Computational Materials Science 111 (2016) 301–309

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# *Ab initio* study of lattice dynamics of $CsH_2PO_4$ and $CsD_2PO_4$ crystals

Ya. Shchur [a,*], T. Bryk [a], I. Klevets [a], A.V. Kityk [b]

[a] Institute for Condensed Matter Physics, 1 Svientsitskii str., 79011 L'viv, Ukraine
[b] Faculty of the Electrical Engineering, Czestochowa University of Technology, Al. Armii Krajowej 17, 42-200 Czestochowa, Poland

ARTICLE INFO

*Article history:*
Received 15 May 2015
Received in revised form 16 August 2015
Accepted 5 September 2015
Available online 18 October 2015

*Keywords:*
Lattice dynamics
Density functional theory
Ferroelectric
Phonon frequency
Elastic constant
$CsH_2PO_4$

ABSTRACT

Lattice dynamics of $CsH_2PO_4$ and $CsD_2PO_4$ crystals has been studied by density functional theory in two structural phases ($P2_1/m$ and $P2_1$). The bulk crystal structure, electronic band structure, phonon spectra in different symmetry points and directions of Brillouin zone, density of states and partial density of states have been calculated. The lattice instability at Brillouin zone boundary close to (1/2,0,1/2) and (0,0,1/2) points has been found in paraelectric $P2_1/m$ phase of both title crystals. The detailed interpretation of spectroscopic experimental data is performed basing on simulated vibrational spectra. The matrices of elastic constants, piezoelectric coefficients and temperature dependent heat capacity are calculated.



## 1. Introduction

Caesium dihydrogen phosphate $CsH_2PO_4$ (CDP) crystal belongs to the well known family of hydrogen bonded ferroelectrics of $KH_2PO_4$-type [1]. The crystals of this class have been intensively studied for the last sixty years mainly because of their practical application in different areas of quantum electronics. More recently, the interest to CDP crystal was renewed due to its potential commercial application in fuel cells of the intermediate temperature range (500–600 K) [2,3]. Therefore, the stability of their physical properties under the variable external conditions like the temperature or hydrostatic pressure has persistently been the subject of high attention. Numerous experimental and theoretical studies have been performed aiming to provide comprehensive characterization of their properties [1,4]. Among the various experimental techniques, Raman and infra-red (IR) spectroscopy are particularly relevant since they both probe the instantaneous crystal structure. However, experimental spectroscopic data do not always agree with group theory predictions, detecting a much higher number of vibrational modes than expected theoretically. In fact, this complicates their assignment likewise overall structural analysis. In this framework, the lattice dynamics calculations may be considered as efficient tool for the interpretation of experimental Raman and IR spectra.

Lattice dynamics of CDP and its deuterated analog, $CsD_2PO_4$ (DCDP), has already been studied in the framework of semi-phenomenologic atomistic model [5,6]. Despite the quite reasonable information shedding light into the mechanism of structural transformations in CDP, the semi-empirical models involve adjustable parameters, the proper choice of which is not always straightforward. It would be highly desirable to simulate the lattice dynamics of title crystals using the parameters-free *ab initio* techniques. Such *ab initio* methods have been already used for investigating the electronic and structural properties of $KH_2PO_4$ and $NH_4H_2PO_4$ crystals [7,8] and for studying high-temperature proton transport mechanism in CDP [9]. However, to the best of our knowledge, the phonon spectrum of neither crystal of $KH_2PO_4$-type has not yet been studied within the quantum-chemical approaches. Therefore, our paper is aimed at accurate first-principal studying of lattice dynamics of CDP and DCDP crystals within the density functional perturbation theory (DFPT). Our attention will be mainly focused on the proper interpretation of the experimental spectroscopic, elastic and thermodynamic data.

## 2. Crystal structure and numerical method

At ambient pressure, CDP (DCDP) may exist in three structural phases. At room temperature it has monoclinic symmetry, $P2_1/m$ ($Z = 2$) [10,11] and demonstrates no polar electric properties (paraelectric phase). Below $T_C = 152$ K ($T_C = 267$ K in DCDP), a phase transition occurs into a ferroelectric phase accompanied by symmetry lowering to the acentric $P2_1$ ($Z = 2$) space group [12,13].

