



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Electronic structure of $KD_{2x}H_{2(1-x)}PO_4$ studied by soft x-ray absorption and emission spectroscopies

S. O. Kucheyev, C. F. Bostedt, T. van Buuren, T. M.
Willey, T. A. Land, L. J. Terminello, T. E. Felter, A. V.
Hamza, S. G. Demos, A. J. Nelson

May 4, 2004

Physical Review B

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.



Electronic structure of $\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$ studied by soft x-ray absorption and emission spectroscopies

S. O. Kucheyev,^{*} C. Bostedt,[†] T. van Buuren, T. M. Willey, T. A. Land, L. J. Terminello, T. E. Felter, A. V. Hamza, S. G. Demos, and A. J. Nelson
Lawrence Livermore National Laboratory, Livermore, California 94550
 (Dated: April 30, 2004)

The surface and bulk electronic structure of tetragonal (at 300 K) and orthorhombic (at 77 K) $\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$ single crystals (so-called KDP and DKDP), with a deuteration degree x of 0.0, 0.3, and 0.6, is studied by soft x-ray absorption near-edge structure (XANES) and non-resonant soft x-ray emission (XES) spectroscopies. High-resolution O K -edge, P $L_{2,3}$ -edge, and K $L_{2,3}$ -edge XANES and XES spectra reveal that the element-specific partial density of states in the conduction and valence bands is essentially independent of deuteration x . We give assignment of XANES and XES peaks based on previous molecular orbital and band-structure calculations. Projected densities of states in the conduction band also appear to be essentially identical for tetragonal (at 300 K) and orthorhombic (at 77 K) phases, consistent with previous band structure calculations. However, a decrease in sample temperature from 300 to 77 K results in an ~ 0.5 eV shift in the valence band edge (probed by XES), with negligible changes to the conduction band edge (probed by XANES). Results also show that high-intensity x-ray irradiation results in decomposition of these hydrogen-bonded materials into water and KPO_3 cyclo- and polyphosphates.

PACS numbers: 77.84.Fa, 78.70.Dm, 78.70.En, 71.20.Ps

I. INTRODUCTION

Potassium dihydrogen phosphate, KDP (KH_2PO_4), and its deuterated form, DKDP ($\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$), are important optical materials widely used for frequency conversion and optoelectrical switching in laser systems.¹ What makes these materials *unique* is that single-crystal KDP and DKDP can be conveniently grown with linear dimensions in the range of 50 – 100 cm, as required for large-aperture high-power lasers.^{1,2} In addition to being optical materials, KDP and DKDP are the most common hydrogen-bonded ferroelectrics.³ At room temperature and atmospheric pressure, both KDP and DKDP are paraelectric and have the tetragonal crystal structure. Below the ferroelectric phase transition temperature (122 and 228 K for KDP and DKDP, respectively),⁴ their crystal structure is orthorhombic.

The structure of KDP and DKDP consists of highly covalently bonded tetrahedral PO_4 units linked together by O–H–O hydrogen bonds and by ionic bonding between the (8-coordinated) K^+ and $(\text{H}_2\text{PO}_4)^-$ groups. Hydrogen bonds are essential for the stability of this crystal structure. Neutron diffraction experiments⁵ have shown that protons have two fixed positions along the O–H–O bonds. In the paraelectric phase, these two positions are occupied with equal probability, whereas only one position is occupied in the ferroelectric phase. At room temperature, the lattice constants of DKDP increase (from $a = 0.74529$ and $c = 0.69751$ nm up to $a = 0.74697$ and $c = 0.69766$ nm) with an increase in deuteration x from 0 to 1.⁶

Despite excellent optical characteristics and rather mature crystal growth methods^{1,2} (which are currently not attainable with other materials), KDP and DKDP are notoriously known for their complex fundamental ma-

terials properties, resulting in a range of challenging problems. In particular, these crystals (i) are water soluble, with different solubilities in H_2O and D_2O ;¹ (ii) are mechanically highly anisotropic and rather soft and brittle, with a nanoindentation hardness of ~ 2 GPa;⁷ (iii) do not have preferential cleavage planes;¹ (iv) have rather low melting points ($T_{\text{KDP}}^{\text{melt}} \approx 260$ °C and $T_{\text{DKDP}}^{\text{melt}} \approx 250$ °C);⁸ (v) decompose when heated in air above ~ 175 °C (into water and KPO_3 salt,⁹ typically a mixture of poly- and cyclophosphates, which are also sometimes called metaphosphates¹⁰); (vi) often crack when rapidly cooled/heated during processing such as cutting, polishing, and even jet drying; (vii) have a relatively low resistance to ionizing-radiation-induced damage;^{11,12} and (viii) exhibit a significant decrease in deuteration in the near-surface layer due to D/H proton exchange while stored at ambient conditions, typically developing a network of surface cracks as a result of the buildup of tensile stress in the near-surface layer.¹³ These material properties, closely related to the structure and atomic bonding, are often undesirable, and there are still a number of serious challenges to overcome with growth and processing KDP and DKDP crystals.^{1,2}

One of the most challenging scientific and technical issues for large-aperture lasers, where KDP and DKDP are the current materials of choice, is a relatively low threshold for the formation of laser-induced damage in these crystals at light intensities well below the intrinsic laser-induced breakdown threshold.² Since laser-induced damage results from the coupling of the laser beam with the electronic subsystem of the solid, the understanding of the electronic structure of KDP and DKDP is crucial for revealing the physical mechanism responsible for the initiation of damage sites and their growth with subsequent laser pulses.

