UCRL-JRNL-210039

Electronic Structure Calculations of an Oxygen Vacancy in KH2PO4

C. S. Liu, C. J. Hou, N. Kioussis, S. Demos, H. Radousky

February 28, 2005

Physical Review B

Electronic Structure Calculations of an Oxygen Vacancy in KH_2PO_4

C. S. Liu,[1,2] C. J. Hou,[1] Nicholas Kioussis,[2] S. G. Demos,[3] and H. B. Radousky[3]
[1]*Key Laboratory of Materials Physics,*
Institute of Solid State Physics, Chinese Academy of Sciences,
P. O. Box 1129, Hefei 230031, P. R. China;
[2]*Department of Physics, California State University,*
Northridge, California 91330-8268, USA;
[3]*Lawrence Livermore National Laboratory,*
P.O. Box 808, Livermore, California 94580, USA

(Dated: February 16, 2005; Received textdate; Revised textdate; Accepted textdate; Published textdate)

Abstract

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 DOS 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, the gap states are occupied by two electrons. The difference between the integral of the total density of states (DOS) and the sum of the DOS projected on the atoms of 0.98 $|e|$, indicates that one of the two electrons resulting from the removal of the oxygen atom is trapped in the vacancy, while the other tends to delocalize in the neighboring atoms. For the +1 charge oxygen vacancy, the addition of the hole reduces the occupation of the filled gap-states in the neutral case from two to one electron and produces new empty states in the gap. The new empty gap states are very close to the highest occupied states, leading to a dramatic decrease of the band gap. The difference between the integral of the total DOS and the sum of the DOS projected on the atoms is 0.56 $|e|$, which implies that more than 56% of the redundant electron is trapped in the oxygen vacancy, and 44% spreads over the neighboring atoms. In sharp contrast, no defect states appear in the energy gap for the +2 charge O vacancy. Thus, the addition of the two holes completely compensates the two redundant electrons, and removes in turn the occupied gap states in the neutral case.

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 properties.[2] 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. KDP has found wide use as a frequency conversion crystal as well as for electro-optic modulation in various laser systems and applications. Due to the fast rate at which large single crystals can be grown, KDP and its deuterated analog known as DKDP (KD_2PO_4) are unique materials suitable for large aperture laser systems. The utilization of KDP crystals for frequency up-conversion (for example, for second and third harmonic generation in Nd:YAG lasers) makes it particularly susceptible to adverse effects arising from absorbing defects due to its exposure to higher energy protons. Such absorbing defects can lead to damage initiation at laser intensities well below the dielectric breakdown threshold of the material.[3] This problem constitutes a key limiting factor in high-power laser systems and it is believed to arise from defects created during crystal growth.[4,5]

An additional concern is the generation of transient optical absorption bands in the 300-650 nm spectral region by short-lived defects when KDP crystals are exposed to intense ultraviolet or X-ray irradiation.[6–18]Davis *et al.*[6] 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: Multi-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 resulting H vacancy traps the hole and forms the $[HPO_4]^-$ radical. Subsequent electron paramagnetic resonance (EPR) experiments[15] provided direct spectroscopic evidence of the $[HPO_4]^-$ hole center and of the hydrogen interstitial H^0 electron center, in support of the proton-transport mechanism.

Recently, Graces *et al.* and Chirila *et al.* used EPR to characterize a new hole trap and several electron traps in KDP and DKDP.[18,19] The new hole center, labeled by $[H_2SiO_4]^-$, consists of a hole trapped on an oxygen ion adjacent to a silicon impurity substituting a phosphrous ion. The $(PO_3)^{2-}$ 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 200K), these new centers introduce long-lived absorption bands that may adversely affect the performance of KDP crystals. Such defects have been suggested[3,4] also to play an important role in laser-induced damage in KDP. Namely, depending on the laser wavelength, two or three photons absorbed by neighboring defects can lead to a sufficient population of conduction band electrons to start the localized cascade multiplication process responsible for the damage initiation[3].

