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Alexander Slepko and Alexander A. Demkov

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First principles study of the biomineral hydroxyapatite

Alexander Slepko and Alexander A. Demkov¹

Department of Physics

The University of Texas at Austin, Austin, Texas 78712, USA

Abstract

The biomineral hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is the main mineral constituent of mammal bone. Hydroxyapatite crystallizes in the hexagonal and monoclinic phases, the main difference between them being the orientation of the hydroxyl groups. Using density functional theory we study the energetics of the hexagonal and monoclinic phases along with the several hypothetical crystal structures of hydroxyapatite. The monoclinic phase has the lowest energy, with the hexagonal phase being only 22meV/cell higher in energy. We identify a structural transition path from the hexagonal to monoclinic phase with the activation energy of 0.66 eV per hexagonal cell. At room temperature the transition occurs on a millisecond time scale. The electronic structures of the monoclinic and hexagonal phases are compared. For the hexagonal phase we calculate the phonon frequencies at the Γ -point and elastic constants. Both are in good agreement with available experiment.

I. Introduction

A carbonated form of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is one of the most abundant materials in mammal bone [1]. It crystallizes within the free space between tropocollagen protein chains (Fig. 1) and strengthens the bone tissue. The mineral content of a typical human bone increases with age and reaches a maximum value in males and females at different ages [2]. From this peak value the mineral content starts to decrease leading to diseases such as e.g., osteomalacia (softening of the bone caused by the loss of bone mineral). Some of the emergent applications of hydroxyapatite are, therefore, bone repair and replacement, and production of synthetic bone material [3]. Although by itself HA is too brittle to be used as a bone replacement directly, a variety of coating techniques have been developed in recent years to combine the strength of metals (such as titanium) with the natural bio-activity of HA [4]. The key property besides the bio-activity is therefore the HA adhesion to metals. The adhesion is governed by chemical bonding and thus the problem is that of the electronic properties of the interface. Therefore, a thorough understanding of the electronic and mechanical properties of HA, its surface and interfaces to other substrates are of scientific interest.

A significant amount of experimental work on HA has been done, and in particular in the medical implant field, for an excellent review of this work we refer the interested reader to ref.

¹ demkov@physics.utexas.edu

[4]. Some of the first experimental reports of HA date back to 1936 [5]. In his work on dental enamel, Schmidt demonstrated that the crystallographic c-axes of the HA platelets within the collagen framework are well aligned with the collagen fibrils (Fig. 1). The hexagonal crystal structure of HA with $P6_3/m$ symmetry (#176 in the *International X-Ray Tables*, figure 2) and the atomic positions were determined in 1958 by Posner *et al.* using the X-ray diffraction [6]. In 1964 Kay and co-workers refined the positions of the OH molecules using neutron diffraction [7]. Studies of the alignment of tropocollagen chains in mammal bone and alignment and growth of HA crystals were done by Weiner and co-workers [8]. In the 1970s [9] Carlisle showed that doping (in that study with Si) can play an important role in supporting the bone growth. A monoclinic variant of HA was suggested in 1967 by Young [10]. He inferred that a HA crystal sufficiently free of impurities and vacancies could crystallize in the monoclinic phase analogous to the known monoclinic chlorapatite. Prior to this work it was believed that HA only appeared in a hexagonal structure. Recently, the monoclinic variant of hydroxyapatite attracted significant interest [e.g. 11,12].

From the theoretical point of view the HA crystal presents an interesting challenge due to its complexity and importance in biological and biophysical systems. Only with the recent increase in computational power a theoretical study on HA became feasible, and of late along with other calcium apatites HA has been subject to a number of first principles calculations. De Leeuw, using density functional theory (DFT), analyzed the HA crystal structure and specifically the position and orientation of hydroxyl molecules [13]. She suggests that the experimentally found OH disorder in the crystal is due to locally ordered domains with differently oriented OH molecules. In the simplest case, this is achieved in a monoclinic cell. Later, using DFT Calderin *et al.* [14] have analyzed the crystal structure and electronic density of states of stoichiometric and OH-deficient HA as well a variety of other calcium apatites. They found that monoclinic and hexagonal HA are very close in energy indicating no particular preference for crystallization in a specific structure. They also found that apatites permit exchanging the OH molecules with other anions. The electronic structure has been confirmed by Rulis and co-workers using the orthogonalized linear combination of atomic orbitals method [15]. More recently, studies have focused on altering the electronic and chemical properties of HA with doping. For example, Chappell and Bristowe have studied the influence of substituting phosphorus with silicon on the HA crystal and electronic structure [16]. Silicon incorporation is found to be energetically most favorable in combination with removing one of the two negatively charged OH pairs in the primitive cell to maintain the overall charge neutrality (the ionic charge of SiO_4 is -4 vs. -3 of a PO_4 unit). Other recent theoretical studies of doping include the substitution of OH by fluorine [17] (making the crystal a mixture of HA and fluorapatite (FA)), introduction of carbonate ion (CO_3^{2-}) to study physiologically found carbonated form of HA [17], and calcium substitution by titanium [18] and strontium [19] to induce structural modifications. Using a classical shell-model Calderin *et al.* investigated the lattice dynamics, calculated thermal factors and simulated the infrared spectra of HA [20]. They find good agreement with experiment for the low-frequency

and high-frequency vibrational modes at the Γ -point, whereas in the intermediate frequency range the reported agreement is poor. More recently, classical and quantum-mechanical molecular dynamics simulations have been used to study preferred surface orientations and terminations of HA [17, 21, 22] and to study the water and amino acid adsorption on the HA surface [17, 21, 23, 24, 25].

Despite the recent progress, many questions remain. Little is known, for example about the transformation mechanisms between the hexagonal and monoclinic phases. The mechanical properties of HA remain virtually unstudied. HA is still a challenging subject for first principles calculations due to a large number of atoms in the unit cells and variation in nature of interatomic bonding. In this paper, using density functional theory we investigate both hexagonal and monoclinic forms of HA. We identify the monoclinic phase as the ground state and analyze possible pathways for the phase transition between the hexagonal and monoclinic phases. We carefully compare the electronic structure of both phases. For the hexagonal phase we calculate the phonon frequencies at the Γ -point and elastic constants. Both are in good agreement with available experiment.

