Hybrid functional electronic structure of PbPdO$_2$, a small-gap semiconductor

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Abstract

PbPdO$_2$, a ternary compound containing the lone pair active ion Pb$^{2+}$ and the square planar d$^8$ Pd$^{2+}$ ion, has attracted recent interest because of the suggestion that its electronic structure, calculated within density functional theory using either the local density or the generalized gradient approximation, displays zero-gap behavior. In light of the potential ease of doping magnetic ions in this structure, it has been suggested that the introduction of spin, in conjunction with zero band gap, can result in unusual magnetic ground states and unusual magnetotransport. It is known that most electronic structure calculations do not properly obtain a band gap even for the simple oxide PdO, and instead obtain a metal or a zero-gap semiconductor. Here we present density functional calculations employing a screened hybrid functional which correctly obtain a band gap for the electronic structure of PdO. When employed to calculate the electronic ground state of PbPdO$_2$, a band gap is again obtained, which is consistent with both the experimental data on this compound, as well as a consideration of valence states and of metal–oxygen connectivity in the crystal structure. We also present comparisons of the absolute positions (relative to the vacuum level) of the conduction band minima and the valence band maxima in α-PbO, PdO and PbPdO$_2$, which suggest ease of p-type doping in PbPdO$_2$ that has been observed even in nominally pure materials.

(Some figures may appear in colour only in the online journal)

1. Introduction

Both lead and palladium—in their own right—present an array of fascinating phenomena in the oxide solid state, and find use in a host of important applications. The stereochemically active lone pair of Pb$^{2+}$ is associated with numerous electronic effects observed in complex oxides, such as the ferroelectric polarization of PbTiO$_3$, and the high piezoelectric response of PbZr$_{1−x}$Ti$_x$O$_3$ (PZT) [1]. Palladium is ubiquitously employed in both heterogeneous and homogeneous catalysis, and is a critical component in catalytic converters for automotive exhaust purification. The catalytic action of Pd$^{2+}$ ions in oxides has been a topic of much interest recently, addressed for example, by Hegde et al [2]. Given the diversity of properties associated with Pb$^{2+}$ and Pd$^{2+}$ cations in oxides, it is of interest to examine how they behave together in a complex oxide.

Litharge, the tetragonal form of PbO (α-PbO, P4/nmm #129), is a red compound with a bandgap of about 1.9 eV [3]. Its crystal structure, depicted in figure 1(a), is layered, with each layer comprising a square lattice of O that is alternately (up and down) capped by Pb. The layers eclipse one another when projected down the long (c) axis of the structure.

Palladium oxide crystallizes in the tetragonal cooperite structure [4], (space group P4$_2$/nmc #131), and consists of edge-sharing chains of PdO$_4$ planes that run perpendicular along the a axis and the b axis of the structure, and these chains corner-share along the c axis (figure 1(b)). All of the Pd–O bonds are equidistant, but the PdO$_4$ units are not perfect squares and instead are rectangular, with a slight compression leading to shorter nearest-neighbor O–O distances along c than in the a direction. Oxygen is tetrahedrally coordinated by four Pd atoms in the structure. The nearest-neighbor Pd–Pd distance of slightly over 3 Å (the a axis length) is relatively...
short. These short contacts occur in two dimensions in PdO, within and between the chains, and should give rise to disperse bands derived from the Pd d orbitals.

Rogers et al. reported that single crystals of PdO are dark green [5], but the presence of impurities prevented the reliable determination of the band gap. PdO displays p-type semiconductivity, and it has been suggested that the hole population arises from extrinsic defects, in particular the presence of unintentional dopants [5]. Indeed, widely varying estimates of the PdO band gap have been reported: Hulliger found an optical band gap of 0.6 eV from diffuse-reflectance measurements on a polycrystalline powder [6]. Okamoto and Aso estimated the band gap to be 1.5 eV from conductance measurements of PdO films [7], in agreement with the gap reported by Pillo et al. from photoemission studies [8]. Nilsson and Shivaraman found a 0.8 eV gap from optical transmittance measurements of PdO films [9], while a study of PdO films by Rey et al. yielded an optical gap of about 2.1 eV [10].

