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Two-Dimensional Polaronic Behavior in the Binary Oxides $m\text{-HfO}_2$ and $m\text{-ZrO}_2$

Keith P. McKenna,^{1,2,*} Matthew J. Wolf,³ Alexander L. Shluger,^{2,3} Stephan Lany,⁴ and Alex Zunger^{4,†}

¹*Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom.*

²*WPI-AIMR, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan.*

³*Department of Physics and Astronomy, University College London,
Gower Street, London, WC1E 6BT, United Kingdom.*

⁴*National Renewable Energy Laboratory, Golden, Colorado 80401, USA.*

We demonstrate that the three-dimensional (3D) binary monoclinic oxides, HfO_2 and ZrO_2 exhibit quasi-2D polaron localization and conductivity, which results from a small difference in the coordination of two oxygen sub-lattices in these materials. The transition between a 2D large polaron into a zero-dimensional small polaron state requires overcoming a small energetic barrier. These results demonstrate how a small asymmetry in the lattice structure can determine the qualitative character of polaron localization and significantly broaden the realm of quasi-2D polaron systems.

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Quasi-two-dimensional (2D) systems, including surfaces, heterointerfaces and layered materials, have become a rich playground for discovering exotic electronic effects such as high T_c -superconductivity and novel magnetic phases [1–5]. The formation of polarons and the modification of their properties by reduced dimensionality have been implicated in many of these phenomena [1, 6–8]. Although a number of systems, including layered transition-metal oxides [5], surfaces and thin insulating films [9, 10] are suspected to exhibit 2D polaronic behavior, directly probing their properties remains extremely challenging. Much of what is currently understood about polarons in 2D systems is based upon phenomenological or semi-empirical theoretical models [11–15]. For example, the existence an energetic barrier to the formation of small polarons in systems with more than two dimensions can be shown using simple scaling arguments [12, 13, 16]. However, the 2D case is a marginal one, making it difficult to make reliable predictions about the properties of materials. Experimental evidence, although fairly limited, suggests that there is a barrier in at least some 2D systems [9]. This uncertainty underlines the fact that the theory of polaron self-trapping in anisotropic polar crystals is far from being complete [17, 18] and it remains difficult to predict values of critical parameters causing polaron self-trapping in such systems.

In this letter, we employ fully *ab initio* theoretical methods to investigate the properties of hole polarons in the binary monoclinic oxides HfO_2 and ZrO_2 . A number of previous studies provide evidence for polaronic hole trapping in these materials, including measurements of the magnetorefractive effect [19], oxygen pressure dependence of hole conductivity [20, 21] and electron spin resonance spectroscopy [22]. Although HfO_2 and ZrO_2 are usually considered as 3D materials, our calculations show that they exhibit pronounced 2D polaronic properties. This unexpected effect is due to an asymmetry in the crystal structure of these materials, which induces small polaron formation in only one of its two oxygen

sub-lattices, leading to highly anisotropic polaron conductivity. We further demonstrate the existence of an energetic barrier to hole self-trapping and elucidate the 2D to 0D localization transition. This discovery broadens the field of quasi-2D systems which may exhibit novel electronic properties. Aside from this fundamental interest, both HfO_2 and ZrO_2 find important applications in electronics and catalysis (respectively) where the trapping and mobility of holes is very important [23, 24].

Accurately predicting the character of localization of electrons or holes from first principles is extremely challenging because widely employed density functional theory (DFT) approaches suffer from self-interaction (SI) error which tends to delocalize holes [25]. A number of SI corrected electronic structure methods have been applied previously to investigate polaronic localization, both in perfect crystals and near point defects, such as DFT+U [26], semi-empirical correction schemes [27] and hybrid DFT [28]. Indeed, the later was used previously to predict hole polaron localization in HfO_2 [29]. Although these approaches restore the qualitative picture of localization, none guarantee exact elimination of SI. To make more confident predictions regarding the character of hole localization and mobility in 2D systems requires a more controlled approach to dealing with SI. To achieve this we employ the recently developed cancellation of non-linearity (CON) method within a DFT formalism [30]. The main advantage of this method is that the SI correction that is applied is determined unambiguously by ensuring that the correct linear behavior of the total energy with respect to fractional occupation number is obtained. This method has been successfully applied previously to model holes in wide gap semiconductors, including, acceptor defects in transparent conducting oxides [30, 31], Zn vacancies in Zn chalcogenides [32], and divalent acceptors in GaN [33].

