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Ab initio study of the electronic and structural properties of the ferroelectric transition in KH_2PO_4

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First-principles electronic structure calculations were carried out for the paraelectric and ferroelectric phases of KH_2PO_4 using the pseudopotential method. The calculated structures are in good agreement with experiment. The calculations reveal that the distance δ between the two equilibrium positions of H along the O-O bond in the paraelectric phase depends on both the O-O bond length and the coordinated motion of the heavier P and K atoms. The results reconcile the previously proposed tunneling and geometric phenomenological models. The spontaneous polarization is found to arise from the redistribution of charge density caused by the displacement of the P atoms relative to the O atoms along the ferroelectric axis. The critical pressure for the transition from the orthorhombic to the tetragonal structure at zero temperature is found to be 30 kbar.

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I. INTRODUCTION

Potassium dihydrogen phosphate, KH_2PO_4 (KDP), is the prototype for a series of hydrogen-bonded ferroelectrics whose properties have attracted wide and sustained interest, due to its nonlinear optical and electro-optical properties with many applications in laser physics.[1,2] At room temperature, KDP is paraelectric and has a tetragonal crystal structure; at $T_c = 122$ K, KDP undergoes a transition to a ferroelectric phase which is orthorhombic. The ferroelectric transition has been understood on the basis of the soft-mode theory.[1] The basic concept of this theory is that one of the elementary excitations of the system becomes unstable as $T \rightarrow T_c$ and the vanishing of the frequency at $T = T_c$ corresponds to the condensation of the normal-mode displacements, which are superimposed on the structure of the high-temperature phase. According to the shape of the single-particle energy $V(Q)$ (Q are the normal coordinates), the ferroelectric phase transitions can be distinguished into (i) displacive type and (ii) order-disorder type.[1] In the first category, such as the $BaTiO_3$ system, $V(Q)$ has a single minimum at $Q = 0$ and the phase transition takes place with the condensation of a soft phonon. On the other hand, in the order-disorder type, $V(Q)$ exhibits two minima of equal depth at $Q = \pm Q_0$ and the soft collective excitations are not phonons but unstable pseudospin waves which occur in addition to all phonon modes predicted by the harmonic theory of crystal lattices.[1] Although extensive investigations have been employed during the past several decades, the atomic mechanism of the ferroelectric transition (order-disorder or displacive type) in KDP still remains unclear.[1,3,4]

Experiments suggested that in the high-temperature paraelectric phase, each hydrogen ion (proton) occupies with equal probability (50%) two equilibrium positions (separated by δ) along the O-O bond.[5] In the proton ordering (or quantum tunneling) model proposed by Blinc,[3,6] the equilibrium positions of each H to the "left" or to the "right" of the bond center are described by the pseudospin S^z, which takes values $+1$ and -1, respectively. The proton then tunnels between these two positions and the propagation of the pseudospin in the whole system is referred to as the pseudospin wave. At the transition temperature $T = T_c$, which depends on the tunneling integral and the proton-proton interaction, the frequency of the pseudospin wave decreases to zero. In other words, the ferroelectric phase transition is associated with the condensation of the pseudospin wave. Based on this model, the isotope effect [increase of the transition temperature to 229 K upon substitution of hydrogen in KDP with deuteron (DKDP) (Ref. 7)] is attributed to a change in tunneling frequency caused by the mass change from H to D. Furthermore, the decrease of T_c with pressure can also be explained by the model, assuming a decrease of the proton-proton interaction and an increase of the tunneling integral.

However, neutron diffraction data established the existence of ionic displacements parallel to the c axis to account for the spontaneous polarization, indicating that the above view of the structural phase transition needs to be extended.[5,8] Kobayashi[9] has taken account of the optical phonon mode of the [K-PO_4] complex coupled with the proton tunneling mode, showing that the transition is of displacive type. An alternative suggestion was that the phase transition is still of an order-disorder type, but triggered by the ordering of the P atoms or PO_4 groups other than H atoms.[10,11]

In the last 20 years, new results of high-resolution neutron diffraction studies raised a number of issues related to the mechanism of the phase transition.[5,8] It has been shown that structural changes in the geometry of the hydrogen bond which accompany the H/D substitution (the so-called Ubbelohde effect[12]) are closely connected with the microscopic mechanism of the phase transition. It is found that the distance δ increases upon deuteration. Similarly, the hydrostatic pressure was found to reduce the distance δ and the transition

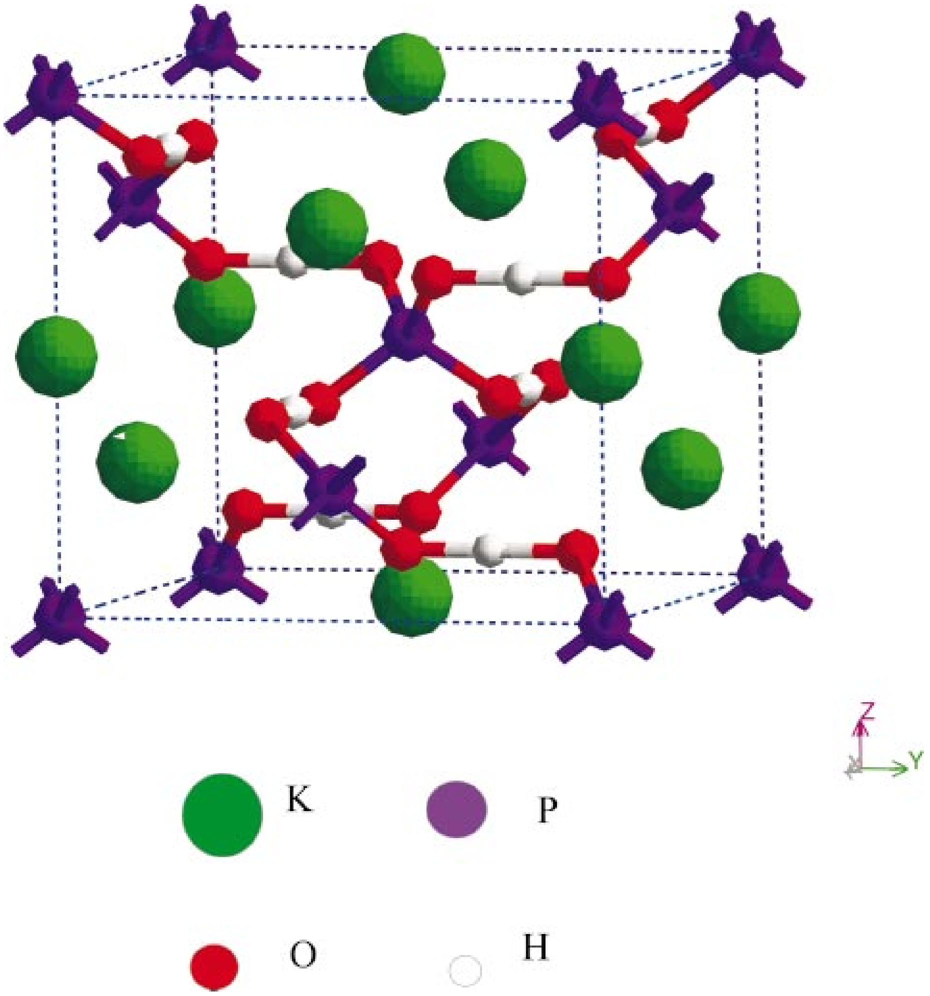

FIG. 1. (Color) The tetragonal structure of KDP. In the actual structure the H atoms are located at two equilibrium positions, which are symmetric with respect to a twofold axes along the x or y directions crossing the center of O-O bonds. Each position has 50% occupancy.

