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LETTER TO THE EDITOR

New evidence of the displacive feature of the ferroelectric transition in KDP-type crystals

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Abstract

Employing *ab initio* calculations we have determined the structural parameters of the paraelectric and ferroelectric phases of KH_2PO_4 , which are in good agreement with experiment. The calculations reveal that the O–O bond length and the coordinated motion of the P and K atoms have a large effect on the double-well potential for H, controlling the distance, δ , between the two equilibrium positions of the H along the O–O bond in the paraelectric phase. The calculations provide new evidence that the ferroelectric phase transition in H-bonded crystals has also a displacive feature.

Despite their extensive applications, the structural phase transition in hydrogen-bonded ferroelectric materials remains still a controversial issue. In the high-temperature phase, each proton occupies two equilibrium sites with equal probability. It is not clear whether the protons are tunnelling between these two sites (separated by δ) along the oxygen–oxygen bonds or they are just localized in one of them. Although it is well accepted that the protons spontaneously order at T_c corresponding to an order–disorder mechanism [1,2], it is an open issue whether the phase transition also involves the displacive component of the host lattice. In the well known quantum tunnelling model [1, 2], the localization of each H is described by a pseudospin and the ferroelectric phase transition is associated with the condensation of the pseudospin wave mode when

$$\frac{2\Omega}{J} = \tanh\left(\frac{\Omega}{2k_B T_c}\right). \quad (1)$$

Here, Ω is the tunnelling integral and J is the proton–proton interaction. Within this model, the isotope effect (in KH_2PO_4 (KDP) $T_c = 122$ K and in KD_2PO_4 (DKDP) $T_c = 229$ K) is attributed to the change in tunnelling frequency caused by the mass change from H to D. In the last 20 years, neutron diffraction studies [3, 4] have shown that the distance δ increases upon deuteration. Thus, the above model was extended to account for the coupling of the order–disorder mode and the optical lattice mode [5, 6].

Table 1. Comparison of the *ab initio* lattice parameters and atomic distances with the corresponding experimental values (units in Å).

	Tetragonal		Orthorhombic	
	Calculated	Expt	Calculated	Expt
<i>a</i>	7.495 27	7.4264	10.629 05	10.5459
<i>b</i>			10.533 94	10.4664
<i>c</i>	6.957 49	6.931	7.013 8	6.9265
P–O2	1.519 8	1.5429	1.551 81	1.5719
P–O1	1.519 8	1.5429	1.492 71	1.5158
O2–O1(2R)	2.405 54	2.4829	2.483 41	2.4974
O2–H	1.202 77	1.0712	1.060 77	1.0564
O1–H	1.202 77	1.4120	1.422 63	1.4410
H–H (δ)	0.0	0.3428		

More recently, two sets of experiments have provided increasing evidence of the features of the structural phase transition. First, the neutron Compton scattering measurements [7] provided direct evidence that the hydrogen atoms are tunnelling between the two equivalent sites above T_c . Second, the displacive effects of the heavy atoms at the transition point were detected by high-precision chemical shift measurements [8,9]. Thus, it is important to provide theoretical evidence, based on *ab initio* electronic structure calculations, of the atomic features controlling the transition. We have employed the density functional theory to investigate the detailed structural parameters for KDP. It will be shown that, although the calculations are performed at zero temperature, they can provide insight into how the heavy atoms are involved in the ferroelectric transition.

The first-principles calculations employ the total energy pseudopotential method, which is well documented elsewhere [10]. The calculations were performed using the CASTEP code. We used the ultrasoft pseudopotentials [11] and the PBE gradient-corrected functional [12] for the exchange–correlation energy. The energy cutoff of the plane wave basis functions was set to be 680 eV, which yields a convergence for the total energy better than 1 meV atom⁻¹. For the reciprocal-space integration we have used the Monkhorst-Pack special *k*-point method [13].