In a series of recent papers,[20,21] 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, reducing dramatically 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. We find that extra levels appear in the band gap for the neutral and +1 charge states. For the neutral O vacancy, one of the two electrons resulting from the removal of the oxygen atom is trapped in the oxygen vacancy, while the other tends to delocalize in the neighboring atoms. For the +1 charged O vacancy, the addition of a hole reduces the occupation of the filled gap-state in the neutral case from two to one electron and produces a new empty gap-state. The new empty state is very close the highest occupied state, which leads to a dramatic decrease of the band gap. 56% of one of the redundant electrons is trapped in the oxygen vacancy, and 44% spreads over the neighboring atoms. In sharp contrast, the addition of two holes completely compensates the two redundant electrons associated with the oxygen vacancy, and removes in turn the occupied gap-states in the neutral case.

The organization of this paper is as follows. In the next section we discuss the details of the present calculations. In Section 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 implementation[22] and ultrasoft pseudopotentials.[23] The Perdew-Burke-Ernzerhof gradient-corrected functional[24] 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 scheme[25] have shown that the total energy converges better than 0.1 meV/atom[26] 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 Å and c = 6.95749 Å are the lattice constants of the conventional unit cell of KDP.[26] 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. 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.[27]

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 analysis[28] 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 Å in pure KDP to 1.537 Å, 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 Å and hence they weaken significantly (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 lost 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 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, but rather may be trapped on the O 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 lenghts 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 expected, the addition of the holes lead to the increase of the effective charge of the P atom. One can see from Table II that 0.36 $|e|$ of the first added hole and 0.49 $|e|$ of the second hole localize on the P atom.

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 occupied defect states, as indicated by the arrow, are located around 1.5 eV. The integration of the DOS in the energy region corresponding to the impurity level is 2.0, which is consistent with the fact that removal of a neutral oxygen atom leaves two electrons. The present result for the total DOS is very similar to that encountered in the case of neutral O vacancy in α-Al_2O_3.[29,30] The difference between the integral of the total DOS and of the sum of the DOS projected on the atoms is 0.98 $|e|$. This implies that one of the two electrons is trapped in the oxygen vacancy and the other tends to delocalize in the neighboring atoms. In Fig. 3 we show the orbital- and atom-resolved density of states for the neutral O vacancy. We find that the impurity level is mainly composed of *s*- and *p*-orbitals of the P atom and *p*-orbitals of the O(1), O(2) and O(3) atoms. 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 one of the two electrons resulting from the removal of the oxygen atom is mainly localized in the P atom neighboring the O vacancy. 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, the impurity level (as indicated by the solid arrow) appears around 1.5 eV. The integration of the impurity DOS yields only 1.0. However, a new empty defect state (as indicated by the dotted arrow) which can accomodate one electron, appears in the gap. Namely, the addition of the hole reduces the occupation of the filled gap-state in the neutral case from two to one and produces a new empty state in the gap. The new empty state is very close to the highest occupied states leading to a dramatic decrease of the band gap. Thus, for the +1 charged vacancy there is only one redundant electron because the hole compensates the other electron. The difference between the integral of the total DOS and the sum of the DOS projected on the atoms is 0.56 $|e|$. This means that more than 56% of this redundant electron is trapped in the oxygen vacancy, and 44% spreads over the neighboring atoms. In Fig. 4 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. 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 addition of two holes completely compensates the two redundant electrons due to the oxygen vacancy, and it removes the occupied gap-states of the neutral case. Consequently, the theoretical 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. However, the defect states, which are occupied with one electron, appear at the bottom of the conduction band, thus, closing the band gap and rendering the system metallic.

Graces *et al.*[18] observed five EPR spectra representing variations of the oxygen vacancy centers, where the differences were attributed to the relative position of a nearby cation vacancy, i.e., either a proton or a potassium missing from one of the five inequivalent cation sites near the oxygen vacancy. These electron centers, $(PO_3)^{2-}$, were explained on the assumption that a nearby cation vacancy is a component of each defect. An oxygen vacancy formed during growth may be partially charge compensated by a hydrogen or potassium vacancy at one of these neighboring sites. Then, when an electron is trapped at the divacancy during exposure to ionizing radiation, the resulting complex will be neutral. The 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.