temperature in KDP. Therefore, the diffraction results lead to the conclusion that δ is the principal factor which determines T_c. Thus, new models were proposed, coupling the tunneling protons and the geometrical aspects of the hydrogen bond, to describe the isotope effect and the pressure dependence of T_c.[13–15] More recently, first-principles calculations have been carried out to study the isotope effect in $K_3H(SO_4)_2$.[16,17]

To our knowledge, no comprehensive *ab initio* calculations for KDP have been reported so far, which can provide parameter-free analysis of the structural and electronic details involved in the phase transition. There is only one research work using the periodic Hartree-Fock quantum chemical method to investigate the electronic structure and the proton transfer potential energy curve.[18] Therefore, the purpose of this work is to employ the density functional theory (DFT) to investigate the electronic structure of both the tetragonal paraelectric phase and the orthorhombic ferroelectric phase. The paper is organized as follows: in Sec. II, we describe the crystal structure and the method. We present the results of the electronic structure calculations in Sec. III. In Sec. IV, we study and discuss the tetragonal phase to show some structural characteristics responsible for the ferroelectric phase transition. Finally, Sec. V includes a brief statement of the conclusions.

II. METHOD

The first-principles electronic structure calculations employ the total energy pseudopotential method, which is well documented elsewhere.[19] The calculations were performed using the CASTEP code. The energy cutoff of the plane-wave basis functions was set to be 680 eV. Convergence tests (up to 1000 eV) have shown convergence of the total energy better than 1 meV/atom. We have used the ultrasoft pseudopotentials[20] and the Perdew-Burke-Ernzerhof gradient-corrected functional[21] for the exchange-correlation energy. The total energy of the system was minimized with respect to the electronic degrees of freedom using a density-mixing conjugate gradient scheme.[22] The atomic forces were calculated using the Hellmann-Feynman theorem which allows optimization of the atomic positions. For the reciprocal-space integration we have used the Monkhorst-Pack (MP) special **k**-point method.[23] Convergence tests were performed for 2×2×2, 4×4×4, and 5×5×5 divisions along the reciprocal-lattice directions and the total energy was found to be converged to less than 0.1 meV/atom.

The crystal structure of the tetragonal paraelectric phase has $I\bar{4}2d$ (D_{2d}^{12}) space group and the orthorhombic ferroelectric phase has $Fdd2$ (C_{2v}^{19}) space group. The crystal structure of the tetragonal is illustrated in Fig. 1 and its projection on

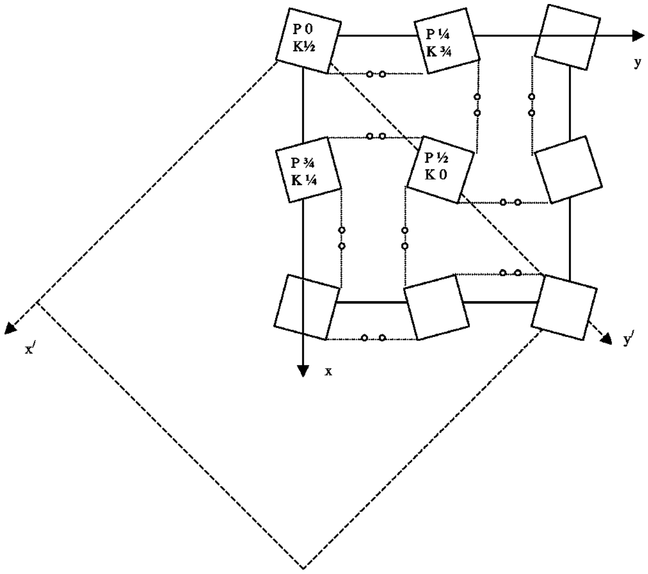

FIG. 2. The tetragonal structure of KDP, with $I\bar{4}2d$ space group, projected along the $\bar{4}$ axis (z), outlined by the solid lines. The dashed lines outline the fcc unit cell of the space group $Fdd2$, corresponding to the orthorhombic phase. Fractional coordinates along z are given for some of the atoms.

the x-y plane is shown in Fig. 2. In both cases the P atom is placed at the origin of the cell. One can see in Fig. 2 that the body-centered $I\bar{4}2d$ conventional cell containing four formula units can be easily transformed into a face-centered cell containing eight formula units, corresponding to the orthorhombic structure. The conventional cell of the orthorhombic phase has its axes x and y along the x' and y' axes, respectively, in Fig. 2. The transition from the tetragonal to the orthorhombic structure is associated with small changes in the lattice parameters and the structural displacements of the atoms. First, the H atoms order onto sites closer to the two ‘‘upper’’ O atoms of each PO_4 group, and hence the twofold axes along the x and y directions for the two PO_4 groups and the two H sites (each 50% occupied above T_c) disappears. Second, the $\bar{4}$ axis along z for each PO_4 group becomes a twofold axis, so that the four oxygen atoms of each PO_4 group, which are all symmetry related above T_c, change to two independent pairs [two O(1) atoms, and two O(2) atoms] below T_c. The H atom motion closer to O(2) atoms is accompanied with that of the P atoms, which move along $-z$ relative to the O atoms so that the P-O(1) bond length becomes shorter than that of the P-O(2), and hence the K atoms move along $+z$ relative to the O atoms.

III. RESULTS AND DISCUSSION

For both the tetragonal and orthorhombic phases we fix the space group ($I\bar{4}2d$ or $Fdd2$) and then carry out both geometric (a/b and c/b ratios) optimization and atomic relaxation to find the equilibrium configuration. For both cases, there are two potassium, two phosphorous, four hydrogen, and eight oxygens in the primitive cell. In Table I we list the calculated and experimental equilibrium lattice parameters and the atomic positions for both the tetragonal and orthorhombic phases. Overall, there is a very good agreement with experiment, especially for the orthorhombic phase. For the tetragonal phase, there are two main differences between the results of the *ab initio* calculations and experiment. First, in experiment,[8] the H atoms occupy two equilibrium sites, symmetrically displaced from the O-O midpoint, each with 50% occupation; these two sites are symmetric with respect to a

TABLE I. Comparison of the *ab initio* lattice parameters and atomic coordinates with the corresponding experimental values. Distances are in Å, and angles are in degrees.