* Corresponding author. Tel.: +380 32 2707439; fax: +380 32 2761158.
*E-mail address:* shchur@icmp.lviv.ua (Ya. Shchur).

http://dx.doi.org/10.1016/j.commatsci.2015.09.014
0927-0256/

Above 502 ± 2 K, CDP transforms to the cubic $P3m3$ ($Z = 1$) symmetry which is accompanied by three-order-of-magnitude jump in the proton conductivity (superprotonic phase) [14]. The peculiar structural feature of CDP is the presence of two kinds of hydrogen bonds, shorter $O_3$–$H_2\cdots O_4$ ($R = 2.48$ Å) and longer $O_1$–$H_1\cdots O_2$ ($R = 2.54$ Å) bonds (see Fig. 1). In paraelectric and ferroelectric phase, the hydrogen $H_1(D_1)$ ions are ordered on longer hydrogen bonds closer to $O_1$ atom, whereas the $H_2(D_2)$ ions are disordered on shorter hydrogen bonds in paraelectric phase and become ordered in one of two possible off-center sites in ferroelectric phase [12]. In high temperature superprotonic phase, the tetrahedral $PO_4$ groups are dynamically disordered over six possible orientations according to the recent synchrotron X-ray diffraction study [14]. Unfortunately, neither the precise location of $H_1$ and $H_2$ protons nor the mechanism of correlation between the proton motion and the dynamical disorder of $PO_4$ groups in superprotonic phase is still unknown. The lack of proton coordinates in high temperature cubic phase prevents us from modeling the lattice dynamics in this phase. Our simulation was thus limited to two monoclinic phases, at intermediate $P2_1/m$ and low-temperature $P2_1$.

Modeling the lattice dynamics of CDP (DCDP) in paraelectric phase we assumed the $H_2(D_2)$ atoms to be located in the middle of $O_3$–$H_2\cdots O_4$ hydrogen bonds. Such a simplification of the $H_2(D_2)$ tunneling motion between two minima of the proton potential relief allowed us to keep the macroscopic center inversion symmetry of $P2_1/m$ phase.

The present calculations have been performed within DFT [15] using the local density approximation (LDA) [16] as implemented in the *ab initio* simulation package ABINIT [17]. We made use of LDA norm-conserving Troullier–Martins pseudopotentials [18] with Cs($5p^6 6s^1$), P($3s^2 3p^3$), O($2s^2 2p^4$) and H($1s^1$) levels treated as valence states. An accurate convergence analysis was carried out with respect to both the sampling of Brillouin zone (BZ) using the Monkhorst–Pack scheme [19] and to the kinetic energy cut-off for plane-wave calculations. Convergence tests were performed for $\Gamma$ point centered $2\times2\times2$, $4\times4\times4$, $6\times6\times6$ and $8\times8\times8$ grids along the reciprocal-lattice directions. It turned out that the difference in total energy between $4\times4\times4$ mesh and both $6\times6\times6$ and $8\times8\times8$ grids was below 0.7 meV in both structural phases investigated. The similar convergence test concerning the cut-off energy led us to choice of cut-off energy $E_{cut} = 1003$ eV (37 Ha) for all our calculations.

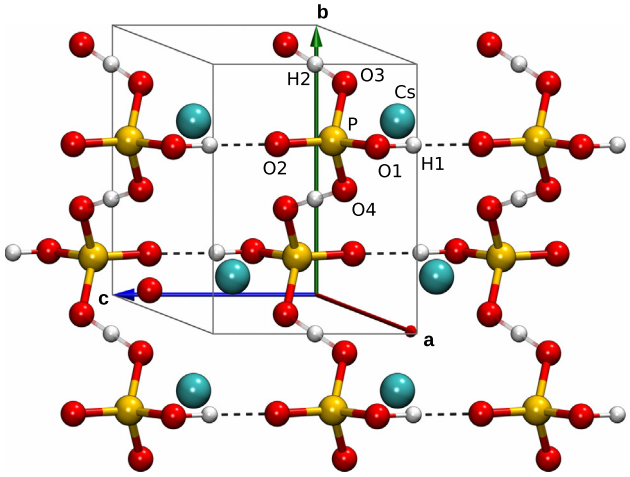


**Fig. 1.** Crystal structure of CDP at room temperature. The hydrogen $H_2$ atoms tunneling between two off-center positions on hydrogen bonds are depicted in the center of hydrogen bonds in order to preserve the center inversion symmetry ($P2_1/m$) of paraelectric phase.