II. Computational details

All calculations are done using density functional theory as implemented in the VASP code [26-30]. We use the Perdew-Wang [31] (PW91) exchange correlation functional and projected augmented wave (PAW) pseudopotentials [32]. The valence configurations are $1s^1$ for hydrogen, $3s^23p^3$ for phosphorus, $4s^2$ for calcium and $2s^22p^4$ for oxygen. We use 700eV as the kinetic energy cut-off for bulk calculations. When calculating the phonon frequencies we increase the energy cut-off to 950eV to obtain highly accurate forces. In all calculations - except for the elastic constant calculations - we allow for full relaxation of the cell including changing the volume, adjusting the atomic positions and cell shape. When calculating the elastic constants we only allow for the relaxation of ionic positions within the strained cells. Symmetry operations are switched off during relaxation. We use a $6\times 6\times 8$ Monkhorst-Pack [33] k-point mesh for the Brillouin Zone (BZ) integration of hexagonal cells that ensures the convergence to 1.8meV/cell. For the monoclinic primitive cells we use $6\times 4\times 6$ Monkhorst-Pack k-point meshes. All structures are relaxed until the largest force on atoms in the cell is smaller than 20meV/Å. When calculating the vibrational modes, we relax the atomic positions until the largest force is smaller than 0.2meV/Å.

III. Results

A. Ground state crystal structure

To identify the theoretical ground state of HA we start from the experimental structure reported by Posner *et al.* and Kay and Young (as shown in Fig. 2) [6, 7]. They report a hexagonal primitive cell of $P6_3/m$ symmetry (#176 in the *International X-Ray Tables*, Fig. 2) that contains

ten Ca atoms, six phosphate (PO_4) groups and two hydroxyl (OH) molecules. In Fig. 3 we present a top view of the crystal. For pictorial purposes we shift the original primitive cell boundaries along the \mathbf{a} and \mathbf{b} axes in such a way that the OH column is now in the center of the cell. There are two types of Ca atoms in the cell. Ca atoms of one type are arranged in a hexagon around the OH molecules (Fig. 3). The darker and lighter color distinguishes two atomic planes. The darker balls are located at $z=0.25c$, and the lighter ones are at $z=0.75c$. The remaining four Ca atoms are arranged in two columns at the corners of the cell in Fig 3. In the upper left column the two Ca_1 atoms are located at $z=0.999c$ and $z=0.501c$. In the lower right column the two remaining Ca_1 atoms are located at $z=0.499c$ and $z=0.001c$. Similarly to first type Ca, six phosphorus atoms of the PO_4 molecules are arranged in two triangles around the OH channel, three are at $z=0.25c$ and three at $z=0.75c$. Again, the darker and lighter color in Fig. 3 distinguishes between the two planes. While most of the atomic coordinates reported in 6 and 7 are almost exactly the same, the two structures differ in the position of the OH molecules. In ref. 6 the exact positions of hydrogen atoms could not be determined and the oxygen atoms are said to be located within the symmetry related planes at $0.25c$ and $0.75c$. The later work [7] specifies the positions of hydrogen atoms and suggests that oxygen of the OH is shifted by $\sim 0.3\text{\AA}$ along the c -axis with respect to the previously reported positions as indicated in figure 2. The OH groups bring a structural ambiguity: two OH molecules do not have an energetic preference whether to point the hydrogen atom ‘upwards’ or ‘downwards’ along the c -axis. This is accounted for by introducing 0.5 occupancies in both possible arrangements. To simplify our discussion we introduce a notation where arrows (\uparrow) and (\downarrow) correspond to the z -coordinate of the hydroxyl group oxygen being smaller and larger than the z -coordinate of hydrogen, respectively. The pair of hydroxyl groups per primitive cell is denoted by a pair of arrows. In the hexagonal primitive cell four different orientations ($\uparrow\uparrow$), ($\uparrow\downarrow$), ($\downarrow\uparrow$), ($\downarrow\downarrow$) are possible with ($\uparrow\uparrow$) and ($\downarrow\downarrow$) cells, and ($\uparrow\downarrow$) and ($\downarrow\uparrow$) cells being equivalent.

To identify the ground state we calculate the energy of both the ($\downarrow\downarrow$) and ($\downarrow\uparrow$) configurations. For later use, we also consider cells in which the hydroxyl molecules are slightly tilted away from the c -axis keeping the oxygen atoms on the c -axis and OH bond length fixed. These are indicated by ($\searrow\swarrow$) if tilted from a ($\downarrow\downarrow$) configuration and by ($\searrow\nwarrow$) if tilted from a ($\downarrow\uparrow$) configuration. Additionally, we consider monoclinic cells created by doubling the hexagonal unit cell in the \mathbf{b} direction. Here, each of the two contributing hexagonal cells is described by one pair of arrows for the OH-orientation, for example ($\downarrow\downarrow$)($\downarrow\downarrow$) or ($\downarrow\downarrow$)($\uparrow\uparrow$) in the simplest cases. The ($\downarrow\downarrow$)($\downarrow\downarrow$) configuration resembles a monoclinic cell which is reducible to a single hexagonal cell with a ($\downarrow\downarrow$) configuration. On the other hand, the ($\downarrow\downarrow$)($\uparrow\uparrow$) configuration resembles a monoclinic cell that cannot be reduced further due to the alternating OH-orientation in subsequent OH columns.

The binding energies of all models are compared in Figure 4. The top line in the graph indicates which reference the unrelaxed cell is based on and arrows indicate the OH-configuration before relaxation. The results per hexagonal cell are plotted in ascending energy order. The mixed configuration ($\downarrow\downarrow$)($\uparrow\uparrow$) monoclinic structure suggested by Elliott [34], yields the lowest energy

(structure 1) and is used as the reference energy. The lattice constants are $a=9.53\text{\AA}$, $b=2a$ and $c=6.91\text{\AA}$. We find the second lowest energy for the hexagonal cell (structure 2) with the lattice constants $a=b=9.53\text{\AA}$ and $c=6.91\text{\AA}$. The relaxed bond lengths of the hydroxyl and phosphate groups and bonding angles P-O-P of the phosphates in structure 2 are listed in Table 1. We find excellent agreement with experiment [6,7]. During the relaxation of structures 3 and 4 we find that the OH pairs realign with the c-axis ending up in structure 2. In structure 6 hydrogen atoms stay at the tilted positions during the relaxation yielding a binding energy which is $\sim 269\text{meV/cell}$ higher than the hexagonal ground state structure 2. The ($\downarrow\uparrow$) type configurations where OH pairs flip within the same c-column are $\sim 0.4\text{eV}$ higher in energy (per hexagonal cell) than the ground state making them unlikely.