PbPdO$_2$ is the only ternary oxide of Pb and Pd reported in the inorganic crystal structures database [11]. Single crystals of PbPdO$_2$ were prepared by Meyer and Müller-Buschbaum, which they observed to be black [12]. Locally, the Pb-capped planes in α-PbO and roughly square planar coordination of Pd in PdO are preserved in orthorhombic PbPdO$_2$, which was determined to crystallize in the Imma #74 space group. However, the relationship between the structural units is very distinct in this ternary phase (figure 1(c)). PbPdO$_2$ can be viewed as a layered structure containing zig-zagging sheets of corner-sharing PdO$_4$ planes, interleaved by layers of Pb. Oxygen is tetrahedrally coordinated to two Pd within the sheets and two Pd between the sheets. Between the Pd layers, edge-sharing PdO$_4$ units form 1D chains running parallel to $b$ with Pb on alternating sides of the chain, and the chains are eclipsed with respect to one another along the $c$ axis.

While an understanding of the PbPdO$_2$ structure is facilitated by describing it as a layered material, it is important to point out that chemically it should be regarded as a three-dimensional extended solid. The Pd–O and Pb–O bonds in the simple oxides of Pd and Pb are quite covalent, and PbPdO$_2$ contains an extended network of −Pd–O–Pb−O–Pd−connectivities. There are two points that we emphasize here about the structure of PbPdO$_2$: first, the dimensionality of the PdO$_4$–PdO$_4$ and PbO$_4$–PbO$_4$ connectivities are reduced in PbPdO$_2$, relative to those in the oxides PdO and α-PbO. Second, there are no edge-sharing PdO$_4$ units present in PbPdO$_2$ or any short Pd–Pd distances, as encountered in PdO, nor are there any in-plane Pd−O–Pd connectivities. Qualitatively, considering the structural arrangement and electronic configurations of the cations, one would expect PbPdO$_2$ to not be any closer to metallic behavior than the two binary compounds that it is derived from.

Our interest in PbPdO$_2$ stems from prior and ongoing efforts to understand relationships between the electronic structural features of platinum group and noble metal ions, and the catalytic activity of the oxides they form. We recently reported an experimental and computational comparison of the complex oxides of isoelectronic Pd$^{2+}$ and Au$^{3+}$, La$_2$BaPdO$_5$ and La$_4$LiAuO$_8$, both of which contain isolated PdO$_4$ and AuO$_4$ square planes, respectively [13]. Density functional calculations within the local density approximation (LDA) yielded sizable (though underestimated) band gaps for both compounds, consistent with their yellow colors and optical absorption spectra. That LDA was a sufficient level at which to study these compounds is related to the isolated nature of the Pd and Au coordination environments. In contrast, although PdO is a well known semiconductor, LDA calculations often predict it to be metallic [14].

The electronic structure of PdO has been previously studied by a variety of ab initio methods. Hass et al. reported the first computational investigation of PdO, in which an augmented-spherical-wave approach within the local density approximation was employed [15]. PdO was correctly predicted to be a semiconductor, with a direct gap at the M point, although the size of the gap was severely
underestimated. A subsequent study reported by Park et al., using full-potential approaches with linearized augmented plane waves (LAPW) and linear muffin-tin orbitals (LMTO) within the LDA, was unable to predict a gap in PdO [14], though a small gap was reported to open through the use of LMTO in the atomic sphere approximation [16]. Uddin et al reported a study of density functional predictions for the electronic structure of PtO [17], which is isostructural with PdO. Using Gaussian-type orbitals, the Heyd, Scuseria, and Ernzerhof (HSE) screened hybrid functional [18] correctly predicted PtO to be a semiconductor, whereas calculations within the local spin density approximation (LSDA), Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation (GGA), and with a meta-GGA functional, all led to the prediction of (poor) metallicity. Recently, a HSE band gap of 0.9 eV in PdO has been reported by Seriani et al [19], and Bruska et al determined an HSE band gap of 0.8 eV that could be extended to 1.5 eV by increasing the amount of Fock exact exchange to 39% [20].