	Tetr.		Orth.	
	Calculated	Expt.	Calculated	Expt.
a	7.49527	7.4264	10.62905	10.5459
b			10.53394	10.4664
c	6.95749	6.931	7.0138	6.9265
O/O(2) x	0.140285	0.14935	0.02999	0.03380
y	0.08153	0.08284	0.11407	0.11554
z	0.124796	0.12676	0.13191	0.13555
O(1) x			0.11444	0.11625
y			-0.03042	-0.03415
z			-0.115093	-0.11790
P-O(2)	1.5198	1.5429	1.55181	1.5719
P-O(1)	1.5198	1.5429	1.49271	1.5158
O(2)-O(1) ($2R$)	2.40554	2.4829	2.48341	2.4974
O(2)-H	1.20277	1.0712	1.06077	1.0564
O(1)-H	1.20277	1.4120	1.42263	1.4410
H-H (δ)	0.0	0.3428		
O(2)-P-O(2)	110.2	110.52	106.5	106.65
O(1)-P-O(1)			114.8	114.80

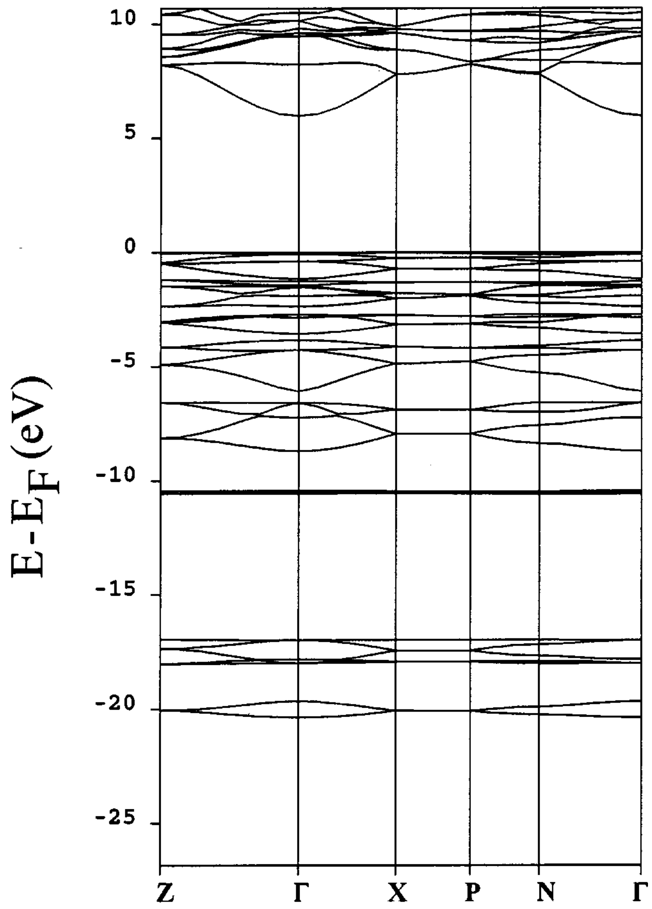

FIG. 3. Band structure for the tetragonal KDP structure along the high-symmetry axes in the Brillouin zone.

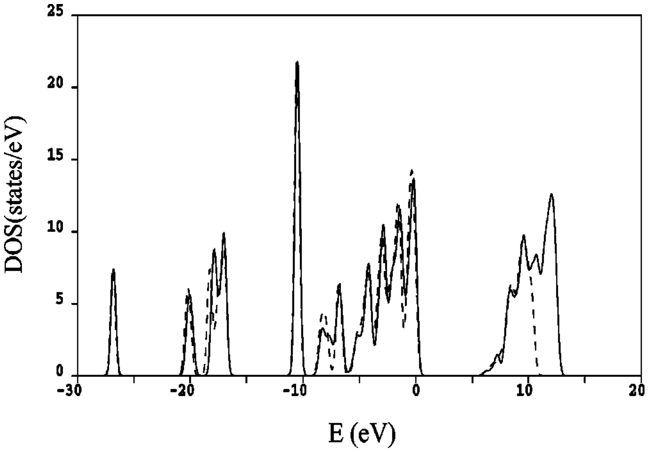

FIG. 4. Total density of states of KDP for the orthorhombic (dashed line) and the tetragonal structures (solid line).

twofold axis crossing the center of the O-O bonds. On the other hand, in the calculations, the H atoms are found to occupy the center of the O-O bonds, and the symmetry is automatically satisfied. Second, the calculated distance of the O-O bonds, $2R$, is less than the experimental value by about 0.08 Å. This discrepancy results from the symmetry constraint imposed on the system and will be discussed in Sec. IV.

We have calculated the electronic structure and density of states for both the tetragonal and orthorhombic structures. Generally speaking, there is almost no difference in the electronic structure between the tetragonal and orthorhombic phases. The band structure for the tetragonal phase is plotted along the high symmetry axes of the Brillouin zone in Fig. 3. The band structure of KDP is typical of an insulating system with an energy gap of about 5.96 eV. The total density of states (DOS) for the tetragonal and orthorhombic structures are shown in Fig. 4. In Fig. 5 we plot the partial DOS for the tetragonal phase. One can see that the valence states below the Fermi energy E_F are primarily O-*p*-derived states, whereas the lowest conduction band states (about 6 eV above E_F) are primarily of P *s* and H *s* character. The K-*p*-derived states are about 10 eV below E_F and the P *p* bonding states are centered about 6 eV below E_F.

Figures 6 and 7 we show the charge density contours of the (001) atomic planes which contain the O-H chains and the P and K atoms, respectively. In both figures, we show the charge density for both the orthorhombic (a) and the tetragonal structures (b). We find that the bonding between the O-H atoms is quite directional, whereas the charge density along the *z* direction is relatively weak. Note that the O-H-O chains are along the [110] direction in the orthorhombic structure and along the [100] direction in the tetragonal structure, and that the number of atoms in the conventional cell of the orthorhombic structure are twice as many as that in the tetragonal one. For the orthorhombic structure, since the H atoms are located at the off-center positions and the P-O(1) bonds have different length than the P-O(2) bonds, the charge density for O(1) and O(2) is not symmetric. For the (001) plane containing the P and K atoms (Fig. 7) there exists strong bonding between the P and O atoms (located above and below this plane) of the PO_4 group which has covalent character. Note that there is very weak bonding between the PO_4 group and the K atom, which reflects the presence of an ionic bond between them. The covalent bonding between the P and O atoms in the orthorhombic structure exhibits asymmetry due to the fact that the O(1) and O(2) atoms are inequivalent. Segall *et al.* used[24] a technique for the projection of plane-wave states onto a localized basis set to calculate atomic charges and bond populations by means of Mulliken analysis. In Table II we list the charge and overlap population (using a cutoff distance of 3 Å) for both the tetragonal and the orthorhombic structures. Since the distances of H-O(1) and H-O(2) and P-O(1) and P-O(2) in the tetragonal phase are identical, the overall population is the same. In conclusion, the redistribution of the charge density leads the spontaneous polarization in the ferroelectric phase.