The $m\text{-HfO}_2$ crystal structure is shown in Fig. 1a. It is characterized by two types of oxygen ion which differ in their coordination to hafnium ions, either three-

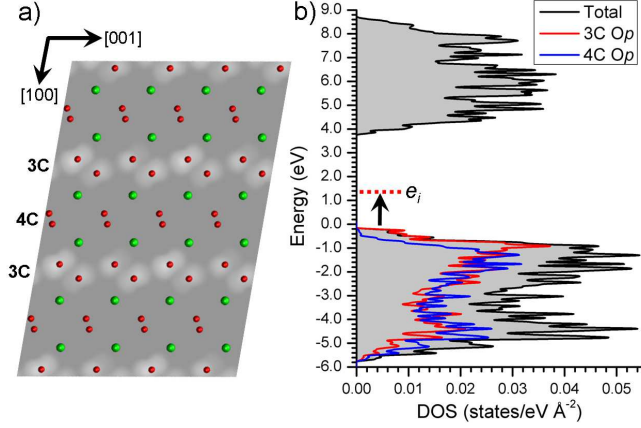


FIG. 1: (color online) (a) [010] projection of a (2x2) unit cell of $m\text{-HfO}_2$: Hf ions (light balls) and O ions (dark balls). Also shown is a charge density isosurface for a hole created by vertical ionization. (b) The total electronic density of states of $m\text{-HfO}_2$. Localization of a hole associated with splitting of a one electron level (e_i) from the top of the valence band is also indicated.

coordinated (3C) or four-coordinated (4C). The 3C and 4C oxygen ions are geometrically separated in the lattice and arranged in 2D layers. Viewed from this perspective $m\text{-HfO}_2$ can be considered as a layered material, which, as we show below, has profound consequences for its electronic properties. The DFT calculations presented in the rest of this paper have been performed using the projector augmented wave method and the Perdew-Burke-Ernzerhof exchange correlation functional as implemented within the Vienna *ab initio* simulation package [34–36]. Using this method we obtain lattice parameters within 0.6% of experiment ($a = 5.142 \text{ \AA}$, $b = 5.192 \text{ \AA}$, $c = 5.250 \text{ \AA}$ and $\beta = 99.65^\circ$). Fig. 1b shows the calculated total density of states (DOS) of $m\text{-HfO}_2$ and the partial DOS projected onto 3C and 4C oxygen p -states. The top of the valence band (VB), within about 0.4 eV, is comprised almost exclusively of 3C O_p character, while the contribution from 4C O ions appears only deeper in the VB. The origin of the splitting in energy of these electronic states can be traced to differences in the Madelung potential, which is 0.36 V higher on the 3C sites than the 4C sites. Correspondingly, the band dispersion near the top of the VB is very small perpendicular to the 3C layers, [100], but high parallel to them [37]. We will focus our further discussion on $m\text{-HfO}_2$, however, we find very similar properties for $m\text{-ZrO}_2$ and the key properties of both materials are summarized later in the text.

A direct consequence of the layered oxygen sublattice in $m\text{-HfO}_2$ is that a hole introduced at the top of the VB optically (*i.e.* without ionic relaxation) is initially delocalized over the 3C oxygen ions, as shown by the hole density isosurface in Fig. 1a. If ions in the lattice are allowed to displace, the delocalized hole may form a small

polaron, *i.e.* localize onto one or several anion sites. The trapping energy, E_t , defined as the difference between the total energy of the vertically ionized system and that of the polaron state, can be used to characterize whether polaron formation is energetically stable. Localization of a hole is associated with the splitting of an unoccupied one electron level (e_i) from the top of the valence band (*e.g.*, e_i in Fig. 1b). It can be shown that for SI free DFT, there should be an exact equivalence between the vertical charge transition level $E_{+/0}$ (defined as the energy gained on addition of an electron to the system with ion coordinates frozen) and the eigenvalue of the corresponding one electron level which is being populated or depopulated.

