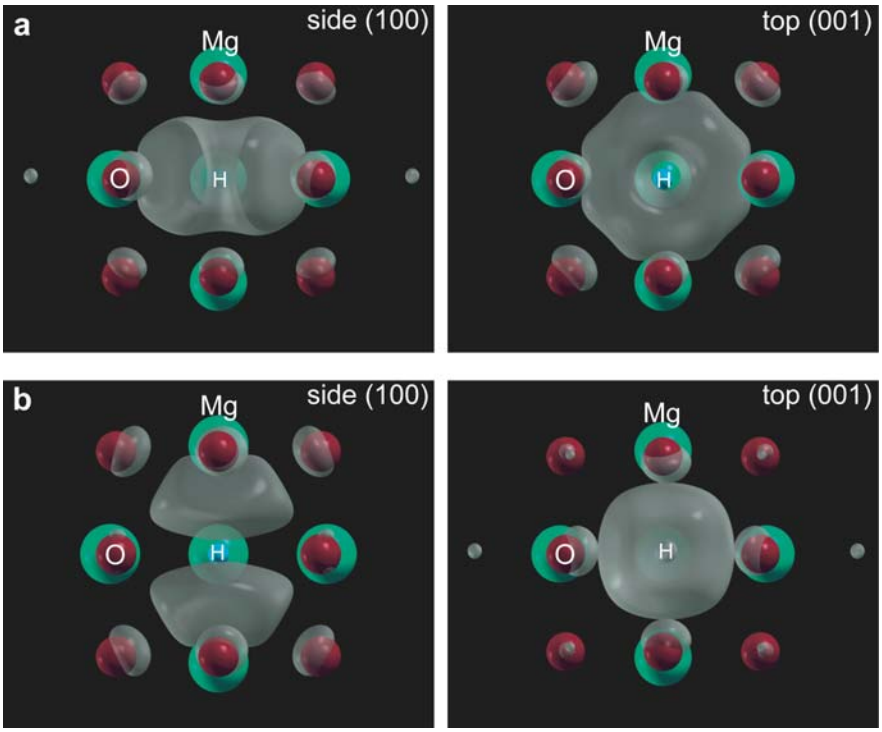

Figure 8 Electronic charge density distribution of the lowest-energy unoccupied states related to the hydrogen multicenter bond in MgO. Three degenerate states occur at 1.1 eV above the conduction-band minimum. The charge densities at the top correspond to two states with a “doughnut”-like shape in the (001) plane. The charge densities at the bottom represent the third state with charge density distributed along the [001] direction. The isosurfaces correspond to 0.02 electrons/Å^3. The three states exhibit nodes on the hydrogen site, characteristic of nonbonding states.