

Electronic structure calculations of an oxygen vacancy in KH_2PO_4

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We present first-principles total-energy density-functional theory electronic structure calculations for the neutral and charge states of an oxygen vacancy in KH_2PO_4 (KDP). Even though the overall density of states profiles for the defective KDP are quite similar to those of the perfect KDP, the oxygen vacancy in the neutral and +1 charge states induces defect states in the band gap. For the neutral oxygen vacancy, one electron is localized in the O vacancy maintaining the charge that was at that site in the pure crystal, while the neighboring P atom to the vacancy gains about one electron relative to its charge state in pure KDP. For the +1 charge oxygen vacancy, the removal of an electron reduces the occupation of the filled gap states in the neutral case from two to one electron and produces a new empty state in the gap. The new empty gap state is very close to the highest occupied states, leading to a dramatic decrease of the band gap. In sharp contrast, no defect states appear in the energy gap for the +2 charge O vacancy, where the neighboring P atom to the O vacancy almost returns to its perfect-crystal charge state. For the -1 charge oxygen vacancy, the added electron does not localize on any of the atoms near the vacancy; rather it goes into the vacancy to spin-pair with the electron that was there in the neutral vacancy.

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I. INTRODUCTION

Potassium dihydrogen phosphate KH_2PO_4 (KDP), the prototype of hydrogen-bonded (HB) ferroelectrics,¹ is probably the best known and most extensively studied HB system due to its nonlinear and electro-optical properties² and the fast rate at which large single crystals can be grown. KDP is also an ideal model system in which to study the role of intrinsic defects in complex oxide insulators.³ The KDP crystal is characterized by strong covalent bonds within the PO_4 tetrahedra which are interconnected by a network of hydrogen O—H—O bonds and an ionic bonding between the potassium cation and the PO_4 group.

A major concern in the practical applications of KDP at room temperature is that unwanted optical absorption bands are produced in the 300–650 nm spectral region, when KDP crystals are exposed to intense ultraviolet or x-ray irradiation.^{4–7} The laser-induced optical absorption bands, which significantly degrade the device performance, have been attributed to point defects created during crystal growth or produced by radiation during use.^{4–16} Davis *et al.*⁴ suggested that *proton transport* (the radiation-induced displacement of a proton from its normal site) is a major component of the mechanism responsible for the transient optical absorption. The proposed mechanism for the formation of the absorbing defect centers proceeds as follows: Two-photon absorption of high-intensity laser radiation generates electron-hole pairs, a portion of which may eventually evolve into electronic defect states that often lie within the band gap. A H^+ ion occupying a normal lattice site traps an electron to become a neutral H atom, which in turn is ejected from its original site. The oxygen atom closest to the H vacancy thus formed, traps the hole and forms the $[\text{HPO}_4]^-$ radical. Subsequent electron paramagnetic resonance (EPR)

experiments¹³ provided direct spectroscopic evidence of the $[\text{HPO}_4]^-$ hole center and of the hydrogen interstitial H^0 electron center, in support of the proton-transport mechanism.

Recently, Garces *et al.* and Chirila *et al.* used EPR to characterize a new hole trap and several electron traps in KDP and DKDP.^{16,17} The new hole center, labeled by $[\text{H}_2\text{SiO}_4]^-$, consists of a hole trapped on an oxygen ion adjacent to a silicon impurity substituting a phosphorous ion. The $(\text{PO}_3)^{2-}$ electron centers are formed when an electron is trapped at an oxygen vacancy with a hydrogen or potassium vacancy located on one of five inequivalent cation sites relative to the oxygen vacancy. Because of their greater thermal stability (they are stable at room temperature compared to the hydrogen hole and electron traps in KDP, which are only stable below 200 K), these new centers introduce long-lived absorption bands that may adversely affect the performance of KDP crystals.

In a series of recent papers,^{18,19} we reported first-principles total-energy density-functional theory electronic structure calculations for the neutral and charge states of H intrinsic (Frenkel pair) and extrinsic (H vacancy or interstitial) point defects in KDP. For the Frenkel pair, the additional hole leads to a decrease of the O—O bond length between the two O atoms next to the H vacancy, while the effect of the additional electron is small. For the H vacancy, the added hole is trapped and shared by the two O atoms adjacent to the vacancy, dramatically reducing the O—O bond length, thus forming a molecular-type polaron. The positively charged H vacancy introduces states in the gap, in sharp contrast with its neutral state. The H vacancy in its negatively charged state leads to an increase of the two O atoms close to H vacancy, and does not induce states in the gap. The negatively charged H interstitial causes the ejection of H

host atom and the subsequent formation of a H_2 interstitial molecule and a H vacancy, in agreement with experimental suggestions. In the positively charged state the H interstitial binds to its nearest-neighbor O atom forming a hydroxyl bond. The H interstitial in both positive and negative charge states induces no defect states in the band gap, in sharp contrast with its neutral state, suggesting that these defects may not be absorbing.