To date, very few experimental studies of the electronic structure of KDP and DKDP have been reported.^{14–20} Most of these previous reports have been focused on UV absorption and reflection studies.^{14–17} However, it is well known that the correlation between optical reflection spectra and the electronic structure is not a trivial task, particularly in the case of complex materials such as KDP and DKDP.^{14,15,17} In addition, the optical absorption spectra of KDP reported in the literature^{14,16} lack sharp excitonic features,²¹ and the absorption edges do not obey the Urbach rule.^{14,17} Hence, even the values of the band gap of KDP and DKDP are still unknown. Recently, Ogorodnikov et al.,²⁰ based on their photoluminescence excitation results (revealing a peak centered on ~ 8.8 eV at 7 K) and the extrapolation (to 7 K) of optical absorption data of Baldini et al.¹⁴ (at 80, 195, and 300 K), suggested that the band gap of KDP should be in the range of 8.0 – 8.8 eV at 7 K. However, we are not aware of any reports where the value of the room-temperature band gap of KDP has been measured or estimated.²² We are also not aware of any studies of the influence of deuteration on the band gap of DKDP. Moreover, the elemental composition of the band edges and the element-specific densities of states in the valence and conduction bands in either KDP or DKDP have not been studied experimentally.

Recently, Engelhard et al.¹⁸ have reported x-ray photoelectron spectroscopy (XPS) data of water polished and ion-beam processed surfaces of rapidly-grown KDP crystals. In addition, Nelson et al.¹⁹ have shown that x-ray absorption near-edge structure (XANES) spectra of KDP surfaces are strongly affected by surface preparation conditions and, apparently, by crystal orientation. In particular, it has been shown that there is a significant change in the structure of the P $L_{2,3}$ -edge XANES spectra during thermal annealing of KDP optics at 160 °C.¹⁹

The electronic structure of KDP has been studied theoretically by molecular orbital (MO) theory^{15,23,24} and several band structure calculation methods.^{25–29} However, there is a disagreement between results of different calculations, and there are essentially no experimental data in the literature to evaluate these theoretical predictions. For example, pseudopotential calculations of Zhang et al.²⁷ have shown that the valence band of KDP is mostly formed by O $2p$ states with a small contribution from P $3p$ orbitals, while the conduction band is primarily derived from P $3s$, P $3p$, and H $1s$ orbitals with a smaller contribution from O $2p$ states. In contrast to predictions of Zhang et al.,²⁷ pseudopotential calculations by Lin et al.²⁸ (using the same computer code as the one used in Ref. 27) suggest that the K orbitals also have a significant contribution to the valence band, while the conduction band mainly consists of the O $2p$ and P $3p$ states with a minor contribution from H $1s$ and K orbitals. Such controversy in theoretical predictions, reflecting the complexity of the material, further warrants experimental studies.

We are also not aware of any previous theoretical stud-

ies of the electronic structure of DKDP. Deuteration could alter the electronic structure through the electron–phonon coupling, which is ignored in all the models reviewed in the paragraph above.^{15,23–29} Indeed, previous experiments have shown that deuteration affects a number of properties of DKDP crystals, related to the electronic structure, including lattice constants,⁴ the melting point,⁸ nonlinear optical constants,^{1,2} UV optical absorption tails,¹⁷ and UV optical reflection.¹⁷ Hence, direct studies of the effect of deuteration on the electronic structure of DKDP are needed.

In this paper, we study the surface and bulk electronic structure of optics-grade $\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$ crystals with different degrees of deuteration. We use high-resolution XANES and non-resonant x-ray emission (XES) spectroscopies. XANES and XES yield information about the partial densities of empty and filled electronic states, respectively, and bonding configurations in an element specific manner. Based on XANES and XES data, we discuss which elements dominate the structure of the band edges in KDP and DKDP and compare our findings with results of previous electronic structure calculations.^{15,23–29}

II. EXPERIMENTAL

The z - and x -cut [i.e., (001)- and (100)-oriented] tetragonal $\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$ single crystals (with $x = 0.0, 0.3, \text{ and } 0.6$) used in this study were grown by a rapid growth method at Lawrence Livermore National Laboratory.² The deuteration degree (x) was determined by elastic recoil detection analysis (ERDA), as discussed elsewhere.¹³ It has been shown in Ref. 13 that, due to deuterium–hydrogen exchange, the degree of deuteration in near-surface layers of DKDP crystals stored at ambient conditions significantly decreases within the first several days after sample polishing in D_2O . Hence, in order to study the effect of deuteration on the electronic structure, as-received KDP and DKDP samples were polished with H_2O and D_2O , respectively, and loaded into the vacuum chamber within ~ 1 min after water polishing.³⁰ Rutherford backscattering/channeling (RBS/C) spectrometry revealed a minimum RBS/C yield (normalized to the random level) of $\sim 4\%$, indicating good crystal quality of ~ 1 μm -thick near-surface layers in the as-polished samples used in the present study.

For KDP, several surface preparation conditions were used, including (i) water polishing on lens paper supplied by two different manufacturers, (ii) etching in water–ethanol solutions, and (iii) sample cleavage in air. The XANES and XES spectra presented in this article were reproducible and essentially independent of the surface preparation conditions used and sample orientation (z - versus x -cut samples).

Both XANES and XES experiments were performed at high-resolution undulator beamline 8.0 at the Advanced Light Source (ALS), Lawrence Berkeley National

Laboratory. Details of the beamline have been published elsewhere.³¹ To minimize sample charging, KDP and DKDP crystals of $\sim 4 \times 4 \times 2$ mm³ in size were wrapped in an indium metal foil and mounted on the sample holder. XANES spectra were obtained by measuring the total electron yield (TEY), by monitoring the total sample photocurrent, and the total fluorescence yield (TFY), measured with a negatively biased channeltron. The incoming radiation flux was monitored by the total photocurrent produced in a highly transmissive Au mesh inserted into the beam. All XANES spectra were normalized to the incoming photon flux. For the O *K* edge, both TEY and TFY spectra were measured at 77 and 300 K. However, sample charging prevented the measurement of TEY spectra at 77 K for P and K *L*_{2,3} edges, and only TFY spectra were recorded at 77 K. The monochromator was calibrated by aligning the σ^* exciton in the C *K*-edge of highly-oriented pyrolytic graphite (HOPG) to 291.65 eV and the O *K*-edge of a TiO₂ rutile single crystal according to the electron energy loss spectroscopy (EELS) values reported by Brydson et al.³² After a linear background subtraction, all XANES spectra were normalized to the post-edge step heights. In XES spectra, the elastic peak was used to calibrate the energy scale.