The energy difference between the monoclinic (structure 1) and hexagonal (structure 2) cells is only $\sim 22\text{meV}$ per hexagonal cell suggesting that at room temperature HA can crystallize in a mixed phase with randomly distributed ($\downarrow\downarrow$) and ($\uparrow\uparrow$) domains. In the rest of the paper we will focus on these two structures.

B. Activation energy for the hexagonal to monoclinic transition

The monoclinic phase of HA was first described by Elliott *et. al.* [34] who, following the work by Young [10], prepared a sample consisting of $\sim 30\%$ monoclinic HA and 70% hexagonal phases. They concluded that HA grown in a sufficiently clean experimental environment and having little impurities or vacancies can assume monoclinic symmetry under ambient conditions. Later, Hitmi *et al.* [35] found that while at ambient conditions both the hexagonal and monoclinic phases can occur. When heated above 470K HA always assumes the hexagonal structure, and the transformation is reversible. The overall structural similarity of the monoclinic and hexagonal phases and closeness of the calculated binding energy raise a question of the activation barrier and transition mechanism. To investigate theoretically possible pathways of the transition we use transition state theory and more specifically, the nudged elastic band method (NEBM) [36] as implemented in the VASP code.

We start by calculating the energy barrier between two equivalent hexagonal structures ($\downarrow\downarrow$) and ($\uparrow\uparrow$), using hexagonal structure 2 described in section A. We assume that changing the OH-configuration from ($\downarrow\downarrow$) to ($\downarrow\uparrow$) is unlikely as we have found the latter to be 0.4eV higher in energy than the former. The transformation involves not only the hydrogen displacement but also that of oxygen (Fig. 5), because the equilibrium positions of oxygen are shifted from the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ containing Ca triangles. One possible pathway for the transition is to move the hydrogen atoms of the OH molecules along the z-axis. This requires breaking the OH-bonds and re-bonding hydrogen with the oxygen atom of the adjacent OH molecule (Fig. 5). Simultaneously, the oxygen atoms of the OH are moved in the opposite direction to their new equilibrium positions. Another possible mechanism is rotating each hydrogen atom around its bonding oxygen while simultaneously translating the oxygen to its new equilibrium position. The

rotation and translation of the hydrogen atom H_i from configuration (\downarrow) to (\uparrow) is described using spherical coordinates as:

$$\vec{r}_{H_i} = \vec{r}_{O(H_i)} + r_{O-H} \cdot \begin{pmatrix} \sin(\vartheta)\cos(\varphi_i) \\ \sin(\vartheta)\sin(\varphi_i) \\ \cos(\vartheta) \end{pmatrix}, \quad \vartheta = \pi, \dots, 0, \quad (1)$$

Note that $\vec{r}_{O(H_i)}$ is not constant throughout the transition as the original oxygen atom has to move along the c-axis to its new equilibrium position. The $\vec{r}_{O(H_i)}$ and the angle ϑ are used to create the images for the NEBM to describe the transition pathway. The angle φ_i is given with respect to the \bar{a} lattice vector and is chosen to move the H atoms in between two Ca atoms (Fig. 6). This yields two choices:

- (i) Rotate hydrogen atom with angles $\varphi_1 = \pi / 3$, $\varphi_2 = 4\pi / 3$ and move the oxygen atom
- (ii) Rotate hydrogen atom with angles $\varphi_1 = \pi / 3$, $\varphi_2 = 2\pi / 3$ and move the oxygen atom

Figure 5 illustrates the linear and rotational transformations, and Fig. 7 shows the calculated energy along these transition paths. The energy barriers are 3.5eV for the linear transition, and 1.3eV and 1.4eV in the rotational transitions (i) and (ii), respectively. These result in the activation energy per OH of 1.75eV, 0.65eV and 0.7eV for the linear and spherical transitions, respectively. The large difference in energy is not surprising as the first mechanism requires breaking the OH-bonds. On the other hand, in the rotational flip no bonds are broken. The barriers for two rotational transitions are very similar and close in energy. In what follows we only consider the rotational transformation of type (i).

Expanding the potential energy of the rotational transformation to second order around the minimum, we calculate the oscillation frequency of approximately 250cm^{-1} corresponding to the period of $\tau \approx 134\text{fs}$. The average time after which a spontaneous flip from ($\downarrow\downarrow$) to ($\uparrow\uparrow$) occurs is therefore

$$t_{(\downarrow\downarrow)\rightarrow(\uparrow\uparrow)} = \tau \times N = \tau \times \exp(E_{B,0} / k_B T) \approx 162 a, \quad (2)$$

at room temperature. In equation (2), N is the number of attempts needed to simultaneously flip both OH molecules per unit cell if each attempt has the probability of success of $p = \exp(-E_{B,0} / k_B T)$. We use $E_{B,0}=1.3\text{eV}$ for the activation energy. The average transition time between the two equivalent hexagonal structures ($\downarrow\downarrow$) and ($\uparrow\uparrow$) is one hundred sixty two years at room temperature.

Now consider the monoclinic cell. Assuming that the OH molecules located along the neighboring columns do not interact, the energy barrier for rotational transitions in the monoclinic cell can be written as

$$\begin{aligned}
(\downarrow\downarrow)(\downarrow\downarrow) \rightarrow (\uparrow\uparrow)(\uparrow\uparrow) : & \quad E_B = 2E_{B,0} / 4 = E_{B,0} / 2 = 0.65\text{eV} \\
(\downarrow\downarrow)(\downarrow\downarrow) \rightarrow (\downarrow\downarrow)(\uparrow\uparrow) : & \quad E_B = E_{B,0} / 4 = 0.33\text{eV} .
\end{aligned} \tag{3}$$