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, occupied defect states appear in the band gap. Integration of these defect DOS yields an occupation of 2.0, consistent with the fact that the removal of the neutral oxygen atom leaves two electrons. The difference between the integral of the total DOS and the sum of the DOS projected on the atoms of 0.98 $|e|$, indicates that one of the two electrons is trapped in the oxygen vacancy, while the other tends to delocalize in the neighboring atoms. The defect state is mainly composed of s- and p-orbitals of the P atom and p-orbitals of the O(1), O(2) and O(3) atoms. The Mulliken population analysis shows that one of the two electrons is mainly localized on the P atom neighboring the O vacancy. 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 addition of the hole reduces the occupation of the defect states in the neutral case from two to one, and produces new empty states in the gap. These empty states are very close to the highest occupied states, leading to a dramatic decrease of the band gap. The hole compensates one of the two electrons of the neutral oxygen vacancy, thus leaving one reduntant electron. The difference between the integral of the total DOS and the sum of the DOS projected on the atoms is 0.56 $|e|$, which means that more than 56% of the redundant electron is trapped in the oxygen vacancy, and 44% spreads over the neighboring atoms. In sharp contrast, no defect states appear in the energy gap for the +2 charged O vacancy, i.e., the addition of the two holes completely compensates the two redundant electrons of the oxygen vacancy, and removes in turn the occupied gap-states in the neutral case. Consequently, the theoretical band gap returns to its value of 6 eV in pure KDP.

Acknowledgments

The research at the Institute of Solid State Physics was supported through the National Natural Sciences Foundation of China under Grant Nos. 10174082 and 10374089, and by the Center for Computational Science, Hefei Institutes of Physical Sciences. The research at California State University Northridge was supported through the Lawrence Livermore National Laboratory through Grant No. B509971 and NSF Grant No. DMR-00116566 for the Parallel Computer Platform in which the calculations were carried out. The research at Lawrence Livermore National Laboratory was supported through the U.S. Department of Energy under Contract No. W-7405-ENG-48.

---

[1] R. Nelmes, Ferroelectrics **71**, 87 (1987); R. J. Nelmes, G. M. Meyer, and J. E. Tibballs, J. Phys. C **15**, 59 (1982).

[2] W. Koechner, *Solid State Laser Engineering* (Springer-Verlag, Berlin, 1999).

[3] C. W. Carr, H. B. Radousky, and S.G. Demos, Phys. Rev. Lett. **91**, 127402 (2003).

[4] C. W. Carr, H. B. Radousky, A. M. Rubenchik, M. D. Feit, and S. G. Demos, Phys. Rev. Lett. **92**, 087401 (2004).

[5] P. DeMange, C. W. Carr, R. A. Negres, H. B. Radousky, and S. G. Demos, Optics Letters, **30**, 221 (2005).

[6] J. E. Davis, R. S. Hughes, and H. W. H. Lee, Chem. Phys. Lett. **207**, 540 (1993).

[7] C. D. Marshall, S. A. Payne, M. A. Henesian, J. A. Speth, and H. T. Powell, J. Opt. Soc. Am. B **11**, 774 (1994).

[8] S. G. Demos, M. Yan, M. Staggs, J. J. De Yoreo, and H. B. Radousky, Appl. Phys. Lett. **72**, 2367 (1998).

[9] I. N. Ogorodnikov, V. Y. Yakovlev, B. V. Shul'gin, and M. K. Satybaldieva, Physics of the Solid State **44**, 845 (2002).

[10] W. E. Hughes and W. G. Moulton, J. Chem. Phys. **39**, 1359 (1963).

[11] K. Tsuchida, R. Abe, and M. Naito, J. Phys. Soc. Jpn. **35**, 806 (1973).

[12] K. Tsuchida and R. Abe, J. Phys. Soc. Jpn. **38**, 1687 (1975).

[13] J. A. McMillan and J. M. Clemens, J. Chem. Phys. **68**, 3627 (1978).