IV. FERROELECTRIC TRANSITION

As discussed above, in the original proton-ordering model of KDP, only the rearrangement of the protons in the double well potentials along the O-O bonds was regarded as the dipolar coordinates. However, inelastic neutron-scattering experiments on DKDP have shown that the 180° out-of-phase motion of the K and P atoms along *z* is "tied" to the motion of the D atoms.[25,26] Moreover, the spontaneous po-

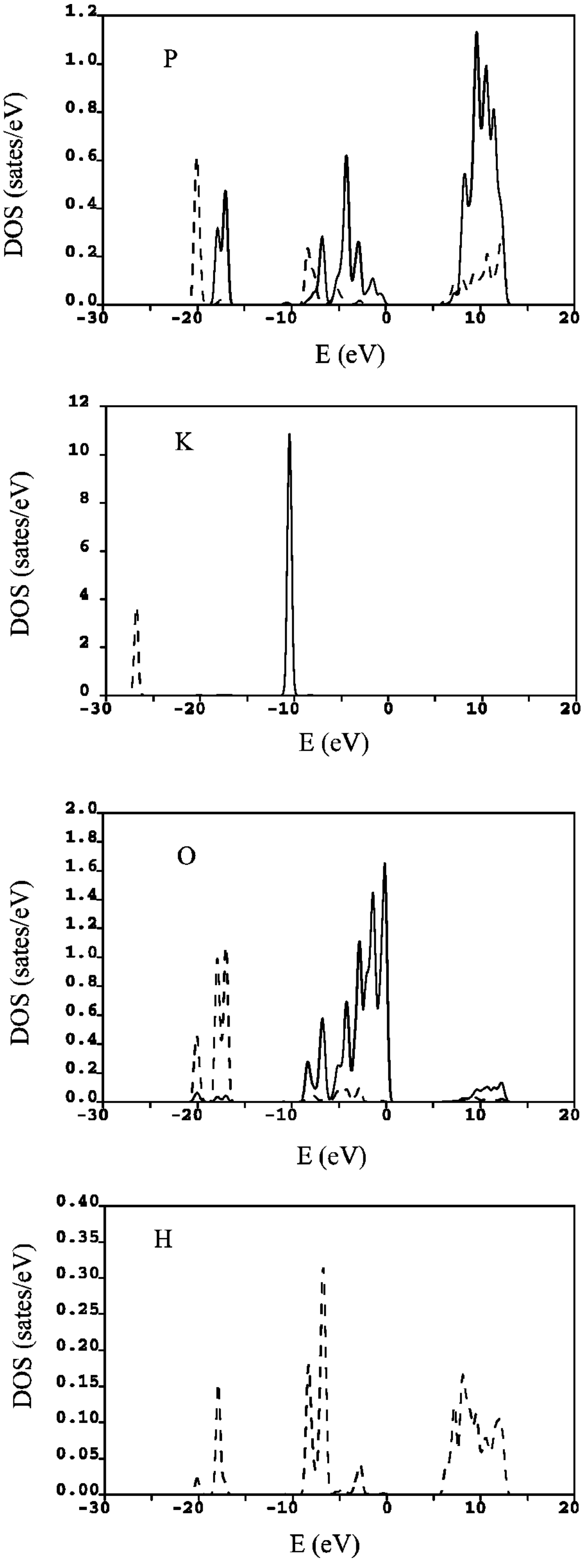

FIG. 5. Orbital- and atom-resolved partial density of states of KDP for the tetragonal structure. The dashed and solid curves represent the *s*- and *p*-projected density of states, respectively.

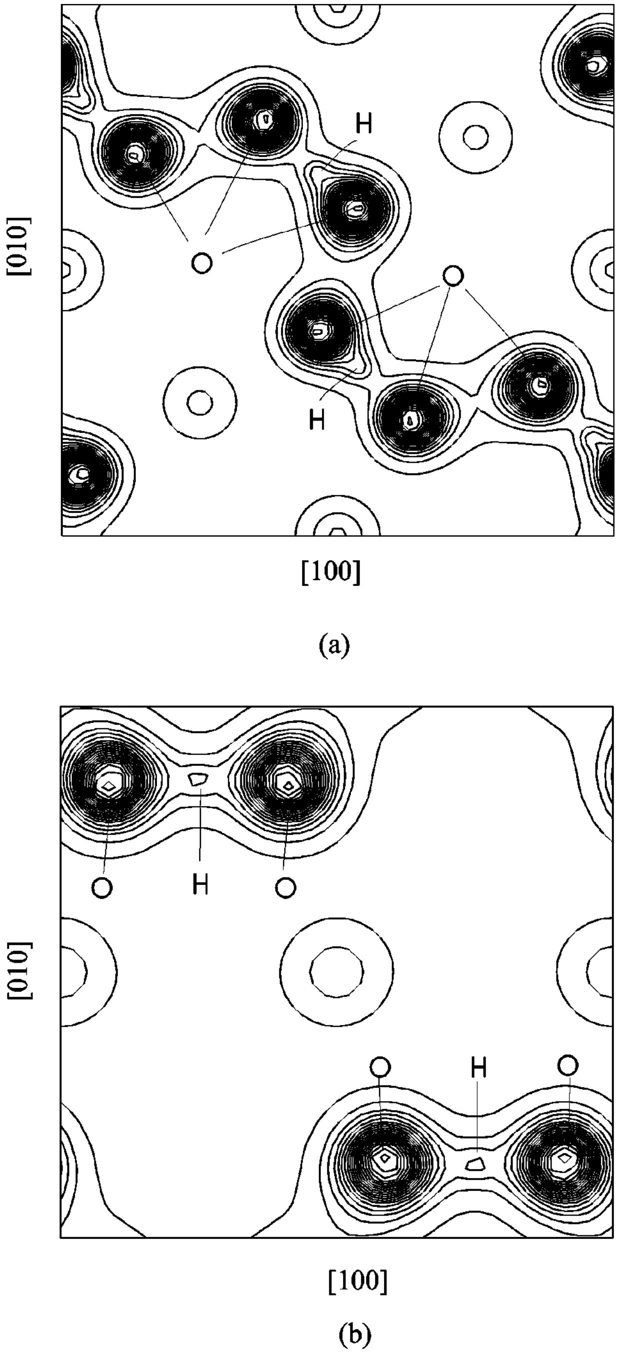

FIG. 6. Valence charge density contour plot of KDP on the (001) plane containing the O-H chains for (a) the orthorhombic and (b) the tetragonal structures.

larization in the ferroelectric phase is along the z direction due to the motion of the heavy atoms. Recent measurements of the chemical shift of ^{31}P in the vicinity of the ferroelectric transition point in KDP suggest that the transition also involves the displacive component of P.[27] Thus the question naturally arises: what is the relationship between the position of the heavier atoms (K and P) and the motion of the proton? The key to answering this question is to reveal the origin in the electronic structure of the double-well potential shape, $V(Q)$, or specifically to reproduce the two-site distribution of H with separation δ.