In equation (3) $E_{B,0}$ is the previously calculated energy barrier of 1.3eV in the hexagonal cell, and E_B is the activation energy per OH pair in the monoclinic cell. Transforming $(\downarrow\downarrow)(\downarrow\downarrow)$ to $(\uparrow\uparrow)(\uparrow\uparrow)$ requires the same energy per OH as flipping $(\downarrow\downarrow)$ to $(\uparrow\uparrow)$. However, the activation energy per OH to transform from $(\downarrow\downarrow)(\downarrow\downarrow)$ to $(\downarrow\downarrow)(\uparrow\uparrow)$ is reduced by a factor of two. The experimentally obtained range for the activation energy to change from hexagonal to monoclinic is 0.016-0.630eV per OH and 0.84-0.89eV per OH, reported by Hitmi and Nakamura [35,37], are in qualitative agreement with our results. Hitmi suspected a rotational transition, while Nakamura suspected a linear one explaining why the two ranges are so different. Using classical molecular dynamics Hochrein *et. al.* [38] find 0.52eV per OH flip in good agreement with our results. Using our calculated activation energy we write the probability of transformation from $(\downarrow\downarrow)(\downarrow\downarrow)$ to $(\downarrow\downarrow)(\uparrow\uparrow)$ as

$$p = \exp(-E_{B,0} / 2k_B T). \tag{4}$$

Using the same oscillation period as for the hexagonal cell the average time for the spontaneous hexagonal-monoclinic transition is estimated as

$$t_{(\downarrow\downarrow)(\downarrow\downarrow) \rightarrow (\downarrow\downarrow)(\uparrow\uparrow)} = \tau \times N = \tau \times \exp(E_{B,0} / 2k_B T) \approx 26\text{ms} , \tag{5}$$

at room temperature. The short transition time suggests that the hexagonal phase would always flip to the monoclinic phase under ambient conditions. Further investigation is needed to explain why the transition from the monoclinic to hexagonal phase occurs at 470K.

C. Electronic structure

The total electronic density of states (DOS) for both the hexagonal and monoclinic structures is shown in Figure 8 a). For comparison we normalize the DOS to the hexagonal cell. The DOS of both structures are very similar, and the following description applies to both phases. Note that we distinguish between the oxygen atoms from the phosphate molecules ($O_{(P)}$) and oxygen atoms from the OH molecules ($O_{(H)}$). The states between -20eV and -17eV mainly consist of $O_{(P)}$, $O_{(H)}$ and phosphorous 2s and 3s states, respectively. At -17eV the hydrogen 1s states are mixed in. In an ideal PO_4 tetrahedron the phosphorus sp^3 hybridized orbitals form σ and π bonds with the surrounding oxygen. The σ -type electronic states appear in two peaks within the energy window -8eV to -4eV. In an ideal PO_4 tetrahedron these σ -states would be closer to each other in energy. However, in the HA crystal the PO_4 tetrahedron is slightly distorted from the ideal 109.5° bonding angle leading to a split in the energy levels. We find the σ^* electronic states in the conduction band between 6eV and 9eV. The remaining $O_{(P)}$ and $O_{(H)}$ p-states are the main contributors to the DOS between -3eV and the top of the valence band.

Calcium 4s-states contribute mainly between -3eV and the top of the valence band at zero. In Figure 8 b) we show the partial DOS projected on the different atomic species in the hexagonal and monoclinic cells in the near gap region. At the bottom of the conduction band the main contribution is from the s-like states of Ca atoms. The conduction band between 6eV and 8eV is almost entirely made up by unoccupied Ca states with $l=2$. In both crystals the GGA band gap is 5.23eV in good agreement with the previously reported LDA band gap of 5.40eV [14]. The reported experimental values of the band gap range from 3.95eV [39] to more than 6eV [40]. Our calculations suggest a large band gap considering that GGA underestimates the gap. Since the DOS of the hexagonal and monoclinic phase appear very similar, we only calculate the band structure for the smaller hexagonal cell. In Figure 9 we show the calculated band structure along the high-symmetry directions in the Brillouin zone in the near gap region. First, we notice that HA is an indirect gap material. The valence band top shows little dispersion indicating heavy localized holes. We find two energy maxima in the valence band separated by only 8meV. The top of the valence band (shifted to 0eV) occurs along the Γ to K line. The bottom of the conduction band is at the Γ -point, and shows a free electron character with the anisotropic effective mass. Fitting the bottom of the conduction band at Γ to a second order polynomial we calculate the effective electron mass tensor

$$\left(m_{\alpha\beta}^*\right) = \hbar^2 \left[\frac{d^2 E}{dk_\alpha dk_\beta} \right]^{-1} = \begin{pmatrix} 0.61 & -0.01 & -0.01 \\ -0.01 & 0.61 & -0.01 \\ -0.01 & -0.01 & 0.48 \end{pmatrix} \times m_e . \quad (6)$$

The principal values are 0.48, 0.60 and 0.62 in units of the electron mass. The indirect band gap is 5.23eV. The direct transitions at the top of the valence band and at the Γ point are at 5.46 eV and 5.28 eV, respectively. Another interesting feature is the flat region in both the valence and conduction bands along the M to K line. With the excitation energy of 5.75eV this feature should be noticeable in optical adsorption. Unfortunately, no experimental data is available. When comparing our results with the band structure calculated by Rulis *et. al.* [15] in Fig. 10 we notice slight differences. The most notable one is the energy gap. Rulis calculates 4.5eV versus our 5.3eV. We attribute the discrepancy to a different basis (Rulis uses the linear combination of atomic orbitals). The overall band structure, and near parabolic dispersion at the bottom of the conduction band agree well with their results.

D. Phonon eigenmodes at the Γ -point

Experimental studies of hydroxyapatite vibrational properties remain scarce. The most recent papers are those of Fowler *et. al.* [41] and Markovic *et. al.* [42] reporting the infrared (IR) and Raman active vibrational modes, respectively. Theoretical studies of the HA vibrational spectra are quite difficult due to the crystal's complexity, and are typically limited to classical shell models [43]. However, the results strongly depend on the model potentials that have to be fitted to match the experimental data (a comparison of different sets of parameters is given by Calderin [43]). Therefore, a more general and transferrable approach of calculating the phonon

spectrum is desirable. We use DFT to calculate the vibrational eigenmodes of hexagonal HA at the Γ -point. We analyze the influence of the ionic nature (long range Coulomb interactions) of the crystal on the eigenmodes and identify the vibrational modes mostly affected by the long range effects.