[14] J. W. Wells, E. Budzinski, and H. C. Box, J. Chem. Phys. **85**, 6340 (1986).

[15] S. D. Setzler, K. T. Stevens, L. E. Halliburton, M. Yan, N. P. Zaitseva, J. J. DeYoreo, Phys. Rev. B **57**, 2643 (1998).

[16] K. T. Stevens, N. Y. Garces, L. E. Halliburton, M. Yan, N. P. Zaitseva, J. J. DeYoreo, G. C. Catella, and J. R. Luken, Appl. Phys. Lett. **75**, 1503 (1999).

[17] S. G. Demos, M. Staggs, M. Yan, and H. B. Radousky, J. J. De Yoreo, J. Appl. Phys. **85**, 3988 (1999).

[18] N. Y. Garces, K. T. Stevens, L. E. Halliburton, S. G. Demos, H. B. Radousky, and N. P. Zaitseva, J. Appl. Phys. **89**, 47 (2001).

[19] M. M. Chirila, N. Y. Garces, L. E. Halliburton, S. G. Demos, T. A. Land, and H. B. Radousky, J. Appl. Phys. **94**, 6456 (2003).

[20] C. S. Liu, N. Kioussis, S.G. Demos, and H. B. Radousky, Phys. Rev. Lett. **91**, 015505 (2003).

[21] C. S. Liu, Q. Zhang, N. Kioussis, S.G. Demos, and H. B. Radousky, Phys. Rev. B **68**, 224107 (2003).

[22] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[23] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett **77**, 3865 (1996).

[25] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[26] Q. Zhang, F. Chen, N. Kioussis, S. G. Demos, and H. B. Radousky, Phys. Rev. B **65**, 024108(2001).

[27] M. R. Jarvis, I. D. White, R. W. Godby, and M. C. Payne, Phys. Rev. B **56**, 14972 (1997).

[28] M. D. Segall, R. Shah, J. C. Pickard, and M. C. Payne, Phys. Rev. B **54**, 16317 (1996).

[29] K. Matsunaga, T. Tanaka, T. Yamamoto, and Y. Ikuhara, Phys. Rev. B **68**, 085110 (2003).

[30] J. Carrasco, J. R. B. Gomes, and F. Illas, Phys. Rev. B **69**, 064116 (2004).

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

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.[26]].

	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

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.