As was alluded to earlier in Sec. III, two main differences were found between the *ab initio* calculations and experiment for the equilibrium configuration of the tetragonal

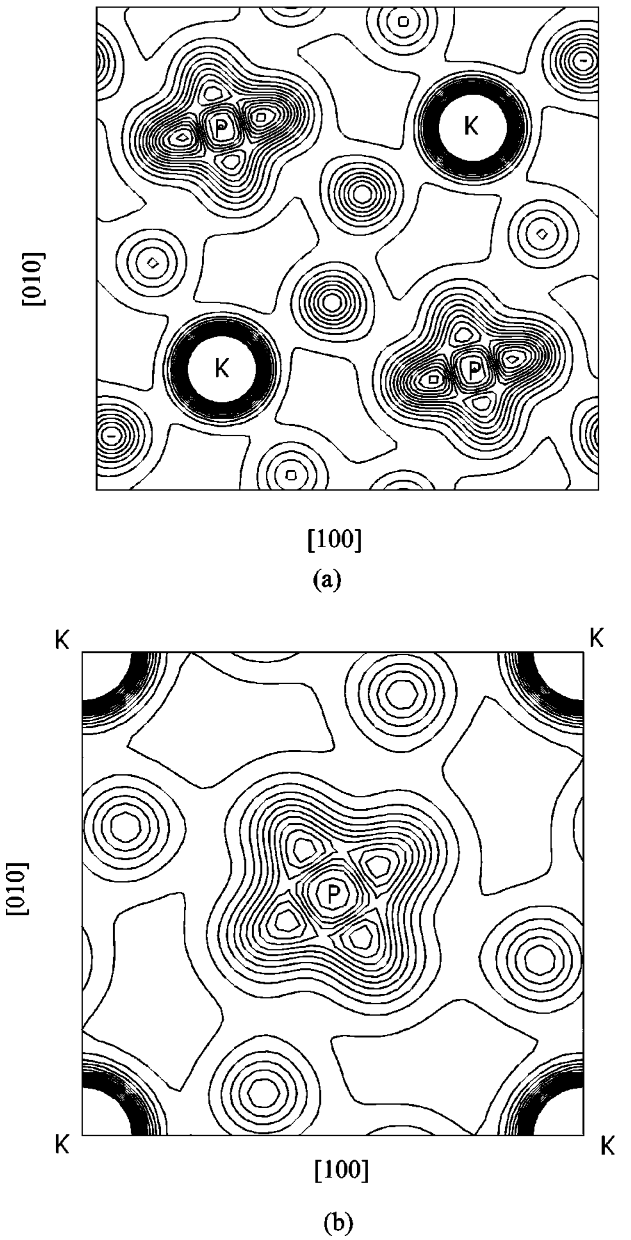

FIG. 7. Valence charge density contour plot of KDP on the (001) plane containing the P atoms for (a) the orthorhombic and (b) the tetragonal structures.

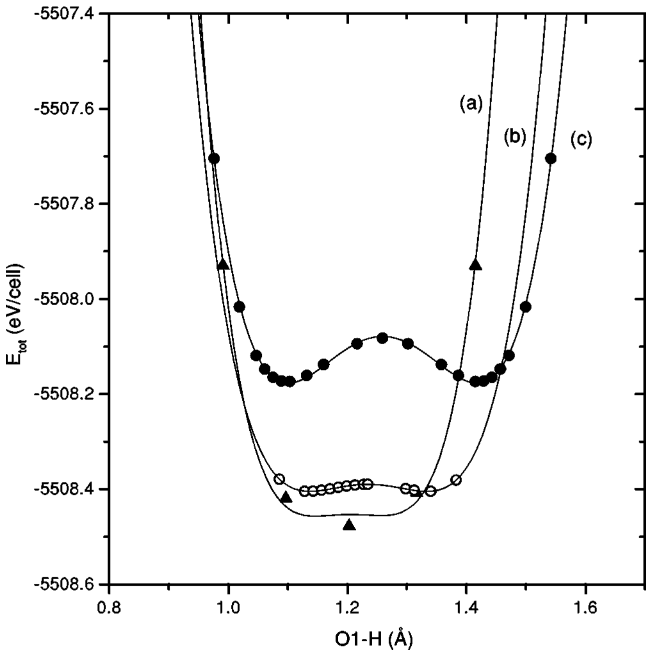

FIG. 8. Total energy vs the position of the H along the O-O bond with O-O bond length of (a) 2.405 Å, (b) 2.469 Å, and (c) 2.510 Å, respectively. The K and P atoms are frozen to their optimized values in Table I. The curves represent fits to fourth-order polynomials.

phase, i.e., the length of the O-O bond, $2R$, and the position of the H atoms. More specifically, the calculated $2R = 2.405$ Å for the tetragonal phase is smaller than the corresponding experimental value of 2.483 Å, while the value of $2R = 2.483$ Å for the orthorhombic phase is in very good agreement with experiment (Table I). The distance δ between the two equilibrium H configurations was found experimentally to depend strongly on the O-O bond length.[8,10] The O-O ($2R$) and the O-H (δ) bond lengths increase from 2.483 and 0.34 Å in KDP to 2.523 and 0.45 Å in DKDP, respectively. In order to investigate the effect of the O-O separation on the total energy in the tetragonal phase, first we have frozen the K and P atomic positions to their equilibrium optimized values (Table I) and varied the H position along the O-O bond and the O-O bond length, preserving the tetragonal structure. In Fig. 8 we show the variation of the total energy as a

TABLE II. Comparison of the charge for each atom and overlap population between atoms for the tetragonal and orthorhombic phases.

Charge	O(1)	O(2)	H	P	K
tetr.	−1.05	−1.05	0.35	2.27	1.23
orth.	−1.09	−1.02	0.37	2.27	1.20
Overlap population	O(1)-O(2)	O(1)-H	O(1)-P	O(2)-H	O(2)-P
tetr.	−0.20	0.40	0.65	0.40	0.65
orth.	−0.14	0.24	0.73	0.53	0.55

function of the H position along the O-O bond, for different O-O bond lengths of (a) 2.405 Å, (b) 2.469 Å, and (c) 2.510 Å, respectively. Note that when the O-O bond is 2.405 Å (optimized bond length in Table I) there is a single minimum at the midpoint. On the other hand, when the O-O bond length increases to 2.469 Å (experimental value) and 2.523 Å, respectively, the energy curve develops a double well, symmetrically placed with respect to the bond center, with the H tunneling between the two equilibrium positions. The hydrogen separation δ increases from 0.21 to 0.31 Å as the O-O separation increases from 2.469 and 2.51 Å, which, however, are still smaller than the experimental values of 0.34 Å in KDP and 0.45 Å in DKDP.