To calculate the short-range force constant matrix we take the numerical derivative of the Hellmann-Feynman forces with respect to small ionic displacements [e.g. 44]. The lattice Fourier transform of the force constant matrix yields the dynamical matrix [44,45]:

$$\bar{D}(\bar{k}; \mu, \nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_m \bar{B}(0, \mu; m, \nu) \cdot \exp\{2\pi i \bar{k} \cdot [\bar{R}(0, \mu) - \bar{R}(m, \nu)]\}. \quad (7)$$

The $\bar{R}(0, \mu)$ is the position of atom μ in the 0-th primitive cell within the supercell. $\bar{R}(m, \nu)$ is the position of atom ν in the m -th unit cell. $\bar{B}(0, \mu; m, \nu)$ are the force constants relating atoms $(0, \mu)$ and (m, ν) . M_μ and M_ν are the masses of atoms ν and μ . In 3-dimensional space the dimension of the dynamical matrix is $3N \times 3N$, where N is the number of atoms in the primitive cell. Since we are interested in phonons at the Γ -point we only calculate the forces in a single hexagonal primitive cell. In covalent systems the range of interaction is assumed to be finite and the dynamical matrix can be directly calculated using the Hellmann-Feynman forces acting on the ions in the supercell when displacing one atom from its equilibrium position. In the ionic system one has to worry about long-ranged dipole-dipole interactions. This is accomplished by adding a long-range correction to the dynamical matrix given by [44]

$$\bar{D}_{\text{ap}}^{\text{long}}(\bar{k}; \mu, \nu) = \frac{e^2}{V \epsilon_0 \epsilon_\infty} \frac{[\bar{k} \bar{Z}^*(\mu)]_\alpha [\bar{k} \bar{Z}^*(\nu)]_\beta}{|\bar{k}|^2} \times \exp\left(-\frac{|\bar{k}|^2}{\rho^2}\right), \quad (8)$$

here we use SI units. $\bar{Z}^*(\mu)$ is the Born effective charge tensor of atom μ , and V is the volume of the primitive cell. The long-range contribution only affects the phonon modes close to the Γ -point. The Born effective charge tensors introduce a directional dependence in equation (8). The total dynamical matrix is given by a sum of (7) and (8).

First, we calculate the phonon eigenmodes in HA at the Γ -point without the long-range correction. We use a single primitive hexagonal cell. There are 132 eigenmodes including Raman and IR active vibrations. We use our calculated eigenmodes to approximate the phonon density of states (PDOS) at the Γ -point given by

$$\frac{\text{\#of Eigenmodes}}{\Delta f} = \sum_i \delta(f - f_i) \equiv N(f), \quad (9)$$

The DOS is a sum of delta-functions positioned at the calculated eigenmodes at each k-point. We represent these peaks by a Gaussian, and apply a Gauss broadening of $\sigma = 15 \text{cm}^{-1}$. In Figure 11 we compare our results with the DOS constructed using experimental IR and Raman active

modes as reported by Fowler [41] and Markovic [42]. The calcium ions contribute predominantly to the low frequency modes. In the ranges from 350cm^{-1} to 650cm^{-1} and from 850cm^{-1} to 1100cm^{-1} mainly the PO_4 molecules contribute to the spectrum. The OH-modes are at 693cm^{-1} and 3660cm^{-1} corresponding to the OH's libration and stretching modes, respectively. Comparing with the experimental work we find good qualitative agreement. The frequencies corresponding to the phosphate eigenmodes are underestimated by $\sim 5\text{-}10\%$. This is consistent with the observation that the theoretical PO bond length is $0.02\text{-}0.03\text{\AA}$ longer than the experimental value. On the other hand, theoretical eigenmodes of the OH groups at 693cm^{-1} (libration mode in x and y directions) and 3660cm^{-1} (OH stretching mode) are overestimated by $\sim 5\text{-}10\%$ compared with experiment.

Having found reasonable agreement with experiment without considering the long-range interactions, we now include the long-range correction (8). We approach the Γ point along the M to Γ , K to Γ and A to Γ directions. These directions correspond to approaching Γ from the face center, corner and top of the hexagonal Brillouin zone. Experimentally, the high frequency dielectric constant is sensitive to the Ca/P ratio of the crystal [e.g. 46]. The values for ϵ_∞ in the literature for stoichiometric HA with the Ca/P ratio 1.67 vary between $\epsilon_\infty=5$ and $\epsilon_\infty=20$ [46-50]. This is in part to the variation in porosity, and water content of the samples, and in part to too low a frequency of measurement. In this work we use $\epsilon_\infty=5$ and cross-check with $\epsilon_\infty=7$ to see the qualitative dependency of the eigenmodes on ϵ_∞ . The calculated Born effective charge tensors are summarized in Table 2. For the Gaussian smearing in (8) we use $\rho=0.02\text{\AA}^{-2}$. We plot our results in Figure 12 a) along with the experimentally measured modes. We find that including the long-range correction has little effect on most of the vibration modes in good agreement with Calderin's work [43] where a shell-model was used to calculate the phonons when approaching the Γ -point from the (100) and the (001) direction. In Figure 12 b) we show the difference between the long-range corrected spectrum and un-corrected spectrum below 1200cm^{-1} at the Γ -point. Positive Δf means the long-range corrected modes are higher in frequency. The frequency shifts are very similar when approaching along the (100) direction and the (110) direction (M to Γ and K to Γ) ranging from 1cm^{-1} to 25cm^{-1} . When approaching along the (001) direction (A to Γ) somewhat different eigenmodes shift compared to approaching along (100) and (110), and the peak at 318cm^{-1} virtually disappears. While in the modes between 97cm^{-1} and 318cm^{-1} all atoms in the cell are vibrating, the 318cm^{-1} mode is a pure OH libration mode in the x-y-plane. The remaining shifted modes close to 600cm^{-1} and around 1000cm^{-1} are pure PO_4 vibration modes. The change in frequency due to the long-range correction is most notable for the OH mode at 318cm^{-1} which moves up to 343cm^{-1} when approaching Γ from the M point. Using $\epsilon_\infty=7$ in the long-range correction, this OH mode moves up to 335cm^{-1} , being the only mode substantially affected by using $\epsilon_\infty=5$. Overall, we find good agreement between our phonon spectra and experimental results.