On the basis of LDA calculations, Wang suggested that PbPdO$_2$ is a zero-gap oxide semiconductor [21], with potentially very interesting electronic structural signatures when the compound is subject to partial substitution by magnetic ions. Chen et al reported a combined experimental and computational study of PbPdO$_2$, employing the PBE functional with the addition of a 2 eV Hubbard $U$ term on Pd to account for on-site Coulomb repulsion [22]. Their GGA+$U$ calculations did not result in the opening of a band gap. However, Bennett et al recently noted that an exceedingly large $U$ value of 8 eV, using the LDA+$U$ method, was needed to reproduce the experimental gap of PdO [23].

Electrical transport properties of polycrystalline PbPdO$_2$ were reported by Ozawa et al [24], and Seebeck and Hall effect measurements indicated p-type conductivity. It was suggested from a change in the temperature coefficient of resistance that PbPdO$_2$ undergoes a metal-to-insulator transition at about 90 K, and that the ground state is an insulator, not a metal. However, the minimum resistivity of a little over 0.4 $\Omega$ cm is more consistent with semiconducting behavior than it is with the resistivity of a metal, which is expected to be of the order of $10^{-2}$ $\Omega$ cm or less. Additionally, the reported change in resistivity between the ‘insulating’ and ‘metallic’ states is less than a factor of 2, whereas typical metal-to-insulator transitions span two or more orders of magnitude. For comparison, Uriu et al studied the effect of Li-substitution in PdO (Pd$_{1-x}$Li$_x$O$_{1-x}$), and found that the resistivity at 273 K decreased from 3 $\Omega$ cm in the unsubstituted material, to $2.2 \times 10^{-3}$ $\Omega$ cm with 1 mol% Li, to $4.4 \times 10^{-3}$ $\Omega$ cm with 8 mol% Li [25].

Reports of chemical substitution in PbPdO$_2$—with the intent of introducing electrical carriers and/or magnetic ions—are few. Ozawa et al studied the substitution of Cu for Pd, which increases the resistivity [26]. Magnetism and transport have been examined in Co and Mn substituted PbPdO$_2$ by Lee et al [27, 28]. Both Co and Mn lower the resistivity, but the minima are pushed to higher and lower temperatures, respectively, relative to unsubstituted PbPdO$_2$. The resistivity of PbPd$_{0.9}$Co$_{0.1}$O$_2$ is larger than 0.1 $\Omega$ cm at 150 K, while for PbPd$_{0.6}$Mn$_{0.4}$O$_2$ the resistivity is 0.08 $\Omega$ cm at 70 K [28]. Large electromagnetoresistance and magnetoresistance in PbPd$_{0.75}$Co$_{0.25}$O$_2$ films have been reported by Wang et al [29], and quite recently, magnetism and transport properties of a PbPd$_{0.81}$Co$_{0.19}$O$_2$ film were studied by Su et al [30].

In the light of the electronic properties that would be expected for PbPdO$_2$ on the basis of its structural attributes and electron count, we report density functional electronic structure calculations for PbPdO$_2$ employing a screened hybrid functional described by Heyd, Scuseria, and Ernzerhof [18, 40] (HSE06). Inclusion of exact exchange to the description of the short-range Coulomb potential has been shown to significantly enhance the accuracy of density functional calculations in periodic systems [31–34]. To complement these results, we also present the HSE electronic structure of PdO. Additionally, by comparing the absolute positions, relative to the vacuum level, of the conduction band minima and the valence band maxima in α-PbO, PdO, and PbPdO$_2$, we find that facile electron transfer from PbPdO$_2$ to, for example, residual PdO left from the preparation, may account for the p-type conductivity observed in nominally pure materials. The HSE calculations suggest surprisingly linear dispersions of the valence and conduction bands across the direct $\approx$1.1 eV band gap of this compound.