In the present work, we have carried out *ab initio* electronic structure calculations for an oxygen vacancy in KDP, and have investigated the effect of defect charge states. The organization of this paper is as follows. In the next section we discuss the details of the present calculations. In Sec. III we present and discuss the detailed results for the O vacancy in the neutral and various charged states. Finally, we give a brief summary in Sec. IV.

II. COMPUTATIONAL METHODS

The *ab initio* calculations we performed are based on spin-density-functional theory with the CASTEP implementation²⁰ and ultrasoft pseudopotentials.²¹ The Perdew-Burke-Ernzerhof gradient-corrected functional²² was used for the exchange-correlation potential. The kinetic energy cutoff for the plane-wave basis was set to be 680 eV, yielding a convergence for the total energy better than 1 meV/atom. Convergence tests for $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $5 \times 5 \times 5$ divisions along the reciprocal-lattice directions in the primitive unit cell of the pure KDP system according to the Monkhorst-Pack scheme²³ have shown that the total energy converges better than 0.1 meV /atom²⁴ if a $4 \times 4 \times 4$ k -point grid is used. An appropriately scaled grid is used for the supercells of KDP containing the defect which yields well-converged results for the total energy. We have used a tetragonal supercell consisting of eight KH_2PO_4 formula units (64 atoms) with lattice vectors $\mathbf{A}=a(\mathbf{i}+\mathbf{j})$, $\mathbf{B}=a(\mathbf{i}-\mathbf{j})$, and $\mathbf{C}=c\mathbf{k}$, where $a=7.49527 \text{ \AA}$ and $c=6.95749 \text{ \AA}$ are the lattice constants of the conventional unit cell of KDP.²⁴

The supercells are fully relaxed including all atoms and lattice constants with the use of conjugate gradient techniques. We remove an oxygen atom from the perfect crystal to simulate the O vacancy. The optimized geometry of the neutral system was used as the initial structure for the corresponding charged system. Due to the periodic boundary conditions inherent in electronic structure calculations, a periodic array of point defects, of atomic concentration of about 1%, is actually being simulated in the calculations. Even though this defect concentration is high relative to the experimental values (less than one defect per million), we believe that these calculations serve as a first step in understanding the effect of O vacancies and the charge state on the electronic structure of KDP. For the studies of the charged defects, an electron or two electrons are added or removed from the neutral system and a uniform background with opposite polarity is adopted automatically to keep the neutrality of the whole system; this in turn prevents the divergence in the total energy.²⁵ The electronic calculations for the -1 and $+1$ charge states are spin polarized. However, while the supercell is formally neutral for charged defects, the long-range

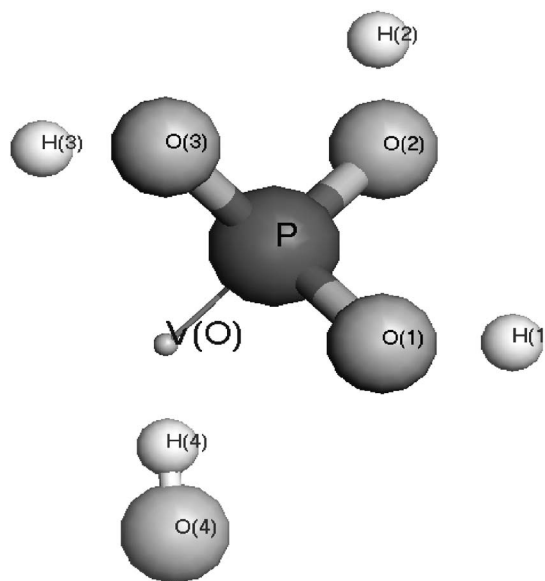


FIG. 1. Schematic view of the local atomic structure of the O vacancy in a tetrahedral PO_4 unit in KDP (The P—O and O—H bond lengths are listed in Table I). The P, O, and H atoms are labeled by black, gray, and white circles, respectively. The O(4) atom belongs to a neighboring tetrahedral PO_4 unit. The position of the O vacancy is denoted with V(O).

polarization and the effect that it may have on the local defect properties, can not be either correctly characterized nor assessed. For instance, the Madelung field, is not fully accurate. While for charged defects the field of point defects in other unit cells can be screened out approximately with a uniform distribution of opposite charge, the screening is not very accurate for near-neighbor cells, where a highly localized charge on a single ion is screened by a uniform charge throughout the cell. Higher order multiple moments of the defect in other unit cells are not fully compensated for.