III. RESULTS AND DISCUSSION

A. Absorption: Study of empty states

1. Oxygen *K* edge

According to dipole selection rules, O *K*-edge XANES spectra of KDP reflect electron transitions from the O 1*s* core level to the O 2*p*-projected partial density of states in the conduction band. Figure 1 shows typical TEY and TFY O *K*-edge XANES spectra of KDP measured at 77 and 300 K. These spectra show a rather broad edge peak with a low intensity double-peak pre-edge feature (at 531.3 and 532.1 eV). The broad nature of the main edge peak is consistent with a broad O 2*p*-projected partial density of states in the conduction band calculated by Zhang et al.²⁷ However, the origin of the weak pre-edge double-peak structure in Fig. 1 is less clear. According to predictions of recent *ab initio* calculations of simple H-related defects in KDP,²⁹ this pre-edge feature could be related to the empty O 2*p*-projected states introduced by positively charged H vacancies ~ 2.5 eV below the conduction band of defect-free KDP. Such H-vacancy-related empty states in the band gap are derived from O 2*p* orbitals of the two O atoms next to the H vacancy, forming an O–O bond.²⁹ Note that a rather large concentration of such positively charged H vacancies would be required to produce a measurable signal in XANES spectra, and, given the immaturity of the current understanding of defects in KDP, additional experimental studies are needed before the pre-edge feature revealed in Fig. 1 is unambiguously associated with H-related defects.

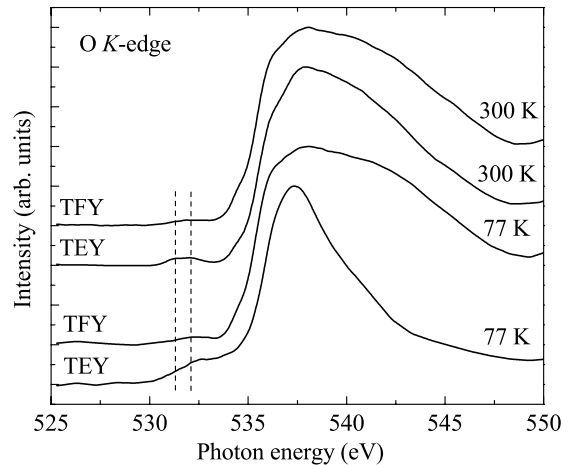


FIG. 1: Oxygen *K*-edge XANES spectra of KDP crystals measured at 77 and 300 K in TEY (surface sensitive) and TFY (bulk sensitive) modes, as indicated. Vertical dash lines show a low intensity double-peak pre-edge feature.

biguously associated with H-related defects.

Figure 1 also shows that TFY spectra, reflecting the bulk properties of the material (averaged over a depth of several hundred nanometers), are essentially identical for both tetragonal (at 300 K) and orthorhombic (at 77 K) phases. This indicates that the O 2*p*-projected partial density of states in the conduction band is similar in these two phases of KDP. This result is consistent with previous band structure calculations,²⁷ suggesting very minor differences between the electronic structure of tetragonal and orthorhombic phases of KDP. Figure 1 also shows that the more surface sensitive TEY spectra (reflecting properties of the first 10 – 20 nm from the sample surface) exhibit a significant narrowing of the main edge peak, without any measurable peak shifts, upon cooling the crystal down to 77 K. Such peak narrowing, however, could be attributed to effects of a different surface reconstruction or possibly water condensed on the sample surface with decreasing sample temperature and will not be further discussed here.

2. Phosphorous *L*_{2,3} edge

Phosphorous *L*_{2,3}-edge XANES spectra of KDP reflect the transitions of P 2*p* core electrons into the P 3*s*- and 3*d*-projected states in the conduction band. Figure 2 shows P *L*_{2,3}-edge XANES spectra of KDP at 300 K. As in the case of the O *K* edge discussed above, TFY P *L*_{2,3}-edge spectra obtained at 77 K (not shown) are qualitatively similar to those at 300 K. The three main peaks, labeled A, B, and C in Fig. 2, are split (but not necessar-

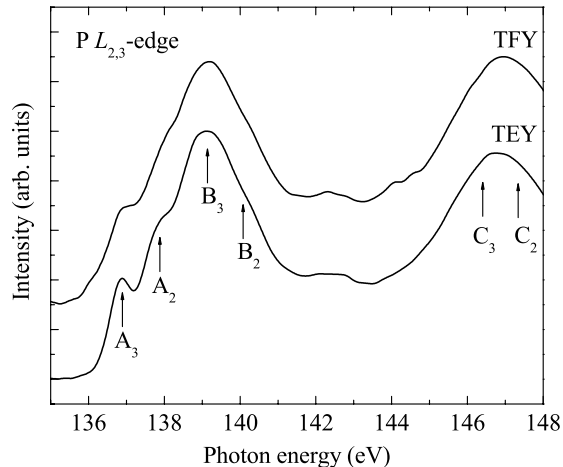


FIG. 2: Phosphorous $L_{2,3}$ -edge XANES spectra for KDP crystals at 300 K. TFY spectra at 77 K are qualitatively similar.

