Interplay between proton ordering and ferroelectric polarization in H-bonded KDP-type crystals

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Abstract

The origin of ferroelectricity in KH$_2$PO$_4$ (KDP) is studied by first-principles electronic structure calculations. In the low-temperature phase, the collective off-center ordering of the protons is accompanied by an electronic charge delocalization from the near and localization at the far oxygen within the O-H···O bonds. Electrostatic forces, then, push the K$^+$ ions towards off-center positions, and induce a macroscopic polarization. The analysis of the correlation between different geometrical and electronic quantities, in connection with experimental data, supports the idea that the role of tunnelling in isotopic effects is irrelevant. Instead, geometrical quantum effects appear to play a central role.

1 Introduction

Among the hydrogen-bonded ferroelectrics, the compound KH$_2$PO$_4$ (KDP) has been the most intensively studied over the second half of the last century. However, a detailed knowledge about its ferroelectric phase transition and some related phenomena is still lacking. In particular, its transition temperature ($T_c \approx 122$K), shows an increase of about 107K upon deuteration. The origin of this huge isotopic effect is still controversial. In the sixties, Blinc and Zecks proposed a quantum tunnelling model to explain it, which focuses purely on mass-dependent effects. Improvements of this model include coupling to vibrations of the K-PO$_4$ complex. Experimental studies over the past fifteen years, especially high-resolution neutron diffraction measurements, provided increasing evidence that the geometrical modification of the hydrogen bonds upon deuteration, the well-known Ubbelohde effect, is intimately connected with the mechanism of the phase transition. McMahon et al. have shown that the distance $\delta$ between the two collective equilibrium positions of the protons is remarkably correlated with $T_c$. They proposed that $\delta$ might be the only relevant parameter for $T_c$ and, in addition, no concluding evidence of tunnelling was established. It was then suggested the necessity of a revised theory for this class of transitions. Recently, a phenomenological model was proposed, which couples, via geometrical details of the H-bond, the proton coordinate with a nonlinear dynamics of the K-PO$_4$ system, where the spontaneous polarization actually develops.
model, which includes both tunnelling and geometrical isotope effects, also allows to explain the $T_c$ behaviour upon deuteration.

Summarizing, it appears well-established that, in this class of systems, proton ordering and geometrical and electronic properties of the host cage are connected in a non trivial way. So far, to the best of our knowledge, no *ab initio* calculations have been reported for KDP. This type of approach has the advantage of allowing a confident parameter-free analysis of the microscopic electronic and structural changes upon proton ordering that drive the ferroelectric transition. To this end, we have performed Density Functional (DFT) electronic structure calculations for KDP, within a gradient corrected approach to exchange and correlation, both in the tetragonal paraelectric phase (forcing the protons to be in the center of the H-bonds) and in the orthorhombic ferroelectric phase, where the protons order cooperatively at off-center positions in the H-bond. We thus analyzed in detail the structural parameters and the microscopic electronic density redistributions associated to the proton ordering phenomenon, which eventually provoke the ferroelectric instability.

This work is organized as follows: in Section 2 we describe the methods and the details of the calculations. Section 3 is devoted to the analysis of the geometry results. In Section 4, we study and discuss the polarization mechanism produced by the off-centering of the hydrogen atoms along the H-bonds, and its relation to the ferroelectric instability. Finally, in Section 5 we elaborate our conclusions.

## 2 *Ab initio* methods

We have performed two different types of *ab initio* calculations. First, we have used a recently developed, very efficient localized basis (LB) set approach (SIESTA). This is a fully self-consistent, pseudopotential DFT method that employs a basis set of pseudoatomic orbitals (PAO). We have chosen a double-zeta basis set with polarization functions (DZP). The exchange-correlation energy terms were computed using the Perdew-Burke-Ernzerhof gradient-corrected functional. Angular-dependent, norm-conserving Troullier-Martins pseudopotentials were employed to represent the interaction between ionic cores and valence electrons. We have also included nonlinear core corrections (NLCC) for a proper description of the K ion, due to the large overlap of core and valence charge densities. We used a 125 Ry energy cutoff for the grid computation of numerical integrals, and a value of $E_c = 50$ meV for the orbital confinement energy, which gives total energies and geometries of sufficient accuracy for this system. Due to the approximate character of these confined basis orbitals, we have checked the overall accuracy by performing standard pseudopotential plane wave (PW) calculations. The parallel version of the Car-Parrinello SISSA FPMD code, and the same set of pseudopotentials, exchange-correlation functional, and NLCC were used. The energy cutoff for the plane wave expansion was set to 150 Ry. In both approaches, the electronic Brillouin zone sampling reduced to the $\Gamma$-point, which is a reasonable approximation for such a wide band gap insulator. We have, however, checked that this sampling is sufficient for the large supercells considered.