III. RESULTS AND DISCUSSIONS

Figure 1 shows a schematic view of the local atomic structure of an O vacancy in a PO_4 tetrahedral unit in KDP. For convenience, we have labeled the four oxygen atoms with O(1), O(2), O(3), and O(4), and the four hydrogen atoms which are closely associated with the O vacancy with H(1), H(2), H(3), and H(4). In Table I, we summarize the results of the optimized structural parameters, such as the bond lengths and overlap populations of the bonds shown in Fig. 1, for the neutral $+1$, $+2$, and -1 charge state of the O vacancy, respectively. In Table II, we list the results of the effective atomic charges from the Mulliken population analysis²⁶ for these atoms, which are associated with and/or strongly influenced by the O vacancy.

In the neutral state, there is a small elongation of the P—O(2) bond length from 1.520 \AA in pure KDP to 1.537 \AA , indicating a weakening of the P—O(2) bond (the overlap population decreases from 0.65 $|e|$ in pure KDP to 0.55 $|e|$). On the other hand, both the P—O(1) and P—O(3) bonds increase to about 1.60 \AA and hence they weaken sig-

TABLE I. Calculated structural parameters for the neutral and charged oxygen vacancy. Distances are in Å and overlap populations in $|e|$. For the tetragonal phase of the defect-free KDP, the P—O bond length and overlap population are 1.520 Å and $0.65|e|$, respectively, and the O—H bond length and overlap population are 1.203 Å and $0.40|e|$, respectively [Ref. 24].

	Neutral state		Charged state	
	0	-1	+1	+2
Length of P—O(1)	1.598	1.579	1.508	1.497
P—O(2)	1.537	1.582	1.499	1.507
P—O(3)	1.604	1.591	1.507	1.479
O(1)—H(1)	1.039	1.057	1.427	1.633
O(2)—H(2)	1.330	1.069	1.442	1.269
O(3)—H(3)	1.049	1.042	1.361	1.536
O(4)—H(4)	1.018	1.015	0.991	1.018
Overlap of P—O(1)	0.39	0.42	0.55	0.71
P—O(2)	0.55	0.44	0.59	0.66
P—O(3)	0.39	0.41	0.56	0.77
O(1)—H(1)	0.56	0.53	0.23	0.13
O(2)—H(2)	0.31	0.53	0.23	0.35
O(3)—H(3)	0.57	0.55	0.27	0.18
O(4)—H(4)	0.54	0.55	0.60	0.61

nificantly (the overlap population decreases to $0.39|e|$). These changes in the P—O(2), P—O(1), and P—O(3) bonds are accompanied by the stretching and weakening of the O(2)—H(2) bond, and the shrinking and strengthening of both the O(1)—H(1) and O(3)—H(3) bonds, respectively. One can see from Table II that in the neutral state, the effective charge of the phosphorus atom adjacent to the O vacancy has decreased from $2.27|e|$ in pure KDP to $1.34|e|$, indicating that this P atom has gained almost one electron compared to a normal P atom in pure KDP. This result is consistent with the weakening of the P—O(2), P—O(1), and P—O(3) bonds.

In the -1 charge state, the addition of an electron primarily increases the P—O(2) bond length and decreases the O(2)—H(2) bond length compared to the neutral O vacancy case, but it has a small effect on all other bonds. Note that the three P—O bond lengths become comparable, as do the four O—H bond lengths. Since the effective charges of the

TABLE II. Effective charge ($|e|$) of those atoms markedly affected by the oxygen vacancy. For the tetragonal phase of the defect-free KDP, the charge of the oxygen and phosphorus is $-1.05|e|$ and $2.27|e|$, respectively.