The CON approach to correcting the SI error applies a local occupation dependent potential to the oxygen p -states of the following form,

$$V_{\text{hs}} = \lambda_{\text{hs}} (1 - n_{m,\sigma}/n_{\text{host}}), \quad (1)$$

where $n_{m,\sigma}$ is the fractional occupancy of sublevel m of spin σ in the oxygen p -orbital. The reference occupation n_{host} is the anion p -orbital occupancy in the absence of holes, as determined from the neutral defect-free system. The only free parameter in the potential, λ_{hs} , is uniquely determined by requiring $E_{+/0} = e_i$. Calculations are performed using a range of λ_{hs} for holes localized on both 3C and 4C oxygen sites. A 324 atom supercell is used to ensure holes are separated from periodic images by over 15 Å. To improve accuracy further, the total energies and eigenvalues are also corrected for image-charge and potential alignment effects, as has been described previously [38]. Following a systematic investigation, we find that the SI of the localized hole is eliminated exactly using $\lambda_{\text{hs}} = 3.8 \text{ eV}$.

Using the self-consistently determined SI correcting potential, we have been able to find local minima in the potential energy surface (PES) corresponding to holes localized on both the 3C and 4C oxygen sites. The 4C site is characterized by $E_t = -0.31 \text{ eV}$, *i.e.* hole polarons trapped at 4C sites are metastable. We have confirmed by evaluation of the dynamical matrix by density functional perturbation theory that the 4C hole is metastable rather than unstable as there are no soft vibrational modes present. On the other hand, 3C sites serve as stable hole traps with $E_t = 0.18 \text{ eV}$. The corresponding charge transition levels, relative to the top of the bulk HfO_2 VB, are 1.13 eV (3C) and 0.78 eV (4C) as illustrated in Fig. 2a. For comparison, we performed calculations using the screened hybrid functional of Heyd, Scuseria, and Ernzerhof [28] and obtained qualitatively similar results [36].

Given the importance of the prediction that hole polarons are only stable on the 3C oxygen sub-lattice, it is instructive to examine the origin of this different stability. For this purpose, we consider a hypothetical process in which we distort the equilibrium geometry of the neutral

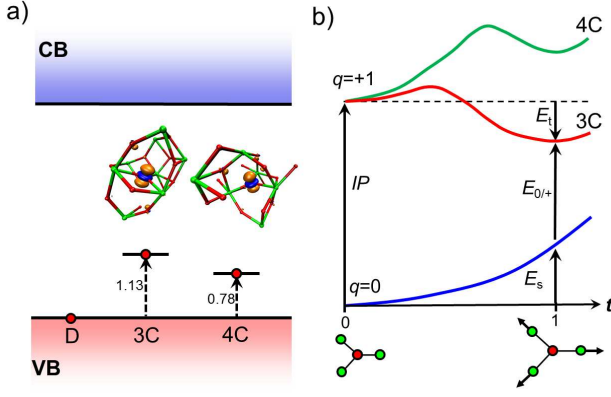


FIG. 2: (color online) (a) Position of the charge transition level for a hole introduced without lattice relaxation (D) and for small polarons localized at 3C and 4C oxygen sites following lattice distortion. The numbers indicate the position of the electronic level relative to the bulk valence band maximum (in eV). (b) Schematic adiabatic PESs before ($q = 0$) and after ($q = 1$) electron ionization.