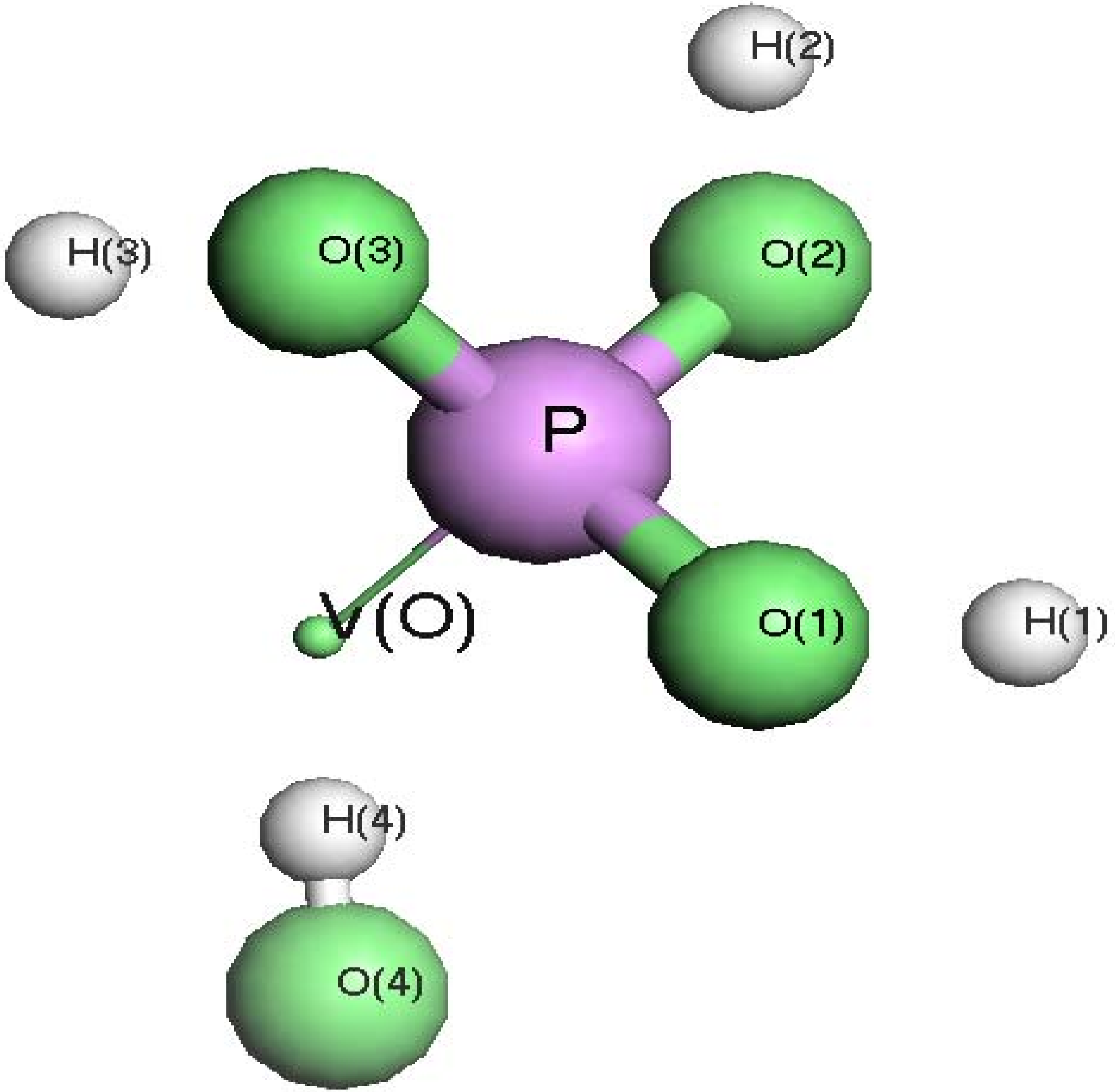
	Neutral state	Charged	state	
	0	-1	+1	+2
P	1.34	1.32	1.70	2.19
O(1)	-0.98	-0.99	-1.03	-1.03
O(2)	-1.04	-0.99	-1.03	-1.01
O(3)	-0.96	-0.96	-1.02	-1.07