We next investigate the effect of the motion of K and P on the ferroelectric transition. It was found experimentally that the motion of the H(D) atoms between the two equilibrium sites is accompanied with the motion of the K and P atoms along the z axis which is out of phase. The amplitude of the soft-mode eigenvector along z, K_z, and P_z can be determined from neutron or x-ray scattering measurements. Although different methods lead to different absolute values of these amplitudes, especially for K, the estimated values are about 0.05 Å.[8] Moreover, the almost-saturated structural displacements of the P and K atoms along the z axis in the ferroelectric phase of (D)KDP have the same magnitude with the P_z and K_z. Therefore, it is reasonable to take in this work the displacements of P and K along z in the orthorhombic structure as the soft-mode eigenvector, with values $P_z = 0.056$ Å and $K_z = 0.03$ Å, respectively. It will be shown below that while the optimized value of P_z is strongly correlated with the O-O bond length $2R$, it has a small effect on the total energy.

In these calculations the symmetry of space group $I\overline{4}2d$ for the tetragonal phase was broken artificially by moving the P and K atoms out of phase along z. The H atoms were then moved along the O-H-O bonds to determine the equilibrium position. Figure 9 shows the variation of the total energy as a function of the H position along the O-H-O bond in the distorted structures for different values of the O-O bond length $2R$ of (a) 2.405 Å, (b) 2.469 Å, and (c) 2.510 Å, respectively. One can see that when P (K) moves along $-z$ $(+z)$, H will be closer to O(2) otherwise, when P (K) moves along $+z$ $(-z)$, H will be closer to O(1). Therefore, there are two equilibrium positions for H caused by the out-of-phase motion of P and K. The energy curves can be fitted by a double-well shape which is asymmetric about each minimum, i.e., steeper towards the nearest oxygen. More importantly, the double-well potential shape depends strongly on the O-O bond length, which can be described by two parameters: the distance of the two energy minima δ and the value of the minimum of the total energy E. The value of E is almost the same as that of the orthorhombic phase. Correspondingly, for the case where the K and P atoms were frozen to their optimized values, we denote the distance between the two potential wells and the minimum of the total energy in Fig. 8 as δ_1 and E_1, respectively.

In Fig. 10 we display the variation of these parameters as a function of the O-O bond length $2R$, for both cases where the K and P were frozen to their optimized positions and where they were allowed to move out of phase. The fact that E is lower than E_1 demonstrates that the out-of-phase motion of the K and P atoms lowers the energy. It is important to note that E reaches its minimum when the O-O bond length $2R = 2.469$ Å, in excellent agreement with experiment. Furthermore, for the equilibrium value $2R = 2.469$ Å the separation δ between the double wells is 0.34 Å, also in excellent agreement with experiment.[8] A further corroboration of the *ab initio* calculations is that it predicts that the energy barrier between the double wells is 0.29 eV in good agreement with the value of 0.37 eV obtained from the best-fitting double-Morse potential for KDP (Ref. 8) and the value of 0.24 eV from more recent experiments.[28]

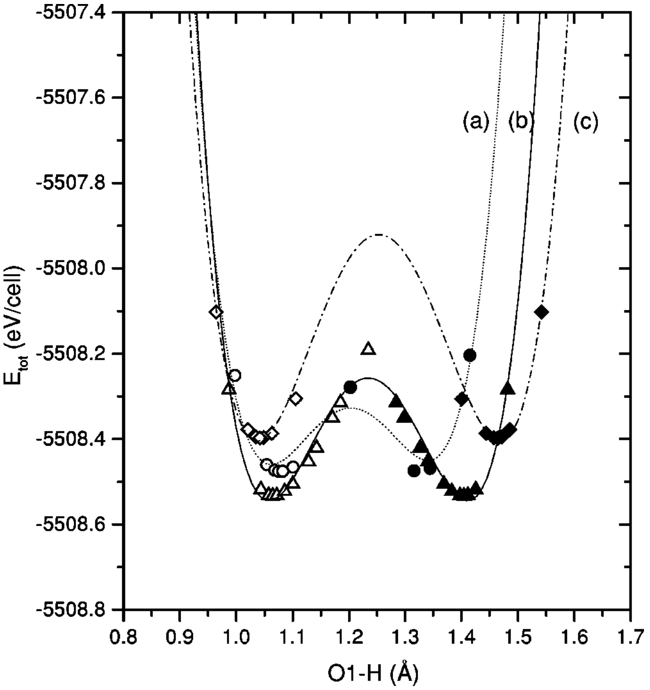

FIG. 9. Total energy vs the position of H along the O-O bond with O-O bond length of (a) 2.405 Å, (b) 2.469 Å, and (c) 2.510 Å, respectively. The P and K atoms move out of phase: solid symbols denote the displacements of P along $-z$ by 0.056 Å and K along $+z$ by 0.03 Å; open symbols denote the displacements of P along $+z$ by 0.056 Å and K along $-z$ by 0.03 Å. The curves have been fitted to fourth-order polynomials.

When $2R$ is 2.51 Å, as that in DKDP, the value of δ increases to 0.41 Å, quite close to the experimental value.[8] These results indicate that the value of δ depends on two important atomic parameters: the O-O bond length and the out-of-phase motion of the P and K atoms along the z direction. In the tetragonal phase of KDP above T_c, the double-well potential for the H atoms is due to the motion of the heavy atoms along the z direction. At the transition temperature, the rearrangement takes place not only for the H atoms, but also for the heavy atoms. In fact, the structural transition from the tetragonal phase to orthorhombic phase involves all the atoms in the cell, including P, K, O, and H, although the significance of the various atomic displacements is different. More specifically, if we allow only the displacement of the K