	Neutral state		Charged state	
	0	-1	+1	+2
P	1.34	1.32	1.70	2.19
O(1)	-0.98	-0.99	-1.03	-1.03
O(2)	-1.04	-0.99	-1.03	-1.01
O(3)	-0.96	-0.96	-1.02	-1.07

P, O(1), O(2), and O(3) atoms in the -1 charge state are similar to those in the neutral case, it suggests that the added electron does not localize on any one of these atoms. Instead, the additional electron resides in the vacancy and spin-pairs with the electron that was there in the neutral vacancy. In the $+1$ charge state, the addition of a hole results in (i) a small shortening of the P—O(2) bond length and (ii) a much larger shortening of both the P—O(1) and P—O(3) bond length compared to the neutral case. This leads to the strengthening of the P—O(1) and P—O(3) bonds. Consequently, there is a small elongation of the O(2)—H(2) bond and a larger elongation of the O(1)—H(1) and O(3)—H(3) bonds and hence a weakening of the O—H bonds. In the $+2$ charge state, even though there are small changes in the P—O(1), P—O(2), and P—O(3) bond lengths compared to those in the $+1$ charge state, there is a greater effect on the overlap population, which indicates a strengthening of the P—O(1), P—O(2), and P—O(3) bonds. As shown in Table II, the addition of holes increases the effective charge of the neighboring P atom to the vacancy: in the $+1$ charge state, it appears that the electronic charge that was on the P atom in the neutral case begins to bleed away; in the $+2$ charged state, the P atom has returned almost to its perfect-crystal charge state.

The total density of states (DOS) for the defect-free KDP (a), the neutral O vacancy (b), the $+1$ (c), the $+2$ (d), and the -1 (e) charged O vacancy are shown in Fig. 2. Note that the valence-band maximum of the defect-free KDP is set at 0 eV in this figure. As can be seen from Figs. 2(b)–2(e), the overall DOS profiles for the defective KDP are quite similar to those of the perfect KDP. However, depending on its charge state, the oxygen vacancy may induce defect states in the band gap. For the neutral O vacancy, the highest occupied defect states, indicated by the arrow, lie in the band gap of perfect crystal and are located around 1.5 eV. Integration of the DOS in the energy region corresponding to the impurity level yields 2.0, indicating that there are two electrons at the occupied gap states. The present result for the total DOS is very similar to that encountered in the case of neutral O vacancy in α -Al₂O₃.^{27,28} The difference between the integral of the total DOS and the integral of the sum of the DOS projected on the atoms is $0.98|e|$. To clarify the spatial distribution of the defect-states for the neutral vacancy, we show in Fig. 3 the isosurface of the wave function at the Fermi energy. Note that there are atomiclike orbitals centered on the O vacancy and that the highest occupied states are localized on the O vacancy as well as the neighboring O atoms.

In Fig. 4 we show the orbital- and atom-resolved density of states for the neutral O vacancy. From Figs. 3 and 4 we can see that the occupied impurity levels in the gap are mainly composed of s and p orbitals of the P atom and p orbitals of the O(1), O(2), and O(3) atoms, and atomiclike orbitals centered on the oxygen vacancy. This result along with that of the Mulliken population analysis presented in Table II (where the effective charge of the P atom adjacent to the O vacancy has decreased from $2.27|e|$ in pure KDP to $1.34|e|$), indicate that the removal of the neutral oxygen atom causes a redistribution of electronic charge so that (i)