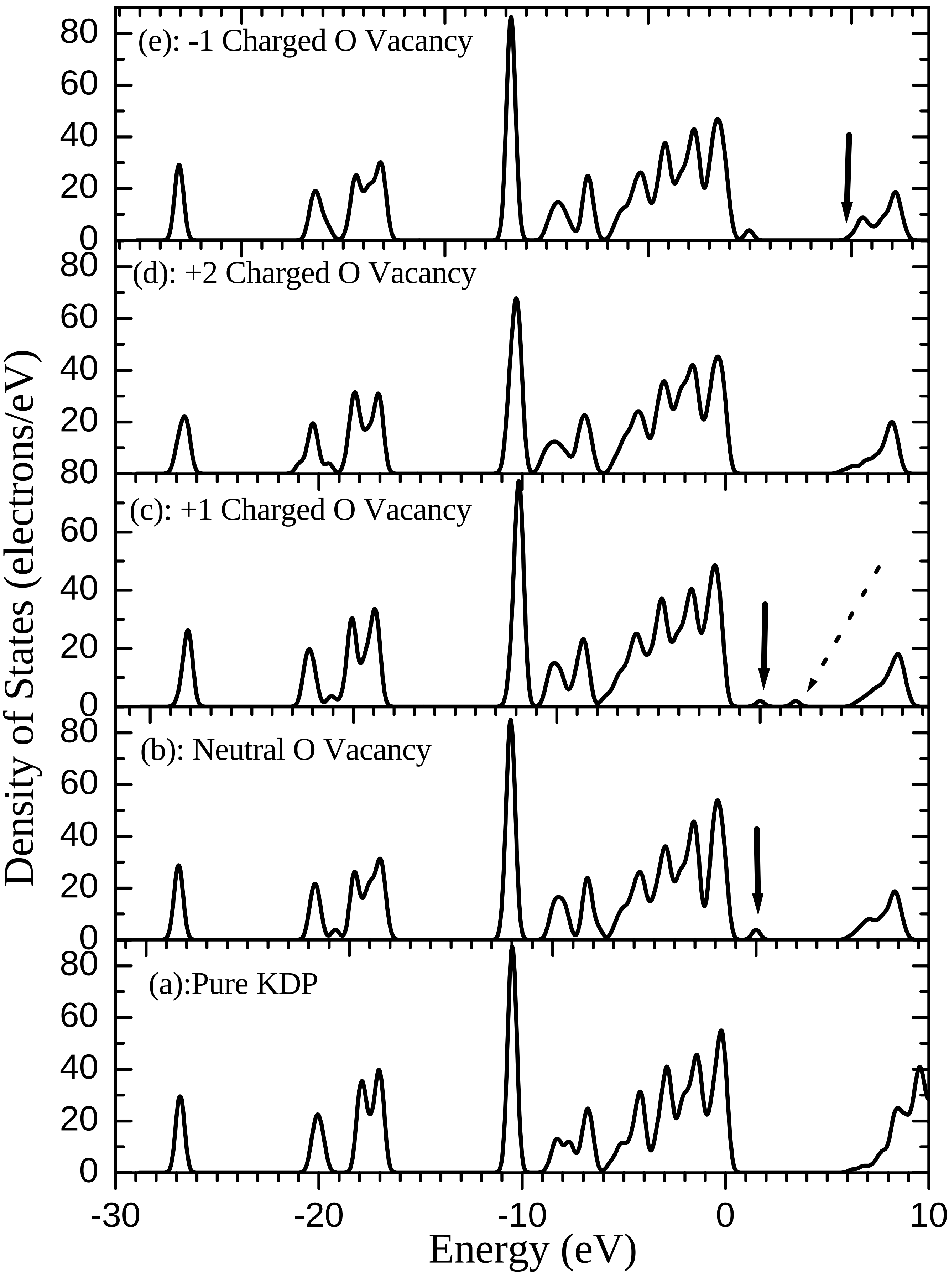
FIG. 1: Schematic view of the local atomic structure of the O vacancy in a tetrahedral PO_4 unit in KDP (The P-O and O-H bond lengths are listed in Table I). The P, O, and H atoms are labeled by purple, green, and white circles, respectively. The O(4) atom belongs to a neighboring tetrahedral PO_4 unit.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