system into the geometry of the polaron and subsequently remove an electron vertically. We interpolate linearly between the positions of atoms in the ideal lattice (\mathbf{R}_0) and the positions corresponding to the (meta)stable polaron state ($\mathbf{R}_{3C(4C)}$), in the following way,

$$\mathbf{R}(t) = t\mathbf{R}_{3C(4C)} + (1 - t)\mathbf{R}_0. \quad (2)$$

Following distortion of the neutral lattice (*i.e.* following the lower curve in Fig. 2b from $t = 0$ to $t = 1$) there is an increase in energy due to elastic strain (E_s), which has an approximately quadratic dependence on the degree of distortion. Accompanying this distortion, the local electrostatic potential at the anion, Φ , is also increased. We find that the increase in local potential is directly proportional to the degree of distortion, which justifies a widely employed approximation in analytical models of polaron trapping [39]. On removing an electron, the hole that is formed is attracted towards the anion due to the potential well formed by the dilation and long range electronic polarization. However, hole localization also implies an increase in kinetic energy and the balance between these various energetic terms determines the magnitude of the trapping energy.

It is reasonable to assume that the long range electronic polarization and increase in kinetic energy following localization are similar for both the 3C and 4C hole polarons as the holes are localized to a similar extent. However, the other two terms: the strain energy and the local electrostatic potential are, in general, dependent on the trapping site. For HfO_2 , we find that E_s is 0.14 eV greater for the 4C polaron than the 3C polaron, which is expected since an additional cation must be displaced. We also find that the electrostatic potential in the polaron geometry is 0.39 V higher on the 3C site than on

the 4C site, which is similar to the difference present in the undistorted lattice (0.36 V). Both of these factors tend to favor trapping at the 3C site. This analysis shows that the main effects responsible for site selective polaron trapping are differences in the electrostatic potential and elastic strain energy between the two anion sites.

To elucidate the localization transition associated with hole trapping we again consider the process described by Eq. 2, but this time for the positively charged system. Fig. 2b shows schematically the form of the PES for hole trapping at the 3C oxygen site. We find that there is a small barrier to trapping from the ideal lattice, ~ 40 meV. Fig. 3 shows the corresponding spin density isosurfaces for the hole at a series of points along the distortion path. For a very small distortion ($t = 0.2$) corresponding to a potential energy fluctuation of only 23 meV, the hole has already undergone a transition from 3D to 2D localization within a single layer composed of 3C oxygen ions. This is an indication that the layered structure of $m\text{-HfO}_2$ is intrinsically unstable to 2D hole localization. As the distortion increases further ($t > 0.2$), the spatial extent of the hole begins to decrease within the 2D (100) plane, until ultimately it forms a small polaron ($t = 1$). Once fully localized, 76% of the spin density is localized on a single oxygen ion.

An important consequence of this result is that large polarons in $m\text{-HfO}_2$ have an essentially 2D character, and the formation of small polarons requires a 2D to 0D localization transition. To assess the mobility of hole polarons we calculate activation energies for hole hopping, E_d , by linear interpolation. We predict hole polarons can move freely between 3C oxygen sites ($E_d = 0.14$ eV), however, the relatively high energy of the 4C localized hole suggests that even the transient formation of a 4C hole is improbable. Therefore, hole polarons, both large and small, must be confined to exist within 2D planes of 3C oxygen ions.

The predicted activation energy for hole mobility is in good agreement with experimental high temperature hole conductivity data [20, 21]. At lower temperatures these experiments found a higher activation energy, 0.7 eV, which has been attributed to the thermal liberation of holes from cation vacancies, *i.e.* $V_{\text{Hf}}^{\times} \rightarrow V_{\text{Hf}}' + h^{\cdot}$ (in Kröger-Vink notation). Using the CON approach we find that the binding energy of a hole to a neutral cation vacancy is 0.64 eV, again in very good agreement with ref. 21. A significant advantage of the CON approach over hybrid functionals is that the larger cell sizes needed to describe such defects are computationally feasible. Very similar results are also obtained for ZrO_2 and the key quantities are summarized in Table I.