2. Computational methods

Density functional electronic structure calculations were performed in the Vienna $ab$ $initio$ simulation package (VASP) [35, 36]. Interaction between the valence and core electrons was described using the projector augmented wave (PAW) approach [37, 38], with valence electrons described by plane-wave basis sets. Fourteen valence electrons were included for Pb (5d$^{10}$6s$^2$6p$^2$), ten valence electrons for Pd (4d$^{10}$), and six valence electrons for O (2s$^2$2p$^4$). Calculations were performed at the scalar relativistic level, without the inclusion of spin–orbit coupling, using both the GGA of PBE [39], and the hybrid functional HSE06 [18, 40]. The screened hybrid functional introduces a percentage of exact nonlocal Fock exchange (25%) to the PBE functional, and a screening of 0.2 Å$^{-1}$ is applied to partition the Coulomb potential into long-range and short-range terms. Hartree–Fock and PBE exchange mix in the short-range portion, with the long-range exchange represented by the PBE functional.

A cutoff energy of 520 eV was used in all calculations, as were Γ-centered k-point grids. Relaxations were deemed to have converged when the forces on all the atoms were less than 0.01 eV Å$^{-1}$. Geometry optimization of PbPdO$_2$ was performed in the primitive rhombohedral unit cell, using a $5 \times 5 \times 5$ k-mesh. The same grid was also used to calculate the HSE electronic density of states (DOS). PBE calculations of the PbPdO$_2$ DOS employed a $20 \times 20 \times 20$ k-mesh. Band structure calculations for PbPdO$_2$ were performed using the conventional orthorhombic unit cell. For PdO, a $6 \times 6 \times 4$ k-mesh was used to relax the structure with the HSE functional and to calculate the DOS. PBE relaxation and DOS calculations for PdO employed $8 \times 8 \times 6$ and $18 \times 18 \times 16$ k-point meshes, respectively. PBE band structures
were calculated with 30-point interpolations between each high symmetry $k$ point. HSE band structure calculations are presented only along the dispersions in the region of the band gaps, $Z$ to $\Gamma$ to $X$ for PbPdO$_2$, and $X$ to $\Gamma$ to $\Gamma$ for PbO, using 10-point interpolations between each high symmetry $k$-point.

To investigate the doping tendencies of PbPdO$_2$, the positions of the valence band maximum (VBM) and the conduction band minimum (CBM), relative to vacuum, were studied. Slab models were constructed and atomic positions optimized using the PBE functional with fixed lattice parameters. Four Pb–O–Pd–O bilayers were included in the PbPdO$_2$ slab, eight Pd–O layers were used in the PbO slab, and eight PbO layers were used for the PbO slab. The lengths of the ideal slabs for the three compounds are $19.20$ Å, $21.82$ Å, and $17.80$ Å, respectively. Vacuum regions with the same length as the slab were included for each compound. Because the local and semi-local PBE functional usually generates band gaps significantly smaller than the experimental values, the hybrid HSE functional was employed for static calculations of the PBE relaxed slabs. To obtain the positions of the VBM and CBM relative to the vacuum level, the electrostatic potential in the center of the slabs (assuming it well represents the bulk) were aligned with the center of the vacuum region.

LMTO calculation [41, 42], performed within the atomic sphere approximation using version 47C of the Stuttgart TB-LMTO-ASA program [43], was used in the determination of the electron localization function (ELF) for PbPdO$_2$. Scalar relativistic Kohn–Sham equations within the local density approximation [44] were solved taking all relativistic effects into account except for the spin–orbit coupling. The calculation was performed on 527 irreducible $k$-points within the conventional orthorhombic cell. The ELF provides a measure of the local influence of the Pauli repulsion on the behavior of electrons, enabling the real-space mapping of core, bonding, and non-bonding regions in a crystal [45, 46].

Figure 2. PbO electronic DOS, orbital projected DOS, and band structure. (a) PBE total and projected DOS. (b) HSE total and projected DOS. (c) PBE band structure, with HSE band structure overlaid in bold (orange) lines along the $X$ to $M$ to $\Gamma$ dispersion. The direct band gap occurs at the $M$ point. In (a) and (b) the Fermi energy is referenced to the top of the valence band, indicated with vertical dashed lines. In (c), $0$ eV represents the Fermi energy for the PBE calculation, while for the HSE bands the Fermi energy has been adjusted to the absolute energy of the PBE $E_F$. As has been similarly noted by Uddin et al for PbO [17], the GGA calculation does not predict PbO to be a semiconductor.