In the paraelectric phase, the KDP structure (space group I42d) has a body-centered tetragonal primitive lattice. For our calculations, we used instead the conventional face-centered tetragonal cell (space group Fd3d), which includes 64 atoms (8
Table 1: Comparison of the ab-initio (LB and PW) lattice parameters and internal coordinates with experimental data. The notation is the same used in the experimental works referred. The different cases considered in the calculations are explained in section 2. We defined $\Delta z_K$ as the displacement of the K atom along $z$, respect to its centered position between P planes. Distances are in Å and angles in degrees.

|                    | LB     | PW     | Exp. Tetr. (293K) | Exp. Orth. ($T_c$-20K) |
|--------------------|--------|--------|-------------------|-----------------------|
|                    | TS     | FP$_t$ | GS                | TS            | FP$_t$               |
| Latt. param.       |        |        |                   |               |                      |
| a                  | 10.54  | 10.54  | 10.75             | 10.54         | 10.54                |
| b                  | 10.54  | 10.54  | 10.71             | 10.54         | 10.54                |
| c                  | 6.97   | 6.97   | 6.98              | 6.97          | 6.97                 |
| Int. Coord.        |        |        |                   |               |                      |
| d(P-O2)            | 1.592  | 1.622  | 1.633             | 1.557         | 1.580                |
| d(P-O1)            | 1.592  | 1.572  | 1.573             | 1.557         | 1.515                |
| 2R                 | 2.407  | 2.457  | 2.482             | 2.445         | 2.503                |
| $\delta$           | 0      | 0.07   | 0.09              | 0             | 0.09                 |
| $\Delta z_K$       | 0      | 0.259  | 0.311             | 0             | 0.395                |
| $< \text{O2-P-O2}$ | 108.6  | 107.1  | 105.0             | 111.1         | 105.2                |
| $< \text{O1-P-O1}$ | 108.6  | 114.7  | 114.1             | 111.1         | 115.1                |
| $< \text{O1\cdots H-O2}$ | 176.1 | 176.5  | 177.1             | 180           | 179                  |
| $\theta$           | 59.8   | 61.3   | 60.8              | 60.2          | 61.4                 |

With this choice, the transformation to the orthorhombic structure of the ferroelectric phase is simply described by a change in the ratio of the basal plane lattice parameters, in addition to changes in the internal structure parameters.

3 Geometry results

In order to obtain the equilibrium configurations relevant to ferroelectricity in KDP, we performed a series of computational experiments, which are described below.

First we considered a static view of the paraelectric phase by fixing a tetragonal cell with parameters at their experimental values at 293 K \cite{5,7} and relaxed the atomic positions under the constraint that the H atoms remain in the middle of the H-bonds. In this way we found the transition state (TS) which connects the two oppositely polarized realizations of the ferroelectric phase. In a second time we still kept fixed the tetragonal lattice, and allowed the hydrogen atoms to relax from their centered positions. When the unstable TS state was slightly perturbed, two H atoms approach each PO$_4$ tetrahedron. The two PO$_4$ oxygens which were approached by the hydrogens (in the following named O2) lie on one side of the (xy)-plane containing the P ion. The other two oxygens (O1) lie on the other side. The geometry relaxation is carried out also for all the other atoms in the unit cell. As a consequence of proton ordering, also the K ions move away from the centered position between P planes, thus leading to a ferroelectric phase with tetragonal lattice, which we denote FP$_t$. Finally, we
Table 2: Mulliken populations for each atom in the FP\textsubscript{t} and TS cases for the LB calculation. The last line shows the charge difference $\Delta q = q(\text{FP}\textsubscript{t}) - q(\text{TS})$ between both cases. Units are electrons (e) for the first two rows, and e/1000 for the last one.

|        | O1  | O2  | P    | K    | H    |
|--------|-----|-----|------|------|------|
| FP\textsubscript{t} | 6.283 | 6.143 | 4.747 | 0.205 | 1.099 |
| TS     | 6.201 | 6.201 | 4.755 | 0.208 | 1.116 |
| $\Delta q/1000$ | +82  | -58  | -8   | -3   | -17  |

fully optimized atomic positions and cell parameters. This leads to an orthorhombic ground state structure GS, which corresponds with the actual experimental ferroelectric structure.