The tetragonal paraelectric phase of KDP has space group $I42d$ (D_{2d}^{12}) and the orthorhombic ferroelectric phase has $Fdd2$ (C_{2v}^{19}) space group. We have carried out both geometric optimization and atomic relaxation to find the equilibrium configuration for both structures. In table 1 we list the calculated and experimental structural parameters for the two phases. Overall, there is a very good agreement, especially for the orthorhombic phase. For the tetragonal phase, there are two differences between the calculated and experimental values, which cannot be regarded as calculational errors. First, while in experiment [1,2], the H atoms occupy two equilibrium sites symmetrically displaced from the midpoint of the O–O bond, in the calculations, the H atoms are found to be at the centre of the O–O bonds and the symmetry is also satisfied. Second, the calculated O–O bond length, $2R = 2.405$ Å, for the tetragonal phase is smaller than the corresponding experimental value of 2.483 Å, while $2R = 2.483$ Å for the orthorhombic phase is in good agreement with experiment. This discrepancy suggests that the O–O bond length may be playing an important role in the phase transition.

In fact, the distance, δ , between the two equilibrium H configurations was found experimentally to depend strongly on the O–O bond length [4]. The H–H (δ) and the O–O ($2R$) distances 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

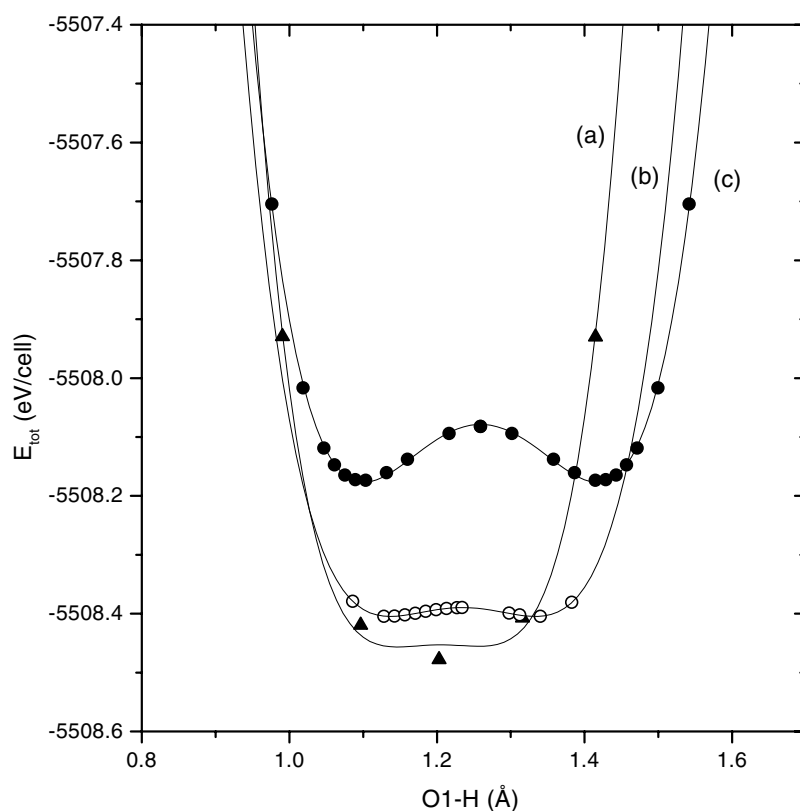


Figure 1. Total energy versus the position of the H along the O–O bond with O–O bond length of (a) 2.405, (b) 2.469 and (c) 2.510 Å. The curves represent fits to fourth-order polynomials.

(table 1) and varied the H position along the O–O bond and the O–O bond length, preserving the tetragonal structure. Figure 1 shows the variation of the total energy as a function of the H position along the O–O bond, for different O–O bond lengths. Note that when the O–O bond is 2.405 Å (optimized bond length in table 1) there is a single minimum at the mid-point. 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 centre. The hydrogen separation δ increases from 0.21 to 0.31 Å as the O–O bond length increases from 2.469 and 2.51 Å. However, these values 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 potential for H. It was found experimentally that the motion of the H (D) atoms between the two equilibrium sites is accompanied with the out of phase motion of the K and P atoms along the z axis. In these calculations the space group symmetry, $I\bar{4}2d$, for the tetragonal phase was broken artificially by moving the P and K atoms out of phase along z , with displacements $P_z = 0.056$ Å and $K_z = 0.03$ Å, respectively, consistent with experiment [4]. Figure 2 shows the total energy versus the H position along the O–H–O bond in the distorted structures for different values of the O–O bond length. One can see that when P moves along $-z$ and K moves along $+z$, H will be closer to O2; otherwise, when P moves along $+z$ and K moves along $-z$, H will be closer to O1. Therefore, there are two equilibrium positions for H caused by the out of phase motion