In summary, we have investigated the properties of holes in HfO_2 and ZrO_2 and their ability to self trap forming polarons using first principles methods that are free from the usual SI problems inherent to DFT. We have shown that holes introduced to the VB form small

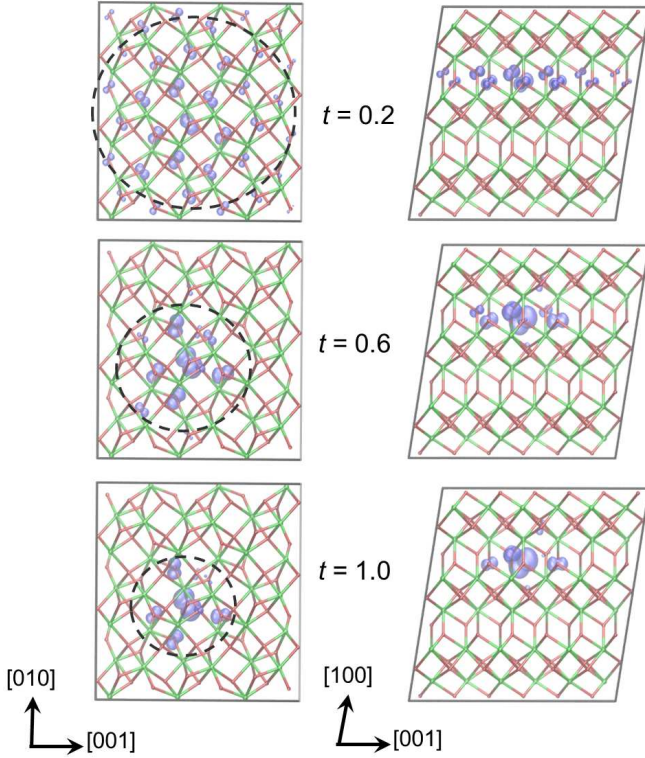


FIG. 3: (color online) Spin density isosurfaces showing the change in the character of hole localization associated with distortion of lattice ions. A very small distortion in the lattice ($t = 0.2$, $\Delta E = 23$ meV) is sufficient to induce a transition from 3D to 2D localization within a layer composed of 3C oxygen ions.

TABLE I: The hole trapping energy (E_t), vertical charge transition level ($E_{+/0}$), barrier to trapping (E_b), and barrier to diffusion (E_d) are summarized below for holes trapped on both three-coordinated (3C) and four-coordinated (4C) oxygen ions.

	HfO ₂		ZrO ₂	
	3C	4C	3C	4C
E_t (eV)	0.18	-0.31	0.13	-0.31
$E_{+/0}$ (eV)	1.13	0.78	1.07	0.75
E_b (eV)	0.04	0.37	0.05	0.36
E_d (eV)	0.14		0.13	

polarons that are distributed across 2D layers comprised of 3C oxygen ions. These polarons are predicted to be highly mobile within the 3C layer, but face high barriers to move in the perpendicular direction. We also elucidate the factors which influence the formation of hole polarons in this material and study their interaction with cation vacancy defects. Our calculations predict hole conductivity in these materials should be highly anisotropic. Testing this prediction requires experiments on single crystals or on films with defined texture.

We note that in many ways the 2D electronic prop-

erties of m -HfO₂ and m -ZrO₂ are similar to those pronounced in numerous layered oxides as well as in 2D electron gases that can be formed at interfaces (e.g. LaAlO₃/SrTiO₃), in high-Tc superconducting cuprates and also at grain boundaries [40]. Recent theoretical calculations on transition metal dichalcogenides (e.g. ZrS₂, HfS₂) suggest that similar 2D polaronic effects may be also present owing to their layered structure [41]. One interesting consequence of this layered electronic structure is that polaronic hole trapping is (unusually) a 2D to 0D delocalization/localization transition. Similar effects can be introduced by strain in otherwise highly symmetric materials [42]. Investigation of the correlated dynamics and interaction of holes confined in these types of material using techniques such as THz time domain spectroscopy [43], and low temperature magnetic and electrical characterization, may reveal interesting effects such as superconductivity, hole crystallization [44] or magnetism which may deepen our understanding of these interesting and important phenomena.

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* Electronic address: keith.mckenna@york.ac.uk

† Present address: University of Colorado, Boulder, Colorado 80309, USA.

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