Table 1. Structural parameters for PBE and HSE relaxed PbO and PbPdO$_2$, compared with experimental values. The experimental parameters given are those determined by Rogers et al for PbO [5], and Ozawa et al for PbPdO$_2$ [24]. PbPdO$_2$, space group $Imma$ ($\#129$, setting 1): Pb (4e) at $0$, $1/4$, $z$; Pd (4c) at $1/4$, $1/4$, $1/4$; O (8f) at $x$, $0$, $0$. PbO, space group $P4_2/mnm$ ($\#131$): Pd (2d) at $1/2$, $0$, $0$; O (2e) at $0$, $0$, $1/4$.

| Comp       | PBE     | HSE     | Expt    |
|------------|---------|---------|---------|
| PbO        | PBE     | HSE     | Expt    |
| $a$ (Å)    | $3.10$  | $3.07$  | $3.043$ |
| $b$ (Å)    | $5.53$  | $5.45$  | $5.460$ |
| $c$ (Å)    | $5.44$  | $5.33$  | $5.336$ |
| Pb $z$     | $0.772$ | $0.764$ | $0.774$ |
| O $x$      | $0.350$ | $0.350$ | $0.345$ |
| Pb–O (Å)   | $2.06$  | $2.03$  | $2.02$  |
| Pb–O–O (Å) | $2.38$  | $2.34$  | $2.37$  |
| Pb–O–O–O (Å) | $97.5$  | $98.1$  | $97.5$  |
| Pb–Pb ($\AA$) | $95.8$  | $96.2$  | $94.3$  |

3. Results and discussion

The total electronic and Pd d and O p orbital projected DOS for PbO, calculated using the PBE and HSE functionals, are compared in panels (a) and (b) of figure 2. The PBE band structure is shown in panel (c) in the region of the VBM and CBM, with bands from the HSE calculation overlaid in bold lines along the dispersion from $X$ to $M$ to $\Gamma$. Structural parameters obtained for the PBE and HSE relaxed structures are listed in table 1, along with experimentally determined values for comparison. Oxygen p states lie predominantly between $-9$ and $-4$ eV, with Pd d states more densely populated between $-4$ eV and the Fermi energy, referenced to the top of the valence band in the DOS plots and denoted with dashed vertical lines. In the plot of the band structure, $0$ eV represents the Fermi energy for the PBE calculation. The Fermi energy of bands calculated with HSE have been adjusted to the absolute energy of the PBE $E_F$. Stabilization of the VBM and destabilization of the CBM by HSE occur
Figure 3. Electronic DOS and orbital projected DOS for PbPdO$_2$. (a) PBE total and projected DOS. (b) HSE total and projected DOS. The Fermi energy is referenced to the top of the valence band, denoted by dashed vertical lines. The upper panels display the total and Pd d projected DOS, which are shaded for clarity, and the lower panels show the O p, Pb p, and Pb s projected DOS. The band gap predicted by HSE is about 1.1 eV. Note the strong hybridization of O p and Pb s states between $-10$ and $-8$ eV, and the presence of Pb s and p states near the Fermi energy.

Geometry-optimized structural parameters obtained with the PBE and HSE functionals are given in table 1, and the total electronic and orbital projected DOS of PbPdO$_2$ are presented in figure 3. The shape and dispersion of the orbital contributions obtained by the different methods are quite similar, with the obvious difference being the presence of a $\approx 1.1$ eV bandgap in the HSE electronic structure. The upper panels display the total and Pd d projected DOS, which are shaded for clarity, and the lower panels show the O p, Pb p, and Pb s projected DOS. The bottom of the Pd d band in PbPdO$_2$ is somewhat destabilized (closer in energy to $E_F$), relative to the dispersion of the d states in PdO, and this is consistent with decreased overlap associated with the absence of short Pd–Pd distances. Note the strong hybridization of O p and Pb s states between $-10$ and $-8$ eV, and overlap of O p and Pb s and p states near the Fermi energy, features that are similarly encountered in the electronic structure of $\alpha$-PbO [47, 48]. In $\alpha$-PbO, the highly stabilized Pb s and O p states held deep below $E_F$ are strongly bonding, while the states just below $E_F$ are of antibonding character [49]. The mixing of Pb s and O p states near the Fermi energy has been suggested to drive the localization of the Pb lone pair into lobe-shaped structures [47, 48]. As can be seen in the electron localization function (ELF) isosurface of PbPdO$_2$ shown in panel (d) of figure 1, the Pb lone pair lobes are localized apical to the base of the Pb-capped planes.