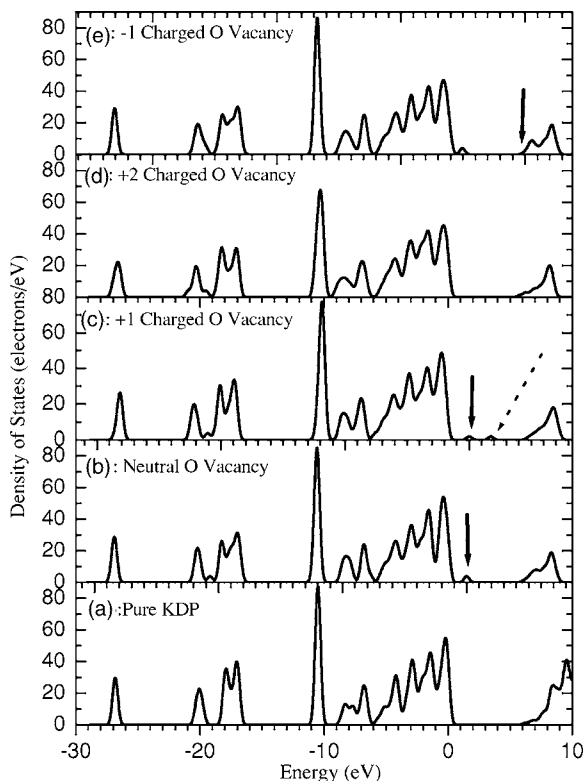


FIG. 2. Total density of states for the defect-free KDP (a), the neutral (b), +1 (c), +2 (d), and -1 (e) charged O vacancy, respectively. The valence-band maximum of the defect-free KDP is set at 0 eV. The highest occupied (empty) band gap states for the defective KDP are denoted by solid (dotted) arrows.

an electron is accommodated in the O vacancy (so that the spin is 1/2), maintaining the charge that was at that site in the pure crystal and (ii) the neighboring P atom gains about one electron, relative to its situation in the pure KDP. The net result is the formation of a two-site defect. In addition, the theoretical band gap for the neutral O vacancy decreases from 5.9 eV (pure KDP) to about 4.0 eV.

For the +1 charged O vacancy, where an electron is removed from the neutral vacancy, the filled impurity level (as indicated by the solid arrow) appears around 1.5 eV. Integra-

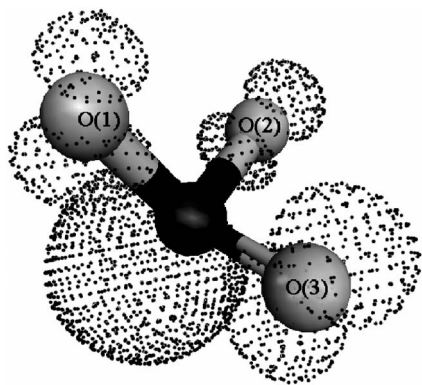


FIG. 3. Isosurface of the wave function of the highest occupied orbitals for the neutral O vacancy in KDP. The atomlike orbitals are centered on the O vacancy as well as the neighboring O atoms.

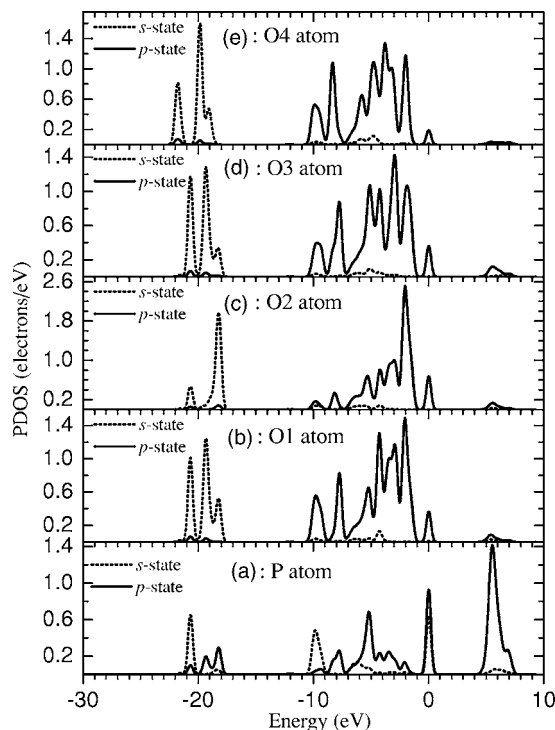


FIG. 4. Orbital- and atom-resolved partial density of states (PDOS) for the neutral O vacancy in KDP. The P, O(1), O(2), O(3), and O(4) atoms are shown in Fig. 1.

tion of the impurity DOS yields only 1.0. However, a new empty defect state (as indicated by the dotted arrow) which can accommodate one electron, appears in the gap. Namely, the removal of an electron reduces the occupation of the filled gap state in the neutral case from two to one (majority spin) and produces a new empty state of one electron (minority spin) in the gap. The new empty state is very close to the highest occupied states leading to a dramatic decrease of the band gap. Further analysis of spin-projected DOS (not shown here) indicates that the highest occupied defect-state is spin-up, while the lowest unoccupied defect state is spin down. In Fig. 5 we show the orbital- and atom-resolved density of states for the +1 charged O vacancy. The defect states in the band gap are mainly P *s*- and *p*-derived states, and O(1), O(2), and O(3) *p*-derived states. Garces *et al.*¹⁶ observed five EPR spectra representing variations of the oxygen vacancy centers. These electron centers $(\text{PO}_3)^{2-}$ were explained on the assumption that a nearby cation vacancy is a component of each defect. A divacancy, an oxygen vacancy plus a hydrogen or potassium vacancy, produces a redundant electron. Thus, this case may be to some extent similar to the +1 charged O vacancy, where there is also a single redundant electron.