E. Elastic constants of HA

The anisotropy of the elastic properties of bones is governed by their main constituents, HA, the collagen chains and water. The theoretical determination of the elastic properties of composite materials is often done by averaging the elastic properties of the separate materials. Although, the quality of the results fluctuates depending on the material in question, upper and lower bounds of the effective moduli of composites can be found rigorously [51]. Previously, Katz and Ukraincik [52] calculated a set of pseudo-single crystal elastic constants extracted from the measured elastic constants of fluorapatite. The validity of such a calculation is somewhat justified by a strong similarity of the crystal structures of these two materials. Mustafa *et. al.* use a force field approach to obtain the elastic constants of HA [53]. Here, we calculate the elastic constants of hexagonal HA from first-principles.

Generally, the energy of a strained system can be written as a second order Taylor expansion in the distortion parameters α_{ij} :

$$E(V, \alpha) = E(V_0, 0) + \frac{V_0}{2} \sum_{a,b,c,d} C_{abcd} \alpha_{ab} \alpha_{cd} . \quad (10)$$

The first order term drops out as the expansion is about the ground state. The second order term is described by the adiabatic elastic constants C_{abcd} . However, the C_{abcd} and α_{ab} are not all independent, and using the Voigt notation, equation (10) can be written as

$$E(V, \alpha) = E(V_0, 0) + \frac{V_0}{2} \sum_{i,j} C_{ij} \alpha_i \xi_i \alpha_j \xi_j . \quad (11)$$

The introduced factors ξ_i account for the symmetry of the α 's, $\alpha_{ab} = \alpha_{ba}$, i.e. for $b \neq a$ both α_{ab} and α_{ba} are labeled with the same Voigt index. Therefore, we get $\xi_i = 1$ if the Voigt index is 1, 2 or 3 and $\xi_i = 2$ if the Voigt index is 4, 5 or 6 [54].

There are five independent elastic constants in a hexagonal crystal: C_{11} , C_{12} , C_{13} , C_{33} , $C_{44} = C_{55}$. In order to determine these constants, five independent stresses must be applied to the system (see appendix). Distortions (I), (III) and (V) keep hexagonal symmetry in the strained cell. Distortion (II) creates a monoclinic cell and distortion (IV) creates a cell with triclinic symmetry. Equation (2) is valid for small distortions. To have a measure of ‘‘small’’ we compare the volume changes after applying a specific distortion. Distortions (I) and (V) yield the largest change in volume. Thus, for (I) we use the parameters $\alpha = -0.01, -0.005, 0.00, 0.005, 0.01$ and for (V) we apply $\alpha = -0.005, -0.0025, 0.00, 0.0025, 0.005$. For distortions (II)-(IV) we use $\alpha = -0.02, -0.01, 0.00, 0.01, 0.02$. These choices of α ensure that the change in volume relative to the equilibrium volume V_0 is smaller than 15\AA^3 or $\sim 2.8\%$ of V_0 . For all distortions we use a quadratic fit to extract the elastic constants C_{ij} . Our results are summarized in table 3. For C_{11} , C_{33} and the bulk modulus B we find agreement within $\sim 6\%$ of the values previously reported by Katz and Mostafa

[52,53]. Our C_{12} , C_{13} and C_{44} are within $\sim 21\%$ of Katz's and Mostafa's results indicating overall good qualitative agreement.

IV. Conclusions

Using density functional theory we find that the ground state of hydroxyapatite is monoclinic in agreement with previous calculations [13] and recent experiments [35,37]. The hexagonal phase is only 22 meV higher in energy than the monoclinic ground state. The structural transition path from the monoclinic to the hexagonal crystal phase and vice versa most likely involves the rotation of hydroxyl groups as suggested by Hitmi [35]. The activation energy for such a transition is 0.33eV per OH molecule and the transition time at room temperature is ~ 26 ms. We find close similarity in the electronic structure of both phases suggesting similar chemical properties. For the hexagonal phase in agreement with previous theoretical results we find the indirect band gap 5.23eV. The bottom of the conduction band mainly consists of Ca s-states and shows free electron like behavior with the anisotropic mass at the Γ point. Our results for the vibrational eigenmodes at the Γ point are within $\pm 10\%$ of available experiment [41,42], and calculated elastic constants agree well with the experimental results reported by Katz [52] and Mostafa [53].

Acknowledgement

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References

- [1] C. A. Van Blitterswijk, J. J. Grote, W. Kuijpers, W. T. Daems, K. A. de Groot, *Biomaterials* **7**, 553 (1986).
- [2] A. L. Boskey, "The Organic and Inorganic Matrices", CRC Press, Washington, 91-123 (2004).
- [3] A. Kruse, R. E. Jung, F. Nicholls, R. A. Zwahlen, C. H. F. Hämmerle, F. E. Weber, *Clin. Oral Impl. Res.* **22**, 506 (2011).
- [4] B. Leon, J. A. Janson, "Thin Calcium Phosphate Coatings for Medical Implants", Springer, 2009.
- [5] W. J. Schmidt, *Naturwissenschaften* **24**, 361 (1936).
- [6] A. S. Posner, A. Perloff, A. F. Diorio, *Acta Cryst.* **11**, 308 (1958).
- [7] M. I. Kay, R. A. Young, *Nature* **204**, 1050 (1964).
- [8] S. Weiner, P. A. Price, *Calcif. Tissue Int.* **39**, 365 (1986).
- [9] E. M. Carlisle, *Science* **167**, 179 (1970).
- [10] R. A. Young, *Trans. N. Y. Acad. Sci.* **29**, 949 (1967).
- [11] H. Morgan, R. M. Wilson, J. C. Elliott, S. E. P. Dowker, P. Anderson, *Biomaterials* **21**, 617 (2000).
- [12] G. Ma, X. Y. Liu, *Cryst. Growth Des.* **9**, 2991 (2009).
- [13] N. H. de Leeuw, *Chem. Commun.* 1646-1647 (2001).
- [14] L. Calderin, M. J. Stott, A. Rubio, *Phys. Rev. B* **67**, 134106 (2003).
- [15] P. Rulis, L. Ouyang, W. Y. Ching, *Phys. Rev. B* **70**, 155104 (2004).
- [16] H. F. Chappell, P. D. Bristowe, *J. Mater. Sci.* **18**, 829 (2007).
- [17] N. H. de Leeuw, *Royal Society of Chemistry* **20**, 5376 (2010).
- [18] S. Yin, D. E. Ellis, *Phys. Chem. Chem. Phys.* **12**, 156 (2010).
- [19] J. Terra, E. Rodrigues Dourado, J.-G. Eon, D. E. Ellis, G. Gonzalez, A. M. Rossi, *Phys. Chem. Chem. Phys.* **11**, 568 (2009)
- [20] L. Calderin, D. Dunfield, M. J. Stott, *Phys. Rev. B* **72**, 224304 (2005).
- [21] M. Corno, A. Rimola, V. Bolis, P. Ugliengo, *Phys. Chem. Chem. Phys.* **12**, 6309 (2010).
- [22] H. F. Chappell, M. Duer, N. Groom, C. Pickard, P. D. Bristowe, *Phys. Chem. Chem. Phys.* **10**, 600 (2008).
- [23] N. Almora-Barrios, K. F. Austen, N. H. de Leeuw, *Langmuir* **25**, 5018 (2009).
- [24] D. K. Dubey, V. Tomar, *Acta Biomaterialia* **5**, 2704 (2009).
- [25] R. Astala, M. J. Stott, *Phys. Rev. B* **78**, 075427 (2008).
- [26] G. Kresse, J. Hafner, *Phys. Rev. B* **47**, 558 (1993).
- [27] G. Kresse, J. Furthmüller, *Comput. Mat. Sci.* **6**, 15 (1996).
- [28] G. Kresse, J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [29] G. Kresse, J. Hafner, *J. Phys: Condens. Matt.* **6**, 8245 (1994).
- [30] G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [31] J. P. Perdew, J. A. Chevary, S. H. Voskok, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [32] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [33] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [34] J. C. Elliott, P. E. Mackie, R. A. Young, *Science* **180**, 1055 (1973).
- [35] N. Hitmi, C. LaCabanne, R. A. Young, *J. Phys. Chem. Solids* **47**, 533 (1986).