ily resolved) into two groups due to the spin-orbit coupling of the P $2p$ core electrons, giving rise to L_3 ($p_{3/2}$) and L_2 ($p_{1/2}$) edges. These two edges are separated by 0.86 eV, in agreement with XPS values for the spin-orbit splitting of the P $2p$ core level reported by Cavell et al.³³ A weak feature seen in both TEY and TFY spectra at ~ 142.5 eV is related to second-order residual C contamination of the Au mesh used to measure the incoming x-ray flux (i.e., an effect arising from the normalization of spectra to the photocurrent in the Au mesh). Two small intensity peaks at ~ 144.1 and 144.6 eV, observed in TFY spectra only, are due to second-order peaks associated with C impurities incorporated into the bulk of KDP and DKDP crystals during growth and will not be discussed here.³⁴

Previous $L_{2,3}$ -edge XANES studies by Sutherland et al.³⁵ have revealed a marked qualitative similarity in the main spectral features of tetrahedral oxides of several third-row elements, including Si, P, and Cl. Such qualitative similarity of the electronic structure of iso-electronic tetrahedral oxide ions ClO_4^{1-} , SiO_4^{2-} , and PO_4^{3-} has also been predicted in MO calculations of Johansen.³⁶ Based on such similarity,^{35,36} below, we assign the spectral features A, B, and C in the P $L_{2,3}$ -edge spectra shown in Fig. 2 based on the current understanding of XANES spectra of a much better studied system, SiO_2 (which is made of corner-sharing SiO_4 tetrahedra).³⁷ In the following discussion, we will ignore (wherever possible) the contribution of the H $1s$ -derived states, not directly probed in our experiments, and use the terminology of the MO in the tetrahedral symmetry. This approach seems to be justified since, based on previous MO calculations,^{15,23,24} the main effect of adding H atoms to the PO_4 group is the formation of additional

energy levels (primarily H $1s$ -derived) at the bottom of the conduction band, with relatively minor changes to the other (O- and P-derived) orbitals.

In the language of MO theory,^{15,23,24} peaks A_3 and A_2 can be attributed to electron transitions from the P $2p_{3/2}$ and $2p_{1/2}$ core levels into the a_1 antibonding orbital derived from P $3s$ and O $2p$ σ -like states. Similarly, peaks B and C are due to electron transitions into the t_2 orbital (formed by P $3p$ and O $2p$ π -like states) and the e orbital (formed by the P $3d$ and O $2p$ states), respectively. It should be noted that, in PO_4 units, the transition to the t_2 orbital is “dipole-allowed” due to strong sp^3 hybridization. In this case, the transition actually occurs from the $2p$ core level to the s -like part of the p -dominated sp^3 hybrid.³⁷ The above peak assignment is also consistent with results of band structure calculations from Ref. 27, predicting a considerable contribution from the P $3s$ states to the conduction band. However, the assignment of peaks C (which are ~ 11 eV above the absorption edge in Fig. 2) to transitions into the P $3d$ -derived e orbital is made solely based on the current understanding of XANES spectra of SiO_2 .³⁷ Indeed, the P $3d$ orbitals have not been considered in previous electronic structure calculations of DKDP.^{15,23-29}

3. Potassium $L_{2,3}$ edge

Potassium $L_{2,3}$ -edge XANES spectra of KDP reflect the transitions of K $2p$ core electrons into the empty K $4s$ and $3d$ states. The $3d$ channel is, however, by far stronger than the $4s$ channel.³⁸ Since K $3d$ states are not expected to participate in bonding in KDP or DKDP,^{15,23-29} K $L_{2,3}$ -edge XANES spectra, which map the K $3d$ empty states, do not provide information on the density of states in the conduction band. These spectra could, however, provide unique information about the symmetry and strength of the crystal field around K atoms.³⁸⁻⁴⁰

Figure 3 shows K $L_{2,3}$ -edge (above the C K edge lying around 285 eV) spectra of KDP at 300 K. In this figure, peaks are split into two groups, separated by ~ 2.7 eV, due to the spin-orbit coupling of the K $2p$ core electrons, giving rise to the L_2 and L_3 edges. For both edges shown in Fig. 3, the high-intensity peaks F are accompanied by low-intensity peaks D and E at lower energies. Note that peaks D and E are much better resolved in (surface-sensitive) TEY spectra than in (bulk-sensitive) TFY spectra. This suggests that peaks D and E are related to the lowering of the symmetry around K atoms at the surface as compared to the bulk. Similar effects of the lowering of the crystal field symmetry at the surface have previously been observed in XANES studies of different Ca compounds.³⁸ Although it is possible to extract from Fig. 3 quantitative information about the crystal field symmetry around K atoms in the bulk and at the surface, accurate theoretical modeling of these effects is beyond the scope of the present article.

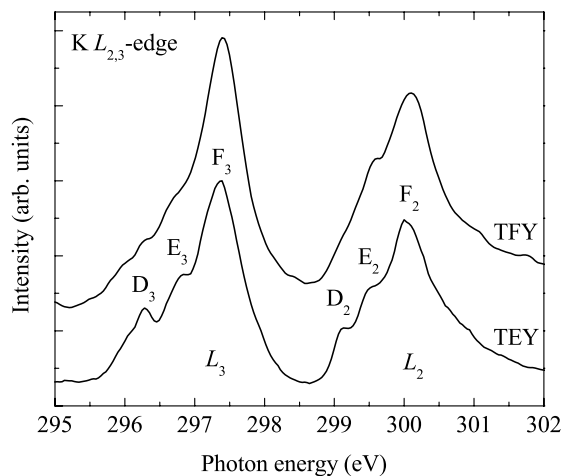


FIG. 3: Potassium $L_{2,3}$ -edge XANES spectra for KDP crystals at 300 K.