The resulting structural parameters are shown in Table 1, together with experimental data for the paraelectric tetragonal and the ferroelectric orthorhombic phases. An excellent overall agreement is observed for the TS and FP\textsubscript{t} configurations obtained with the PW method, as compared to experimental data. The good quality of the LB method can be assessed by comparison with the PW results in columns 4 and 5. In the FP\textsubscript{t} calculation, the off-center ordering of the hydrogen atoms along the H-bonds leads to inequivalent O1 and O2 oxygens. Consequently, (a) there is a distortion of the PO\textsubscript{4} tetrahedra (see the different P-O1 and P-O2 distances on Table 1) and (b) the K ions abandon the centered positions between the phosphate planes (see $\Delta z_K$ in Table 1), thus inducing a spontaneous polarization which leads to ferroelectricity. These effects will be explained in the next Section. We also verified that, when the hydrogen atoms are constrained to remain in the middle of the H-bonds, then the centered positions are stable for the K ions. This provides a strong evidence that the origin of ferroelectricity is in the off-centering of the protons in the H-bonds.

It is worth mentioning that, in this fixed tetragonal FP\textsubscript{t} calculation, a substantial anisotropic stress appears in the $xy$-plane. Note that the hydrogen off-centering in the H-bond network, which lies nearly on the $xy$-plane, leads to an asymmetry of the $x$ and $y$ directions. Further relaxation, obtained by optimizing also the cell parameters in order to minimize the stress with respect to ambient conditions, releases the tetragonal symmetry in favor of the orthorhombic structure shown in column 3 of Table 1.

4 Polarization mechanism for the ferroelectric instability

In order to understand the origin of the ferroelectric instability, we have focused our analysis in the electronic charge redistributions that happen in going from the centered (TS) to the off-centered hydrogen case (FP\textsubscript{t}). To this purpose we compute the orbital Mulliken populations, which are shown on Table 2 for the different atoms in both cases. It is known that Mulliken populations depend strongly on the choice of the basis set. Differences, however, are much less sensitive, and thus meaningful. In going from TS to FP\textsubscript{t}, it can be clearly observed an increase of the charge localized around O1, the main contribution ($\approx 70\%$) being provided by the O2 charge decrease. The
Table 3: Overlap Populations between atoms in units of e/1000. Only the most significant $\Delta q = q(\text{FP}_t) - q(\text{TS})$ values are shown.

|        | O1-O1 | O1···H | O1-P | O2-O2 | O2-H | O2-P | P-P |
|--------|-------|--------|------|-------|------|------|-----|
| $\Delta q/1000$ | 200   | -91    | 46   | -92   | 70   | -44  | -23 |

analysis of bond and self atom-orbitals overlap populations,[21] which are shown in Table 3, also helps to discriminate the origin of this charge redistribution.

The trends observed in Tables 2 and 3 are confirmed by the charge density difference $\Delta \rho(r) = \rho_{\text{FP}_t}(r) - \rho_{\text{TS}}(r)$, which is plotted in the planes determined by the atoms P-O2-H (Fig. 1a) and P-O1···H (Fig. 1b). Analysing both, Table 3 and Fig. 1a, we observe a significant enhancement of the O1-O1 overlap population, accompanied by a smaller increment of the same sign in the O1-P orbitals. This happens at the expenses of the population of the overlap orbitals in the O1···H bond. This behaviour around the O1 atom indicates that, as the hydrogen atoms move away from O1, the strongly covalent O1-H bond weakens, its charge being redistributed. A substantial amount of this charge localizes around O1, while part of it localizes in the O1-P orbitals, consistently with the shortening of the O1-P bonds reported in Table 1. The contrary occurs in the vicinity of the O2 atom: as H moves towards O2 along the O1···H-O2 line, the O2-H distance decreases, thus increasing the degree of covalency and producing a charge localization along the corresponding O2-H bond. This is indicated by the bond overlap population in Table 3, and also by the contours in Fig. 1b. Finally, the O2-O2 and O2-P orbitals loose a significant amount of charge. We name this process of charge redistribution, produced by the collective hydrogen off-centering along the H-bond, the polarization mechanism (PM). The PM can be described in a simplified way as a charge accumulation and localization around O1 at the expenses of a charge depletion and delocalization in the vicinity of O2.

This charge accumulation around the O1 atom can also be viewed as a negative charge defect, which electrostatically attracts the positive K$^+$ ion towards the PO$_4$ cage, along the z-axis. This electrostatic force is counterbalanced by repulsion forces from orbital overlaps, which stabilize a new equilibrium position of the K$^+$ ion, as can also be seen in Table 1. Our calculation then supports the idea that proton off-centering and ferroelectricity are very correlated phenomena.