- [36] H. Jonsson, G. Mills, K. W. Jacobsen, *Nudged elastic band method for finding minimum energy paths of transitions*, Ed. B. J. Berne, G. Ciccotti, D. F. Coker, 385 (World Scientific, 1998).
- [37] S. Nakamura, H. Takeda, K. Yamashita, *J. Appl. Phys.* **89**, 5386 (2001).
- [38] O. Hochrein, R. Kniep, D. Zahn, *Chem. Mater.* **17**, 1978 (2005).
- [39] G. Rosenman, D. Aronov, L. Oster, J. Haddad, G. Mezinskis, I. Pavlovska, M. Chaikina, A. Karlov, *J. Lumin.* **122–123** (2007) 936–938.
- [40] M. Tsukada, M. Wakamura, N. Yoshida, T. Watanabe, *J. Mol. Cat. A* **338**, 18 (2011).
- [41] B. O. Fowler, *Inorg. Chem.* **13**, 194-207 (1973).
- [42] M. Markovic, B. O. Fowler, M. S. Tung, *J. Res. Natl. Inst. Stand. Technol.* **109**, 553 (2004).
- [43] L. Calderin, D. Dunfield, M. J. Stott, *Phys. Rev. B* **72**, 224304 (2005).
- [44] S. Baroni, S. Gironcoli, A. Dal Corso, P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [45] M. Born, K. Huang, *Dynamical theory of crystal lattices*, Oxford University Press (1962).
- [46] M. Quilitz, K. Steingroever, M. Veith, *J. Mater. Sci.: Mater. Med.* **21**, 399 (2010).
- [47] C. C. Silva, H. H. B. Rocha, F. N. A. Freire, M. R. P. Santos, K. D. A. Saboia, J. C. Goes, A. S. B. Sombra, *Mat. Chem. Phys.* **92**, 260 (2005).
- [48] T. P. Hoepfner and E. D. Case, *J. Biomed. Mater. Res.* **60**, 643 (2002).
- [49] T. Ikoma, A. Yamazaki, *J. Mater. Sci. Lett.* **18**, 1225 (1999).
- [50] J. P. Gittings, C. R. Bowen, A. C. E. Dent, I. G. Turner, F. R. Baxter, J. B. Chaudhuri, *Acta Biomaterialia* **5**, 743 (2009).
- [51] G. W. Milton, *Phys. Rev. Lett.* **46**, 542 (1981).
- [52] J. L. Katz, K. Ukraincik, *J. Biomechanics* **4**, 221-227 (1971).
- [53] N. Y. Mostafa, P. W. Brown, *J. of Phys and Chem. Of Solids* **68**, 431 (2007).
- [54] D. C. Wallace, *Solid State Physics* **25**, 302 (1970).
- [55] L. Fast, J. M. Wills, B. Johansson, O. Eriksson, *Phys. Rev. B* **51**, 17431 (1995).

I. Appendix

Following the approach described by Fast *et. al* [55], we use five independent distortions to obtain the elastic constants of the hexagonal cell. Their action on the crystal structure and symmetry are explained in the section E. The small parameter α describes the deviation of the distorted crystal from the original one.

$$\begin{aligned} e_I &= \begin{pmatrix} 1+\alpha & 0 & 0 \\ 0 & 1+\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ e_{II} &= \begin{pmatrix} 1+\alpha & 0 & 0 \\ 0 & 1-\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ e_{III} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\alpha \end{pmatrix} \\ e_{IV} &= \begin{pmatrix} 1 & 0 & \alpha \\ 0 & 1 & 0 \\ \alpha & 0 & 1 \end{pmatrix} \\ e_V &= \begin{pmatrix} 1+\alpha & 0 & 0 \\ 0 & 1+\alpha & 0 \\ 0 & 0 & 1+\alpha \end{pmatrix} \end{aligned} \tag{12}$$

Table 1: Comparison of fully relaxed theoretical bond lengths and bond angles in HA with experimental values.

	theory	Exp. [ref. 7]
P-O_I	1.56Å	1.54Å
P-O_{II}	1.57Å	1.55Å
P-O_{III}	1.55Å	1.53Å
O-H	0.977Å	0.957Å
O_I-P-O_{II}	111.1°	111.0 °
O_I-P-O_{III}	111.6°	111.5°
O_{II}-P-O_{III}	107.5°	107.5°

Table 2: Born effective charge tensors for the different atomic sites.