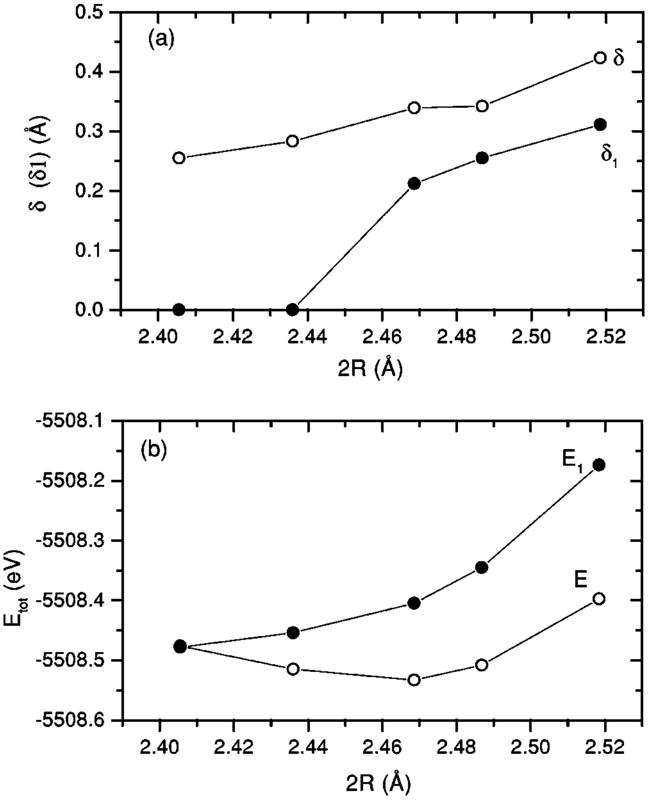

FIG. 10. Variation of (a) the separation of the double wells, δ and δ_1, and (b) the energy minima E_1 and E in Figs. 8 and 9, respectively, as a function of the O-O bond length $2R$. The definition of these parameters is discussed in detail in the text.

atoms, there is no double-well potential. On the other hand, if we displace only the P atoms, the energy curve does exhibit a double-well shape, suggesting that the relative displacement between the P and O atoms is the dominant factor. This in turn determines the position of H, and the motion of K can be neglected.

However, these results cannot clarify whether the motion of the heavy atoms along z is an optical or a pseudospin mode. In other words, whether the ferroelectric transition is of displacive or of order-disorder type still remains an open question. To clarify this issue, further theoretical and experimental work needs to be carried out. However, the *ab initio* calculations presented here show that the vibrational modes of the P atoms cause the double-well potential for each H atom and can be used to provide some insight into the original tunneling model. In the model the transition temperature is given by[1]

$$\frac{2\Omega}{J}=\tanh\left(\frac{\Omega}{2k_BT_c}\right), \tag{1}$$

where Ω is the tunneling integral and J is the dipolar interaction. Accordingly, substitution of H by D decreases the tunneling integral and hence increases T_c. It should be noted that the calculated total energy for the system is at zero temperature, whereas the stability of the ferroelectric or paraelectric phase is determined by the free energy of the system as a function of temperature. According to Blinc's tunneling model,[1] the zero-temperature intrinsic energy for the paraelectric and ferroelectric phases is $-\Omega/2$ and $-J/4$, respectively. When $\Omega/2>J/4$, the paraelectric phase is more stable than the ferroelectric phase; Eq. (1) has no real solution which in turn indicates that no ordering occurs and hence the system remains paraelectric at all temperatures. The *ab initio* calculated total energy can be used to evaluate the parameters Ω and J which determine the transition tendency of the system. From Fig. 10, one sees that the minimum energy $E=-J/4$ for the ferroelectric phase at zero external pressure occurs at $2R=2.469\,\text{Å}$. On the other hand, the minimum of the total energy for the paraelectric phase, $E_1=-\Omega/2$, occurs at $2R=2.405\,\text{Å}$. This indicates that decreasing the O-O bond length $2R$ will make the paraelectric phase more stable. Accordingly, substitution of H by D will increase $2R$ and hence decrease Ω and J, resulting in a higher T_c. Therefore, the change of Ω and hence of T_c upon deuteration does not arise solely from changes of the tunneling matrix elements due to the mass difference, but also from the geometric effect. These results seem to support Nelmes conclusion that a part of the increase (about 40 K) in T_c is caused by a direct tunneling effect and the other is due to the geometric effect.[29]

Similarly, increasing the external pressure (decreasing $2R$) increases the energy of the ferroelectric phase and stabilizes the paraelectric phase, leading to a lower transition temperature. At $2R=2.405\,\text{Å}$, we find that $E_1=E$ and hence $\Omega=J/2$, yielding $T_c=0$ [Eq. (1)]. At this point, we find that $\delta=0.24\,\text{Å}$ and $\delta_1=0$. The *ab initio* calculated value for δ agrees well with the corresponding experimental one of 0.22 Å obtained from the T_c vs δ data extrapolated to $T_c=0$.[30] It is important to note that this nonzero δ value arises solely from the displacements of the heavy atoms. Namely, had the heavy atoms been frozen, there would be only one equilibrium position for H at the center of the O-O bond (δ). The *ab initio* calculations point out that the equilibrium configuration for the paraelectric phase obtained by geometric optimization is that with the lowest total energy and it cannot transform to the ferroelectric phase. For the ferroelectric phase, the spontaneous polarization is proportional to the thermal expectation value of the pseudospin $\langle S_z\rangle$, $\langle S_z\rangle=[\frac{1}{4}-\Omega/J]^{1/2}$. Therefore, according to our calculations, increasing the external pressure will increase Ω and decrease J, leading to a decrease of T_c, consistent with the experimental results.[31]

We have calculated the variation of the total energy with volume for both the orthorhombic and tetragonal phases to determine the critical pressure at which $T_c=0$. For the paraelectric phase, the equation of state is calculated for the structure of $I\bar{4}2d$ space group and certainly the H atoms are at the center of the O-O bonds ($\delta=0$). For each volume, we varied the lattice constant ratios c/a or b/a and the atomic positions to determine the ground-state energy. The equation of state curves are shown in Fig. 11 fitted to polynomial functions. The variation of the O-O bond length $2R$ with volume for the tetragonal and orthorhombic structures is shown in Fig. 12. Note that $2R$ depends strongly on the volume in the ferroelectric phase, but not in the paraelectric

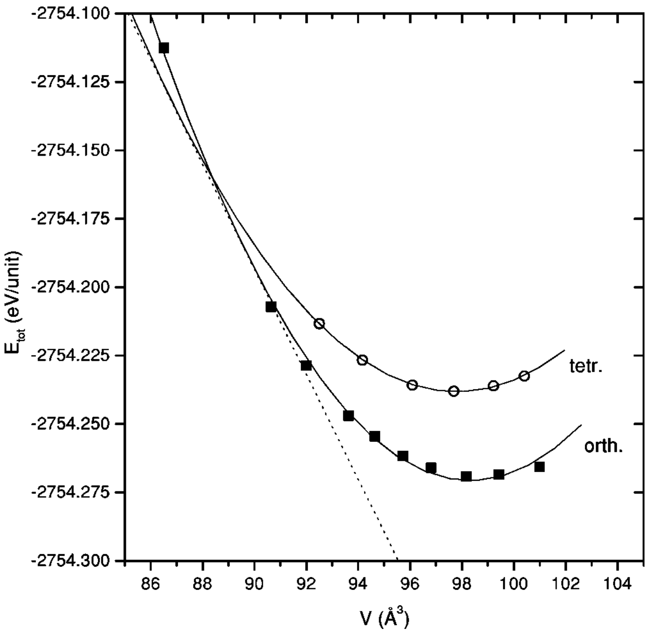

FIG. 11. Total energy vs volume for the tetragonal and orthorhombic phases of KDP. The straight line represents the common tangent for the determination of the critical pressure.