4. Effects of radiation damage

Figure 4 illustrates the effects of x-ray-induced damage on O K -edge [Fig. 4(a)] and P $L_{2,3}$ -edge [Fig. 4(b)] XANES spectra of KDP. Irradiation was done with photon energies of 550 and 145 eV in the case of the O K and P $L_{2,3}$ edges, respectively, with widely open slits, resulting in a several-fold increase in x-ray beam flux as compared to that used to acquire XANES spectra. Figure 4 clearly shows that irradiation with a high-intensity x-ray beam significantly changes both O K - and P $L_{2,3}$ -edge spectra.

For the O K -edge spectra, three additional peaks, labelled A_O , B_O , and C_O , appear in Fig. 4(a) as a result of high-intensity soft x-ray irradiation. Peaks B_O and C_O (at 534.3 and 536.0 eV, respectively) are attributed to signatures of KPO_3 formed as a result of x-ray-induced material decomposition. Indeed, it is known that thermal processing of KDP at temperatures above ~ 175 °C results in material decomposition into water and KPO_3 salt.^{9,10} To support that intense x-ray irradiation results in a similar decomposition/dehydration process, Fig. 4 also shows spectra taken from KPO_3 salt prepared by annealing of KDP (or DKDP) crystals at 350 °C for 3 hours in air. The KPO_3 salt prepared in this way is composed of a mixture of (water soluble) cyclophosphates and (water insoluble) long-chain polyphosphates, as has been discussed in detail elsewhere.¹⁰ It is seen from Fig 4(a) that peaks B_O and C_O are present in spectra from both KPO_3 and x-ray damaged KDP, supporting the above peak assignment.

It should be noted that peaks B_O and C_O might also be attributed to fingerprints of liquid water trapped in KPO_3 and formed as a result of x-ray- or thermally-

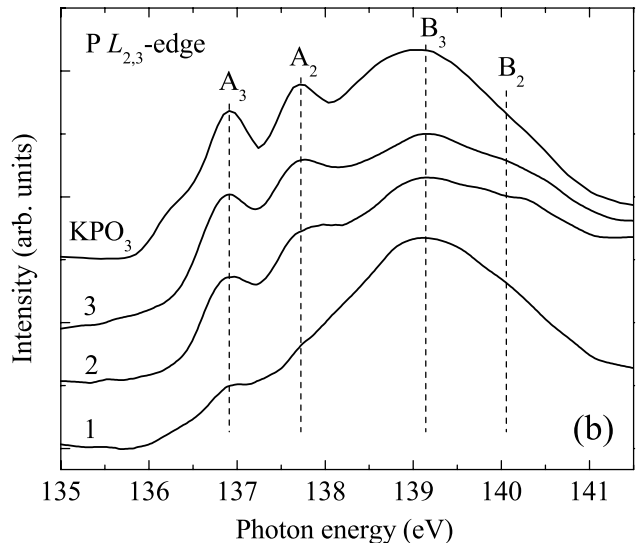
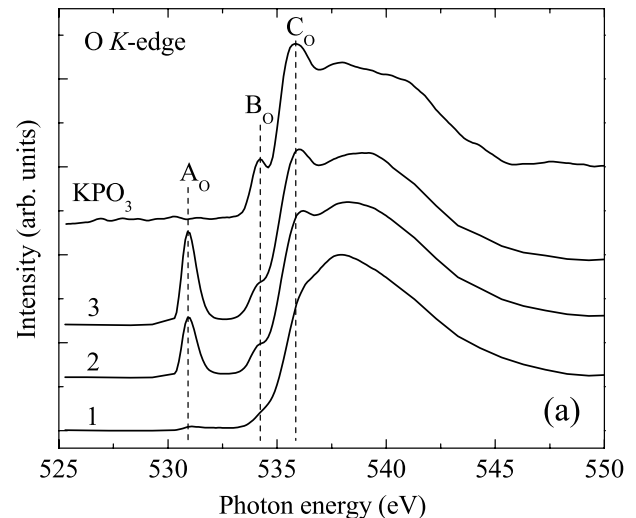


FIG. 4: (a) Oxygen K -edge and (b) P $L_{2,3}$ -edge TEY XANES spectra for KDP crystals after irradiation with a high-intensity soft x-ray beam at 300 K. Shown are spectra from the following samples: undamaged (curves 1), irradiated for ~ 5 min (curves 2), and irradiated for ~ 10 min (curves 3). Spectra from KPO_3 are also shown for comparison.

induced decomposition of KDP. Such liquid inclusions, in fact, have previously been observed in KDP crystals by x-ray topography.⁴¹ The possible assignment of peaks B_O and C_O to fingerprints of liquid water also seems to be consistent with previous XANES studies of ice and liquid water (see, for example, Refs. 42 and 43). However, our ERDA analysis¹³ of KPO_3 films produced by thermally-induced dehydration of DKDP crystals has not revealed any detectable levels of deuterium in the first ~ 500 nm from the sample surface, giving compelling evidence that peaks B_O and C_O are indeed the fingerprints of KPO_3 and not of possible inclusions of liquid water.

Figure 4(a) also shows that intense x-ray irradiation

introduces another strong pre-edge peak A_O , which is ~ 3.4 eV below peak B_O , in O K -edge XANES spectra. Note that, peak A_O , centered on 530.9 eV, is at a lower energy as compared to the low-intensity double-peak pre-edge feature (at 531.3 and 532.1 eV) observed in as-grown KDP and discussed in Sec. III A 1. Interestingly, we have found that peak A_O also appears in spectra from KPO_3 after high-intensity x-ray beam irradiation. The exact origin of this peak is unclear at the moment. It is related to some x-ray-induced defects. Pre-edge features in O K -edge XANES spectra such as peak A_O in Fig. 4(a) are often an indication of the presence of the oxygen double-bond (π^* resonance).⁴⁴ Hence, Fig. 4(a) suggests the formation of oxygen double bonds as a result of intense x-ray irradiation. Such double bonds are indeed not uncommon in the phosphate chemistry.⁴⁵ However, additional studies are currently needed to further support the assignment of peak A_O to the oxygen double bond.