The PBE band structure of PbPdO$_2$ in the vicinity of the Fermi energy is shown in figure 4, with the HSE calculated bands overlaid in bold along the Z to $\Gamma$ to X dispersion. The direct band gap occurs at the $\Gamma$ point. 0 eV references the Fermi energy obtained in the PBE calculation; the HSE bands have been scaled to the same absolute reference energy. Note that the HSE correction stabilizes (pushes down in energy) the top of the valence band. The Brillouin zone of a primitive orthorhombic cell is inset in the figure.
Schematic representation of the positions of VBMs and CBMs in PbPdO$_2$, PdO, and $\alpha$-PbO, referenced to the vacuum level. Because the CBM of PdO lies below the VBM of PbPdO$_2$, PdO will be readily hole-dopeable in the presence of even small amounts of residual PbO.

for a conventional orthorhombic cell, and the BZ is inset in figure 4 for convenience. The PBE calculated band structure shows a slight crossing of bands at the $\Gamma$ point, where a zero gap was predicted by Wang [21]. A direct gap is clearly evident in the dispersion calculated with HSE. It is important to note that the bands at the top of the valence band and at the bottom of the conduction band do not show nearly as much energy dispersion as the equivalent bands in PdO. Also noted is the surprising linearity of the valence and conduction band dispersions near the direct band gap.

In figure 5 we present a schematic showing the calculated positions of the VBMs and CBMs for PbPdO$_2$, PdO, and $\alpha$-PbO. The VBM and CBM positions of PbPdO$_2$ are 4.78 and 3.84 eV below vacuum, respectively, which are quite high. This indicates that the compound is prone to p-type doping by native defects and intentional substituents. Conversely, the VBM and CBM of PdO are 6.42 and 5.53 eV below the vacuum, indicating that PdO is, in comparison with PbPdO$_2$, more prone to being n-doped. More importantly, the CBM of PdO is lower in energy than the VBM of PbPdO$_2$. Thus, the presence of PdO in a sample of PbPdO$_2$ can lead to hole-doping of PbPdO$_2$ by facile electron transfer from its valence band to the conduction band of PdO. Even small amounts of PdO would lead to the generation of a large quantity of holes in the valence band of PbPdO$_2$, which may explain the p-type conductivity observed for samples of PbPdO$_2$.

On the other hand, the VBM and CBM for $\alpha$-PbO are located at 5.09 eV and 2.85 eV below vacuum, respectively. Because PbO is more ionic, it has a larger gap, and its VBM is lower than the VBM of PbPdO$_2$ while the CBM of PbO is higher than the CBM of PbPdO$_2$. Therefore, the presence of unreacted PbO in samples of PbPdO$_2$ are not likely to significantly affect its electronic properties, such as the density of charge carriers. Given the volatility of PbO, PbO$_2$ is much more likely to persist in samples of PbPdO$_2$.

Our calculations only address alignment of the energy levels of the starting materials typically used in the preparation of PbPdO$_2$, relative to the target phase. A complete discussion of the source of hole conductivity requires a comprehensive study of the defect and impurity properties of the system—as they may contribute greatly to the source of the p-type doping—which is beyond the scope of the present work. However, our results reveal that PbPdO$_2$ is susceptible to p-type doping, and emphasizes the importance of preparing high purity materials as small amounts of residual starting material, PdO in particular, may greatly influence the physical properties observed in this system.

4. Conclusions

In conclusion, electronic structure calculations carried out on PbPdO$_2$ at the hybrid HSE level suggest that the ground state of PbPdO$_2$ is actually that of a small band gap semiconductor. Slab calculations to obtain the locations of the valence and conduction bands with respect to the vacuum level suggest that PbPdO$_2$ can be easily hole-doped. Both these observations are consistent with experimental observations on the system. The valence band dispersion in this easily hole-doped material is surprisingly linear, potentially suggesting interesting low-temperature physics in this compound.

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