Structural optimization was done within the Broyden–Fletcher–Goldfarb–Shanno scheme [20]. It finally allowed us to reduce the maximal forces acted on each atom to value lower than $5\times10^{-8}$ eV/Å. The calculated equilibrium lattice parameters and atomic coordinates deviate from the corresponding experimental values by less than 1% and 2% as for CDP and DCDP crystals, respectively. The deviation of about 5% was detected only for $Z$-coordinate of $H_1(D_1)$ for both compounds. Note, we used the experimental structural data for CDP (at $T = 297$ K [10] and $T = 80$ K [13]) and DCDP (at $T = 283$ K [11]).

Performing the structure optimization in low-symmetry ferroelectric $P2_1$ phase of CDP we have found that the location of $H_2$ hydrogen appears to be shifted from the experimentally observed off-center ordered position [13] very close to the central position in the hydrogen $O_3$–$H_2\cdots O_4$ bond which is inherent for $H_2$ in paraelectric $P2_1/m$ phase. The optimized coordinates of $O_3$ and $O_4$ atoms in $P2_1$ phase also tended to experimental oxygen coordinates relevant for symmetric $P2_1/m$ phase. To preserve the most characteristic structural feature of ferroelectric phase, the proton ordering in one of the off-center position in hydrogen bond, we were caused to fix the position of $H_2$ atoms to the experimental value [13] during the structure optimization of $P2_1$ phase. In our opinion, it may indirectly confirm the crucial role of the proton tunneling or, in other words, the proton flip-flop motion between two off-center positions in hydrogen $O_3$–$H_2\cdots O_4$ bond which is accompanied by the rotations of $PO_4$ groups.

## 3. Results and discussion

### 3.1. Electronic properties

The calculated valence electron density distribution in CDP in both structural phases is depicted in Fig. 2. We present here the electron densities around the atoms involved in longer (Fig. 2a) and shorter (Fig. 2b and c) hydrogen bonds. Despite the significant overlap between the phosphorous and oxygen valence charges, which is inherent for covalent bonds within $PO_4$ groups, there is a considerable overlap between valence charges of the $O_1$ and $H_1$ ions within the $O_1$–$H_1\cdots O_2$ hydrogen bond. As seen from Fig. 2, this overlap is much deeper comparing with the penetration of $H_2$ ion into $O_3$ valence charge in the ordered $P2_1$ phase. Evidently, this "deep hoping" of $H_1$ by $O_1$ ion should explain the stability of hydrogen $O_1$–$H_1\cdots O_2$ bond in the wide temperature range of para- and ferroelectric phases, whereas $O_3$–$H_2\cdots O_4$ bond is much less stable comparing with the longer hydrogen bond revealing the ordered state only in ferroelectric $P2_1$ phase.

Fig. 3 presents the electronic band structure along with the corresponding electronic total and partial density of states (DOS) along some directions of BZ of CDP in $P2_1/m$ phase. The calculated band structure of DCDP crystal is basically the same. The direct band gap $E_g$ is 4.72 eV at $\Gamma$ point. However, this calculated value may be underestimated comparing with the real one due to the well-known DFT band-gap problem [21]. Note that the calculated band structure of $KH_2PO_4$ crystal is quite comparable with CDP electronic spectrum given in Fig. 3, showing $E_g = 4.178$ eV [22] and $E_g = 5.96$ eV [7]. In $KH_2PO_4$, the experimental value of $E_g$ at room temperature was estimated to be ~7.6 and ~6.4 eV, depending on the type of experiment [23].

As seen from Fig. 3, the lowest bands located below −17 eV are mostly attributed to O $s$– orbitals with contribution of P $-p$ states near −17 eV. The middle region group of bands placed between Fermi level and −10 eV is primarily originated from O $p$– orbitals with very strong contribution of Cs $p$– states near −5 eV. The conduction bands consist mainly of P $p$– and $s$– and O $p$– orbitals.