In sharp contrast, no defect states appear in the energy gap for the +2 charged O vacancy, i.e., both the occupied and empty states associated with the +1 charged O vacancy disappear. Thus, the removal of two electrons completely removes the occupied gap states of the neutral case, which is consistent with the result that the neighboring P atom has returned almost to its perfect-crystal charge state and no vacancy-centered states are present. Consequently, the theo-

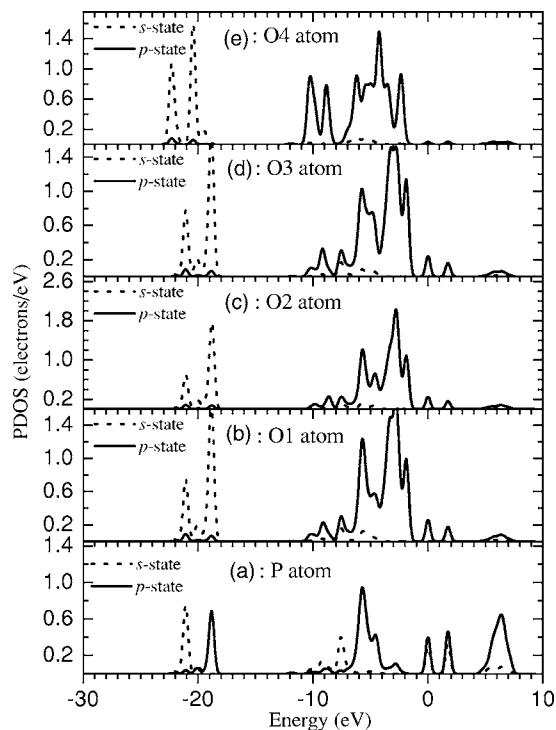


FIG. 5. Orbital- and atom-resolved partial density of states (PDOS) for the +1 charged O vacancy in KDP. The positions of the P, O(1), O(2), O(3), and O(4) atoms are shown in Fig. 1.

retical band gap returns to its value of 6 eV for pure KDP. For the -1 charged O vacancy, the defect states appear in the energy gap as in the case of the neutral O vacancy. Our conjecture that the additional electron goes into the vacancy to spin-pair with the one that was there in the neutral vacancy, is confirmed by the spin-polarized orbital analysis.

Finally, of interest is the formation energy of the oxygen vacancy. Using Eq. (4) of Ref. 19 we find that the oxygen vacancy formation energy is 5.25 eV, which is larger compared to the hydrogen vacancy (interstitial) formation energy of 3.02 eV (3.14 eV).¹⁹

IV. SUMMARY

First-principles total-energy calculations were performed to study the electronic structures for the neutral and charge

states of an oxygen vacancy in KDP. The overall DOS profiles for the defective KDP are quite similar to those of the perfect KDP. For the neutral case, the occupied defect states appear in the band gap. Integration of these defect DOS yields an occupation of 2.0, while the difference between the integral of the total DOS and the sum of the DOS projected on the atoms is 0.98 $|e|$. This suggests that an electron is accommodated in the O vacancy, maintaining the charge that was at that site in the pure crystal. The Mulliken population analysis shows that the neighboring P atom gains about one electron, relative to its charge state in pure KDP, giving rise to a two-site defect. The theoretical band gap for the neutral O vacancy decreases from 5.9 eV (pure KDP) to about 4.0 eV. For the $+1$ charge oxygen vacancy, the removal of an electron reduces the occupation of the defect states in the neutral case from two to one, and produces a new empty state in the gap, which is distinct in energy due to the spin polarization. The empty state is very close to the highest occupied states, leading to a dramatic decrease of the band gap. In sharp contrast, no defect states appear in the energy gap for the $+2$ charged O vacancy. The neighboring P atom of the vacancy returns almost to its perfect-crystal charge state and no vacancy-centered states are present. Consequently, the theoretical band gap returns to the value of 5.9 eV in pure KDP. For the -1 charge oxygen vacancy, the additional electron does not localize in the neighboring atoms, rather it goes into the O vacancy to spin pair with the electron that was there in the neutral vacancy.

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