Figure 4(b) shows that the relative intensity of peaks A in P $L_{2,3}$ -edge XANES spectra increases with increasing x-ray irradiation dose. This behavior is consistent with previous detailed P $L_{2,3}$ -edge XANES studies of polyphosphates,^{46,47} indicating x-ray-induced decomposition of KDP with the reduction of the relative composition of oxygen in the product salt.

B. Emission: Study of filled states

1. Oxygen $K\alpha$ emission

According to dipole selection rules, O $K\alpha$ XES spectra of KDP, shown in Fig. 5, reflect electronic transitions from O $2p$ -derived states in the valence band into the O $1s$ core hole created by the x-ray absorption process. Spectra in Fig. 5 exhibit an intense broad peak at ~ 526 eV with a low-energy tail. These spectra are, in fact, consistent with results of all previous electronic structure calculations,^{15,23–29} suggesting that the valence band of KDP is derived mostly from the O $2p$ states. It is also seen from Fig. 5 that the main emission peak shifts by ~ 0.5 eV when the sample is cooled from 300 K down to 77 K. This shift is in agreement with results of previous UV absorption studies of Baldini et al.,¹⁴ revealing a comparable (~ 0.4 eV) shift in the UV absorption tails upon decreasing sample temperature from 300 K to 80 K. Therefore, Fig. 5 as well as XANES data discussed above indicates that, with decreasing sample temperature, the major shift occurs in the valence band edge (relative to the core level), rather than in the O $2p$ - and P $3s$ -derived states of the conduction band edge, probed by XANES.

2. Phosphorous $L_{2,3}$ emission

Figure 6 shows P $L_{2,3}$ XES spectra measured at 77 and 300 K. These spectra reflect electron transitions from P

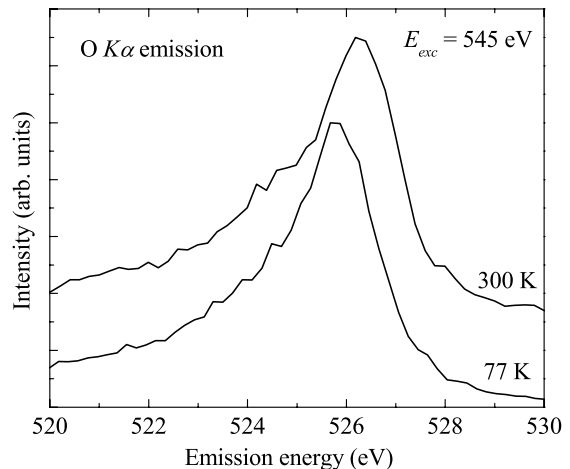


FIG. 5: Non-resonant O $K\alpha$ XES spectra for KDP crystals at 77 and 300 K. Excitation energy is 545 eV.

$3s$ -derived states of the valence band into the P $2p$ core holes. Based on previous MO calculations,^{15,23,24} the two broad peaks centered on ~ 123.5 and 127.3 eV in the room temperature spectrum in Fig. 6 could be attributed to transitions from t_2 (formed by P $3p$ and O $2p$ π -like states) and the a_1 (formed primarily by the P $3s$ states) bonding orbitals. Figure 6 also reveals a shift of the maximum of the broad main peak from ~ 127.3 eV to 125.8 eV with decreasing sample temperature from 300 to 77 K. Such an ~ 1.5 eV shift is significantly larger than the shift in the valence band edge observed in O $K\alpha$ XES spectra in Fig. 5 and discussed in the previous section. This effect indicates changes in the P $3s$ -projected density of states in the valence band upon the tetragonal–orthorhombic phase transition. Experiments with a better resolution are currently needed to further study this effect. It should also be noted that such a relatively large shift of ~ 1.5 eV does not contradict a smaller shift of ~ 0.4 eV observed in previous optical absorption studies¹⁴ and discussed above. Indeed, P $3s$ states, probed in P $L_{2,3}$ XES measurements, have essentially no contribution to the valence band maximum^{15,23–29} which determines the optical gap.

C. Effects of deuteration

Our results reveal a negligible effect of sample deuteration on XANES and XES spectra studied in this work. Indeed, we have found that O K -, P $L_{2,3}$ -, and K $L_{2,3}$ -edge XANES spectra as well as O $K\alpha$ and P $L_{2,3}$ XES spectra for $KD_{0.6}H_{1.4}PO_4$ and $KD_{1.2}H_{0.8}PO_4$ crystals are essentially identical to those for KH_2PO_4 illustrated in Figs. 1–6. This indicates that deuteration has a neg-

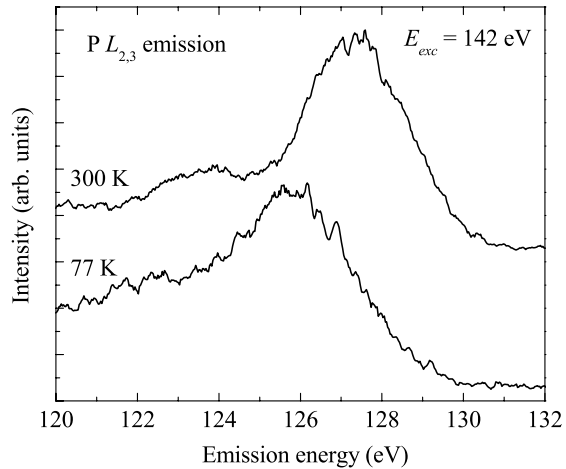


FIG. 6: Non-resonant P $L_{2,3}$ XES spectra for KDP crystals at 77 and 300 K. Excitation energy is 142 eV.

ligible effect on the O, P, and K related electronic states probed in our experiments.