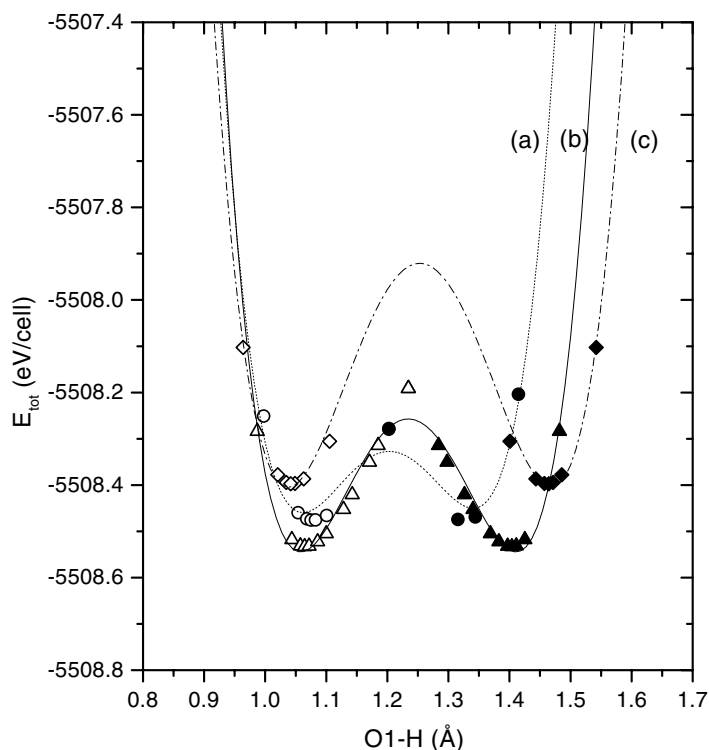


Figure 2. Variation of total energy versus the position of H along the O–O bond for different O–O bond length of (a) 2.405, (b) 2.469 and (c) 2.510 Å. The P and K atoms move out of phase: closed symbols correspond to displacements $P_{-z} = 0.056$ Å and $K_{+z} = 0.03$ Å, open symbols to $P_{+z} = 0.056$ Å and $K_{-z} = 0.03$ Å. The curves represent fits to fourth-order polynomials.

of P and K. The energy curves can be fitted with a double-well shape which is asymmetric about each minimum, i.e. steeper towards the nearest oxygen. The double-well potential shape depends strongly on the O–O bond length. It is important to note that the energy reaches its minimum value when the O–O bond length is 2.469 Å (curve (b)), in excellent agreement with experiment [4]. Furthermore, the *ab initio* calculations predict an energy barrier of 0.23 eV and a hydrogen separation of 0.34 Å (curve (b)), in excellent agreement with the corresponding experimental values of 0.21 eV [7] and 0.34 Å [4], respectively. Finally, when $2R$ is 2.51 Å, as in DKDP, the value of δ increases to 0.41 Å, quite close to the experimental value of 0.45 Å [4]. 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 other words, in the tetragonal phase of KDP above T_c , the double-well potential for H is caused by the motion of the heavy atoms. However, we find that the significance of the motion of the various atomic displacements is different. More specifically, if we allow only the displacement of the K 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. Thus, the *ab initio* calculations show that the relative P–O distance is the important displacive component involved in the ferroelectric transition, in agreement with recent measurements of the chemical shift of ^{31}P in the vicinity of T_c [9].

In summary, by reproducing the proton separation δ in the paraelectric phase, the *ab initio* calculations reveal that the double-well potential for H is caused by the O–O bond length and the optical mode of the P atoms. The calculations provide new evidence that the ferroelectric phase transition has also displacive character, which previously was observed experimentally. The conclusion of our calculations should also be appropriate to the whole KDP-type ferroelectric and antiferroelectric hydrogen-bonded crystal family.

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