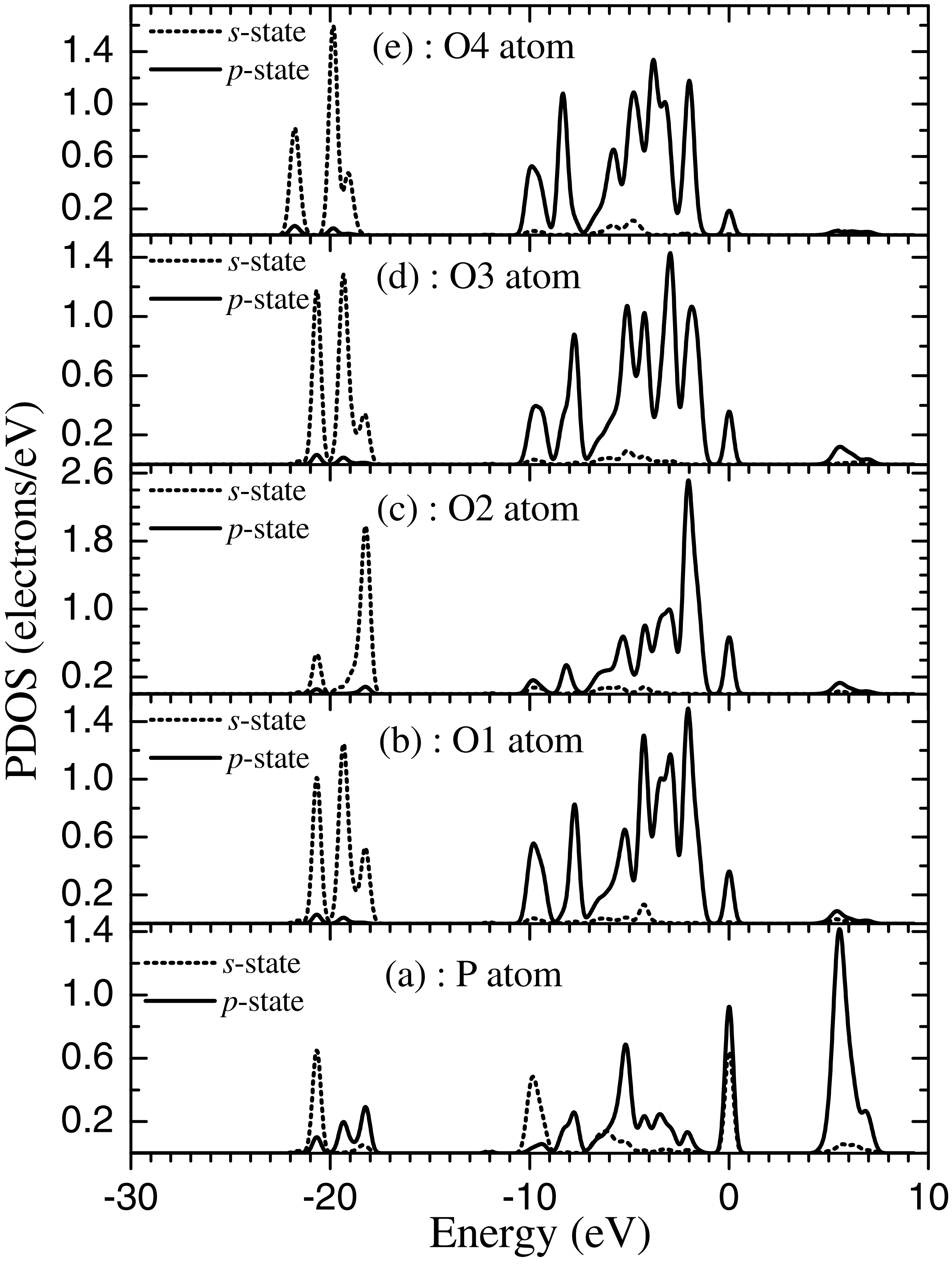
FIG. 2: Total density of states for the defect-free KDP (a), the neutral (b), +1 (c), +2 (d), and -1 (e) charged O vacancy, respectively. The valence-band maximum of the defect-free KDP is set at 0 eV. The highest occupied (unoccupied) levels for the defective KDP are denoted by solid (dotted) arrows.