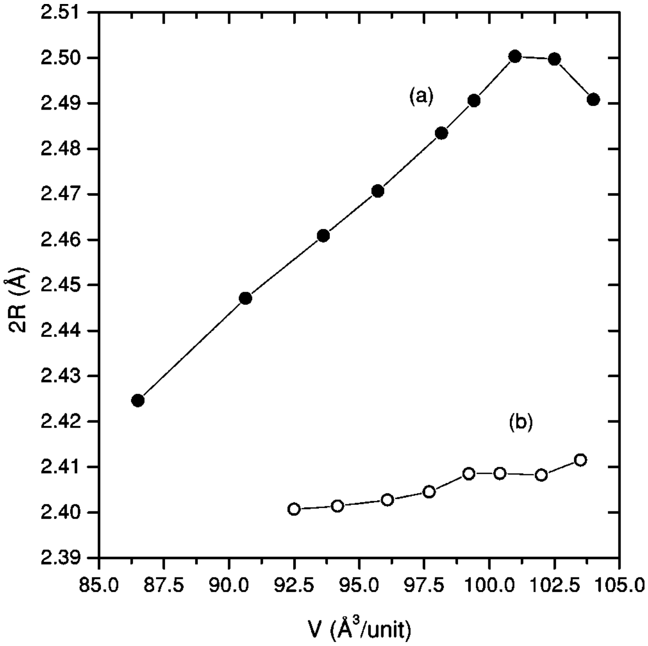

FIG. 12. Variation of the O-O bond length $2R$ with the volume of the unit cell for (a) the orthorhombic and (b) the tetragonal phases.

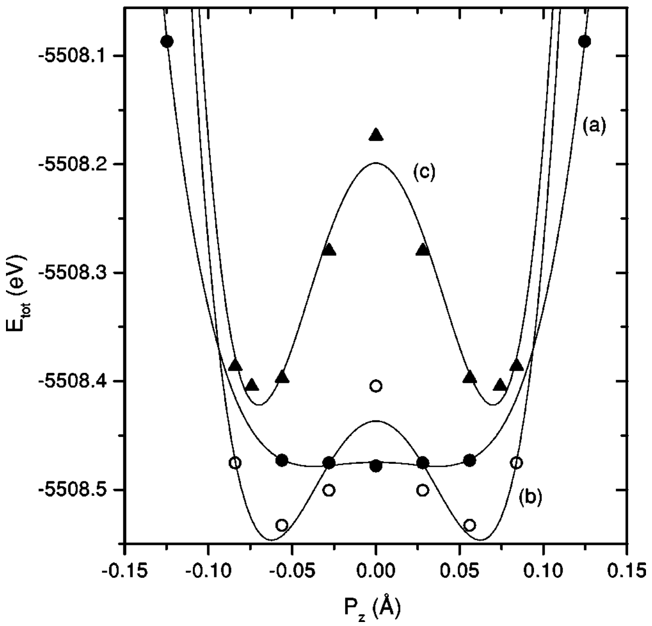

FIG. 13. Variation of the total energy vs the P displacement along the *z* direction for different O-O bond lengths $2R$ of (a) 2.405 Å, (b) 2.469 Å, and (c) 2.510 Å, respectively. The curves are the fits to fourth-order polynomials.

phase because of the imposed symmetry constraint ($\delta=0$). Actually, the variation of $2R$ in the paraelectric phase should be similar with that in the ferroelectric phase. Experimentally, at room temperature and at 16.5 kbar the equilibrium volume V_0, the O-O bond length, and δ are 92 Å^3/unit, $2R=2.469$ Å, and $\delta=0.315$ Å, respectively.[8] In the *ab initio* calculations, when the volume is 92 Å^3/unit in the ferroelectric phase, the corresponding pressure is 23 kbar, $2R=2.455$ Å and $\delta=0.32$ Å, in good overall agreement with experiment. The critical pressure P_c, determined by the common tangent of two curves, is 30 kbar compared to the experimental value of 17 kbar.[8] However, the latter was determined by extrapolating $\delta(T,P)$ and using the P-T_c dependence and H distribution along the O-O bond length. More experiments need to be performed to clarify this issue. It is interesting that in the ferroelectric phase the value of $2R$ exhibits a maximum of 2.51 Å at about 101 Å^3/unit, and then it decreases for larger volumes. The structure of DKDP can be regarded as that of the KDP structure with negative pressure with $2R=2.51$ Å (the maximum value of $2R$) and volume of 101 Å^3/unit. The negative pressure evaluated from this figure is 9 kbar, so that the predicted value of P_c in DKDP at which $T_c=0$ is 39 kbar, compared to the experimental value of 65 kbar.[8]

We finally investigate the effect of the displacement of the heavy atoms. In Fig. 13 we show the variation of the total energy versus the relative displacement of P and O along the *z* direction for different values of $2R$. The double-well feature of the energy curve indicates that the origin of the ferroelectric transition in KDP is the coupled relative displacement of P and O, in the PO_4 unit. The minimum energy occurs at $2R=2.469$ Å and at $P_z=0.056$ Å, which is the phosphorous displacement used in Fig. 9. Note that for $2R=2.51$ Å (the O-O bond length in DKDP) the equilibrium value of P_z increases to 0.08 Å, which agrees also well with experiment.[8] For $2R=2.405$ Å, the energy curve is very flat and exhibits a single minimum, indicating that no ferroelectric transition will occur. This is consistent with the results of the charge density and the Mulliken population analysis which shows that changes of the P-O distance leads to a redistribution of charge density and hence to the spontaneous polarization.

V. CONCLUSION

We have carried out electronic structure calculations for the orthorhombic and tetragonal crystal structures in KDP. The calculated lattice parameters and atomic positions are in good agreement with experiments. The distance δ between the two equilibrium positions of H along the O-O bond is found to depend on both the O-O bond length and the displacements of K and P along the z direction. Of course, the distance δ depends also on the isotope mass. The change of transition temperature upon deuteration or external pressure is caused by changes of the O-O bond length and hence changes of δ. It is shown that the origin of the ferroelectricity of KDP arises from the redistribution of charge density caused by change of the P-O distance and the coupled P-O motion is the dominant factor for the ferroelectric phase transition. Although our calculations were focused on KDP, the results should be appropriate for other hydrogen-bonded ferroelectric and antiferroelectric systems. However, further experimental and theoretical work needs to be carried out to clarify the mechanism (order-disorder or displacive) responsible for the ferroelectric transition in this family of systems.

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