It should be noted that the degree of deuteration could, in principle, affect the H $1s$ -related electronic states, not probed in our experiments, and could account for the dependence of a range of material properties on deuteration experimentally observed, as discussed in Sec. I. However, most manifestations of the effect of deuteration on the properties of DKDP observed experimentally to date (such as slight changes in the melting point, UV absorption and reflection) may simply be related to variations in the type and concentration of lattice defects and impurities in samples with different deuteration. Indeed, different growth conditions are typically used to grow crystals with different deuteration.^{1,2} The effects of deuteration reported in the literature could also be related to large tensile lattice stress associated with D/H exchange in samples stored at ambient conditions after surface polishing, as discussed in detail previously.^{7,13}

Finally, the apparently contradicting fact that the densities of states in the conduction and valence bands, probed by XANES and XES, exhibit a negligible change with a relatively large increase in the lattice constants

upon deuteration (see Sec. I) can be explained as follows. The substitution of H for D changes the length of the O–H bond, affecting the lattice constants and the distance between the PO_4 groups, whereas the deformation of the PO_4 tetrahedron is relatively small upon deuteration.^{6,48} Hence, the fact that it is the properties of the PO_4 tetrahedron which determine the electronic states probed in our experiments can explain the negligible effect of deuteration observed in this study.

IV. SUMMARY

In conclusion, we have studied empty and filled electronic states in tetragonal (at 300 K) and orthorhombic (at 77 K) $\text{KD}_{2x}\text{H}_{2(1-x)}\text{PO}_4$ single crystals by a combination of XANES and XES spectroscopies. The main conclusions of this work can be summarized as follows.

(i) Based on results of previous electronic structure calculations, assignment has been given to the XANES and XES peaks experimentally observed.

(ii) Deuteration has a negligible effect on the O, P, and K related electronic states of DKDP.

(iii) A decrease in temperature from 300 K to 77 K, accompanied by a transition from the tetragonal to orthorhombic phase, has a negligible effect on the density of O- and P-related states in the conduction band. However, such a decrease in temperature results in an ~ 0.5 eV shift in the valence band edge (opening the band gap) and changes to the P $3s$ -projected density of states in the valence band.

with a negligible shift of the conduction band edge.

(iv) High-intensity x-ray irradiation results in sample decomposition into water and cyclo- and polyphosphates.

Acknowledgments

Authors are grateful to P. Whitman for providing some of the samples investigated in this study. Work at LLNL was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

* Email address: kucheyev1@llnl.gov

† Present address: HasyLab at DESY, Notkestr. 85, 22607 Hamburg, Germany.

¹ L. N. Rashkovich, *KDP-Family Single Crystals* (Adam Hilger, Bristol, 1991).

² See, for example, a recent review by J. J. De Yoreo, A. K. Burnham, and P. K. Whitman, *Internat. Mater. Rev.* **47**, 113 (2002), and references therein.

³ See, for example, C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, NY, 1996).

⁴ G. M. Loiacono, J. F. Balascio, and W. Osborne, *Appl. Phys. Lett.* **24**, 455 (1974).

⁵ R. J. Nelmes, Z. Tun, and W. F. Kuhs, *Ferroelectrics* **71**, 125 (1987); and references therein.

⁶ W. R. Cook, Jr., *J. Appl. Phys.* **38**, 163 (1967); C. Belouet, M. Monnier, and R. Crouzier, *J. Cryst. Growth* **30**, 151