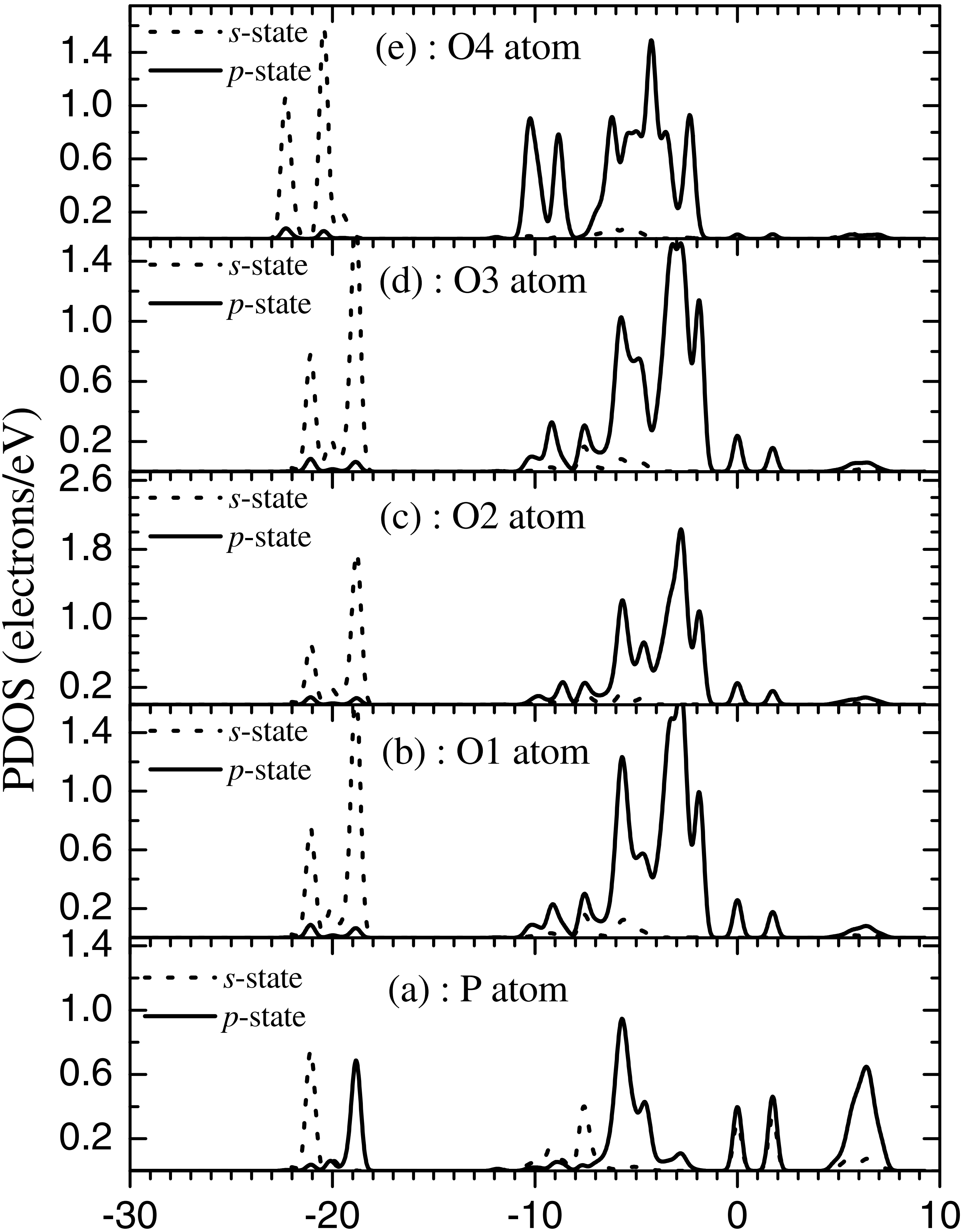
FIG. 4: Orbital- and atom-resolved partial density of states (PDOS) for the +1 charged O vacancy in KDP. The positions of the P, O(1), O(2), O(3) and O(4) atoms are shown in Fig. 1.

FIG. 3: 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


H(2)
H(3)
O(3)
O(2)
P
V(O)
O(1)
H(1)
H(4)
O(4)


(e): -1 Charged O Vacancy
(d): +2 Charged O Vacancy
(c): +1 Charged O Vacancy
(b): Neutral O Vacancy
(a):Pure KDP
Density of States (electrons/eV)
Energy (eV)
80
60
40
20
0
80
60
40
20
80
60
40
20
0
80
60
40
20
0
80
60
40
20
0
-30
-20
-10
0
10


(e) : O4 atom
(d) : O3 atom
(c) : O2 atom
(b) : O1 atom
(a) : P atom
s-state
p-state
PDOS (electrons/eV)
Energy (eV)
0.2
0.6
1.0
1.4
1.8
2.6
-30
-20
-10
0
10



(e) : O4 atom
(d) : O3 atom
(c) : O2 atom
(b) : O1 atom
(a) : P atom
s-state
p-state
PDOS (electrons/eV)
Energy (eV)
1.4
1.0
0.6
0.2
2.6
1.8
-30
-20
-10
0
10