Cell relaxation – from FP$_t$ to GS – also affects the internal structure (Table 1). As H approaches O2, $\delta$ increases, the O1···H bond weakens and the H-O2 bond becomes stronger. As a consequence, a larger amount of charge localizes around O1, and delocalizes away from O2. This behavior is related to the PM and will be useful to establish a connection between $\delta$ and the charge difference $\Delta q_O = q(O1) - q(O2)$. Moreover, we observe a striking correlation between $\Delta q_O$, the distortion of the tetrahedra, $\Delta(P-O) \equiv d(P-O2) - d(P-O1)$, and the displacement of the K atoms, $\Delta z_K$. These trends are shown in the theoretical curves in Fig. 2 for two different values of $\delta$, obtained from the cell-unrelaxed FP$_t$ and the GS calculations.

The crucial experimental observation that the effect of isotopic substitution can be almost exactly reproduced by applying pressure,[3, 4], supports the idea that the main effect of deuterium is to modify the internal geometry. In this sense, our
Figure 1: Differential charge density contours $\Delta \rho(r)$ in the planes containing the following atoms: (a) P-O1···H, (b) P-O2-H. Labels O1 and O2 denote the positions of the respective nuclei, positioned at (0,0). Labels O2-P and O1-P indicate the position of the center of the corresponding bonds. The same convention is used for the O2-H and O1···H bonds. Positive (negative) contours are in solid (dashed) lines. The thickest lines represent an absolute value of $2.96 \times 10^{-3}$ eÅ$^{-3}$. The thinner lines are obtained by successively halving this value, down to $3.70 \times 10^{-4}$ eÅ$^{-3}$.

calculations for FP$_t$ and GS, corresponding to two different pressures, can be used to analyse isotopic effects. It is known from experiment that H(D) ordering, $\Delta z_K$, $\Delta$(P-O), and spontaneous polarization $P_s$, show very similar trends just below $T_c$, in the ferroelectric phase.[22] Moreover, these trends are quite well explained by the present PM (left curves in Fig. 2). Therefore, it is natural to attempt to establish a connection between $\Delta q_O$ and structural data measured in KDP and in its deuterated analog, DKDP. This is done in Fig. 2, by including the experimental values of $\Delta z_K$, $\Delta$(P-O) and $P_s$ for KDP and deuterated DKDP. The comparison between theoretical and experimental curves is very favorable, especially for what concerns the slopes of the curves.[23]

In connection with the proposed PM, the above indicates that the enhancement of the saturated polarization due to deuteration, experimentally observed below $T_c$, [22] can be explained merely by the increase in the charge unbalance between O1 and O2 ($\Delta q_O$), which in turn is induced by an increase in $\delta$. This picture is in line with the ideas developed in Ref.[24], where the experimental behaviour of $P_s$ and the inverse dielectric constant were rationalized in terms of a proton-dipole interaction model. In fact, at temperatures well below $T_c$, the protons are strongly bound to the neighboring PO$_4$ dipoles, in a stable minimum of an asymmetric potential. In this asymmetric configuration, the protons localize into the deepest well because the energy needed to be promoted to the excited state is too high, thus ruling out the possibility of tunnelling.[22] In this case, deuteration can only induce the indirect effect of enhancing $\delta$ [23], i.e. the so-called geometric effect. Preliminary $ab\ initio$ calculations indicate, even more strikingly, that there is actually no double minimum structure in the potential energy surface for single protons. Apart from supporting
this scenario, the current ab initio-derived PM establishes the importance of the short-range proton – PO₄-dipole interaction for the transition, as was also speculated in [4].

Figure 2: The variation of ∆(P-O) (circles), ∆zₜ (triangles), ∆qₒ (diamonds) and saturated P* (squares) with the H(D) displacement δ. Left curves: LB theoretical results for cases FPₜ and GS (open symbols) and right curves: experimental values for KDP with δᴴₑₓᵖ ≈ 0.34Å, and for DKDP with δᴰₑₓᵖ ≈ 0.45Å, from Ref.[22], (full symbols), both in the ferroelectric phases at Tₑ₋20K and Tₑ₋10K, respectively. Experimental δ values considered are estimations of these magnitudes at Tₑ, as they cannot be measured in the ferroelectric phase.[22] The lines are guides to the eye only. Arbitrary units are used in the vertical axis.

5 Conclusions

We presented the results of ab initio DFT calculations for the H-bonded ferroelectric material KDP, which reproduce very well the structure of the tetragonal and orthorhombic (ferroelectric) phases in KDP. On this basis we identified the microscopic polarization mechanism that leads to the ferroelectric instability. This arises from an electronic charge redistribution between the oxygen atoms involved in the H-bonds, occurring when the protons move away from the center of the bonds. We indirectly showed that the interplay between proton ordering and ferroelectric polarization qualitatively explains the enhancement of the saturated P* upon deuteration. In addition we provided, for the first time, fully ab initio evidence supporting the idea that isotope effects reduce, at least at low temperatures in the ferroelectric phase, to the indirect geometric effect of enhancing δ, as speculated in recent works [4].

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