- (1975).
- ⁷ S. O. Kucheyev, W. J. Siekhaus, T. A. Land, and S. G. Demos, *Appl. Phys. Lett.* **84**, 2274 (2004).
 - ⁸ E. Rapoport, J. B. Clark, and P. W. Richter, *J. Sol. State Chem.* **24**, 423 (1978).
 - ⁹ K.-S. Lee, *J. Phys. Chem. Solids* **57**, 333 (1996); and references therein.
 - ¹⁰ A. Durif, *Crystal Chemistry of Condensed Phosphates* (Plenum, New York, 1995).
 - ¹¹ S. D. Setzler, K. T. Stevens, L. E. Halliburton, M. Yan, N. P. Zaitseva, and J. J. De Yoreo, *Phys. Rev. B* **57**, 2643 (1998).
 - ¹² S. O. Kucheyev and T. E. Felter, *J. Appl. Phys.* (accepted, scheduled on 06/15/04).
 - ¹³ S. O. Kucheyev, T. E. Felter, W. J. Siekhaus, A. J. Nelson, and A. V. Hamza, *Appl. Phys. Lett.* **84**, 1344 (2004); and references therein.
 - ¹⁴ G. Baldini, M. Cottini, and E. Grilli, *Sol. State Commun.* **11**, 1257 (1972).
 - ¹⁵ S. Saito, K. Wada, and R. Onaka, *J. Phys. Soc. Jpn.* **37**, 711 (1974).
 - ¹⁶ W. L. Smith, *Appl. Opt.* **16**, 1798 (1977).
 - ¹⁷ S. Saito and R. Onaka, *Ferroelectrics* **21**, 553 (1978).
 - ¹⁸ M. Engelhard, C. Evans, T. A. Land, and A. J. Nelson, *Surf. Sci. Spectra* **8**, 56 (2001).
 - ¹⁹ A. J. Nelson, T. van Buuren, E. Miller, T. A. Land, C. Bostedt, N. Franco, P. K. Whitman, P. A. Baisden, L. J. Terminello, and T. A. Callcott, *J. Electron Spectros.* **114**, 873 (2001).
 - ²⁰ I. N. Ogorodnikov, V. A. Pustovarov, B. V. Shul'gin, V. T. Kuanyshev, and M. K. Satybaldieva, *Optics and Spectroscopy* **91**, 224 (2001).
 - ²¹ Sharp excitonic features could be expected in optical absorption spectra of KDP and DKDP at higher photon energies than those studied in Refs. 14 and 17 (i.e., above ~ 7.7 eV). However, measurements of the optical absorption coefficient at such higher energies are hindered by problems with the preparation of thin KDP samples.
 - ²² Analysis of optical absorption spectra from Ref. 14, treating KDP as a direct band gap material, indicates that the room-temperature band gap of KDP should be ~ 7.6 eV or larger.
 - ²³ A. A. Levin, I. S. Fedorova, and A. R. Zaitsev, *Russian J. Inorg. Chem.* **32**, 782 (1987); *ibid* **33**, 34 (1988).
 - ²⁴ K. Wu and C. Chen, *Appl. Phys. A* **54**, 209 (1992).
 - ²⁵ I. V. Stasyuk and R. Y. Stetsiv, *Ferroelectrics* **144**, 195 (1993).
 - ²⁶ S. Silvi, Z. Latajka, and H. Ratajczak, *Ferroelectrics* **150**, 303 (1993).
 - ²⁷ Q. Zhang, F. Chen, N. Kioussis, S. G. Demos, and H. B. Radousky, *Phys. Rev. B* **65**, 024108 (2002).
 - ²⁸ Z. Lin, Z. Wang, C. Chen, and M.-H. Lee, *J. Chem. Phys.* **118**, 2349 (2003).
 - ²⁹ C. S. Liu, N. Kioussis, S. G. Demos, and H. B. Radousky, *Phys. Rev. Lett.* **91**, 015505 (2003).
 - ³⁰ Our previous study (Ref. 13) has shown that a negligible change in deuteration occurs in the $\sim 100 - 200$ -nm-thick near-surface layer during sample storage in air for several minutes after D₂O polishing.
 - ³¹ J. J. Jia, T. A. Callcott, J. Yurkas, A. W. Ellis, F. J. Himpsel, M. G. Samant, J. Stohr, D. L. Ederer, J. A. Carlisle, E. A. Hudson, L. J. Terminello, D. K. Shuh, and R. C. C. Perera, *Rev. Sci. Instrum.* **66**, 1394 (1995).
 - ³² R. Brydson, H. Sauer, W. Engel, J. M. Thomas, E. Zeitler, N. Kosugi, and H. Kuroda, *J. Phys. Condens. Matter* **1**, 797 (1989).
 - ³³ R. G. Cavell and K. H. Tan, *Chem. Phys. Lett.* **197**, 161 (1992).
 - ³⁴ We have observed relatively strong C-related absorption peaks in TFY spectra in all the KDP and DKDP samples studied in this work after different surface preparation conditions (such as water polishing on different lens paper, etching in water-ethanol solutions, and sample cleavage [in air]). Our detailed study of C impurities, unintentionally introduced into KDP and DKDP during crystal growth, with possible implications to the performance of KDP and DKDP as optical materials, will be reported separately.
 - ³⁵ D. G. J. Sutherland, M. Kasrai, G. M. Bancroft, Z. F. Liu, and K. H. Tan, *Phys. Rev. B* **48**, 14 989 (1993).
 - ³⁶ H. Johansen, *Theoret. Chim. Acta (Berl.)* **32**, 273 (1974).
 - ³⁷ See, for example, Z. Y. Wu, F. Jollet, and F. Seifert, *J. Phys. Condens. Matter* **10**, 8083 (1998); L. A. G. Garvie, P. Rez, J. R. Alvarez, P. R. Buseck, A. J. Craven, and R. Brydson, *Am. Mineralogist* **85**, 732 (2000); and references therein.
 - ³⁸ See, for example, F. J. Himpsel, U. O. Karlsson, A. B. McLean, L. J. Terminello, F. M. F. de Groot, M. Abbate, J. C. Fuggle, J. A. Yarmoff, B. T. Thole, and G. A. Sawatzky, *Phys. Rev. B* **43**, 6899 (1991).
 - ³⁹ F. Sette, B. Sinkovic, Y. J. Ma, and C. T. Chen, *Phys. Rev. B* **39**, 11 125 (1989).
 - ⁴⁰ F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, *Phys. Rev. B* **41**, 928 (1990).
 - ⁴¹ I. Smolski, J. J. De Yoreo, N. P. Zaitseva, J. D. Lee, T. A. Land, and E. B. Rudneva, *J. Cryst. Growth* **169**, 741 (1996).
 - ⁴² U. Bergmann, Ph. Wernet, P. Glatzel, M. Cavalleri, L. G. M. Pettersson, A. Nilsson, and S. P. Cramer, *Phys. Rev. B* **66**, 092107 (2002).
 - ⁴³ Ph. Parent, C. Laffon, C. Mangeney, F. Bournel, and M. Tronc, *J. Chem. Phys.* **117**, 10 842 (2002).
 - ⁴⁴ J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1996).
 - ⁴⁵ See, for example, F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (John Wiley and Sons, 1962).
 - ⁴⁶ Z. Yin, M. Kasrai, G. M. Bancroft, K. H. Tan and X. Feng, *Phys. Rev. B* **51**, 742 (1995).
 - ⁴⁷ Z. Yin, M. Kasrai, M. Fuller, G. M. Bancroft, K. Fyfe, and K. H. Tan, *Wear* **202**, 172 (1997).
 - ⁴⁸ H. D. Megan, *Crystal Structures* (W. B. Saunders Comp., Philadelphia, 1973).