Born effective charge	
H	$\begin{pmatrix} 0.37 & -0.01 & 0 \\ 0.01 & 0.37 & 0 \\ 0 & 0 & 0.28 \end{pmatrix}$
P	$\begin{pmatrix} 3.17 & 0.04 & 0 \\ -0.01 & 3.17 & 0 \\ 0 & 0 & 3.08 \end{pmatrix}$
Ca _I	$\begin{pmatrix} 2.41 & -0.08 & 0 \\ 0.08 & 2.41 & 0 \\ 0 & 0 & 2.51 \end{pmatrix}$
Ca _{II}	$\begin{pmatrix} 2.45 & 0.02 & 0 \\ -0.01 & 2.45 & 0 \\ 0 & 0 & 2.46 \end{pmatrix}$
O _I	$\begin{pmatrix} -1.93 & 0.03 & 0 \\ -0.02 & -1.93 & 0 \\ 0 & 0 & -1.41 \end{pmatrix}$
O _{II}	$\begin{pmatrix} -1.92 & 0 & 0 \\ 0 & -1.91 & 0 \\ 0 & 0 & -1.30 \end{pmatrix}$
O _{III}	$\begin{pmatrix} -1.47 & -0.02 & 0 \\ 0.02 & -1.47 & 0 \\ 0 & 0 & -2.13 \end{pmatrix}$
O _H	$\begin{pmatrix} -1.71 & 0.04 & 0 \\ -0.04 & -1.71 & 0 \\ 0 & 0 & -0.94 \end{pmatrix}$

Table 3: Calculated elastic constants and bulk modulus compared to other theoretical calculations and corresponding experimental values. The bulk modulus is related to the elastic constants by the formula $B = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2)$.

constant [10¹¹ dyn/cm²]	this work	Ref. [53]	pseudo-exp. [52]
C ₁₁	12.90	15.75	13.70
C ₁₂	3.70	5.74	4.25
C ₁₃	6.70	5.97	5.49
C ₃₃	17.30	14.73	17.20
C ₄₄	4.40	4.39	3.96
B	8.60	9.07	8.90

Fig. 1: Schematic of the HA crystallization during bone formation. Experiments suggest that the c-axes of both the tropocollagen and HA platelets are aligned [8]. The formation of bone tissue happens in several steps. After the tropocollagen helices are aligned, constituents of the HA crystal accumulate in the spaces between the tropocollagen and crystallize in the (001) orientation. The final HA mineral within the spaces consists of many separate HA platelets.

Fig. 2: HA primitive cells as described in references 6 and 7. The cell dimensions are $a=b=9.432\text{\AA}$, $c=6.881\text{\AA}$. The main difference between the two structures is the location of the oxygen atoms from the OH pairs as indicated in the figure. Following our notation (see text) we call the shown orientation of the OH pairs the $(\downarrow\downarrow)$ orientation.

Fig. 3: Top-view on the hexagonal primitive cell. In the figure we shifted the original primitive cell in the x and y directions so that the OH column is in the center of the depicted cell. The darker colored Ca_{II} atoms and PO_4 molecules are centered at $z=0.25c$ and the lighter ones are centered at $z=0.75c$. The OH column is surrounded by six Ca_{II} atoms and six PO_4 molecules. The Ca_{I} atoms are now in the corners of the cell. Below both of the two visible Ca_{I} atoms there is a second Ca_{I} atom at the distance $0.5c$. Here, the lighter Ca_{I} atom is close to the top face and the darker Ca_{I} atom is at $\sim 0.5c$.

Fig. 4: The calculated structures are listed in ascending order according to the binding energy per single cell and the minimum energy is shifted to zero. We find the lowest binding energy for the monoclinic $(\downarrow\downarrow)(\uparrow\uparrow)$ configuration followed by the hexagonal $(\downarrow\downarrow)$ structure. The energy difference these two is $\sim 22\text{meV/cell}$. The binding energies of structures 2-4 are identical. Structures with flipped OH pairs within the same column generally yield higher binding energy.

Fig. 5: a) OH positions with respect to the surrounding Ca_{II} -triangles in the $(\downarrow\downarrow)$ and $(\uparrow\uparrow)$ configurations.

b) The figures show two paths of the hydrogen atoms from one equilibrium position to another symmetry related equilibrium position thus flipping from $(\downarrow\downarrow)$ to $(\uparrow\uparrow)$.

Fig. 6: Top-view along the OH column surrounded by Ca_{II} and PO_4 . The dark Ca atoms are at $z=1/4$ and the light ones at $z=3/4c$. The OH pairs are in the center. There are three equivalent trajectories to flip the top OH-pair rotationally. One of them is indicated by projection 1. Once path 1 is selected there are 2 inequivalent ways to flip the bottom OH-pair as indicated by the dashed lines.

Fig. 7: The energy barriers corresponding to the translational (1) and rotational (2 and 3) hydrogen trajectories. The energy barrier for a translational displacement of the

hydrogen atoms along the z-axis is approximately 3 times higher than that of the rotational transition.

Fig. 8: The total DOS (a) and site-projected DOS in the near-gap region (b) of hexagonal and monoclinic HA. The DOS is normalized to a hexagonal cell. The Fermi level is at zero energy. The band gap is 5.23 eV.

Fig. 9: The electronic band structure of hexagonal HA in the near gap region. The energy range in the gap region and is not shown for clarity. The band structure suggests that HA is an indirect band material. The lowest energy optical excitations are indicated. The dashed lines between M and K indicate nearly constant energy optical excitations.

Fig. 10: The band structure of hexagonal HA from Ref. 15 (left) compared to our band structure (right).

Fig. 11: The theoretical phonon density of states at the Γ -point compared with the experimental IR and Raman active modes. Our Ca and PO₄ peaks are underestimated by $\sim 10\%$, while the OH modes are overestimated by $\sim 10\%$.

Fig. 12: a) The phonon frequencies at the Γ -point with and without the long-range correction. When applying the long-range correction we consider approaching the Γ -point from the M-point, the K-point and the A-point, corresponding to the directions (100), (110) and (001). We use the experimental values from Fowler and Markovic [41,42]. The direction of approach has little influence on the eigenmodes. The deviation from the experimental values is about 10%.

b) The change in the phonon frequency when applying the long-range correction. We find almost identical changes when approaching along the (100) and the (110) direction (M to Γ and K to Γ , respectively). The largest change occurs for the mode at 318cm^{-1} which corresponds to a pure OH libration mode. In the (001) direction (A \rightarrow Γ) this mode is nearly unaffected by the long-range correction.

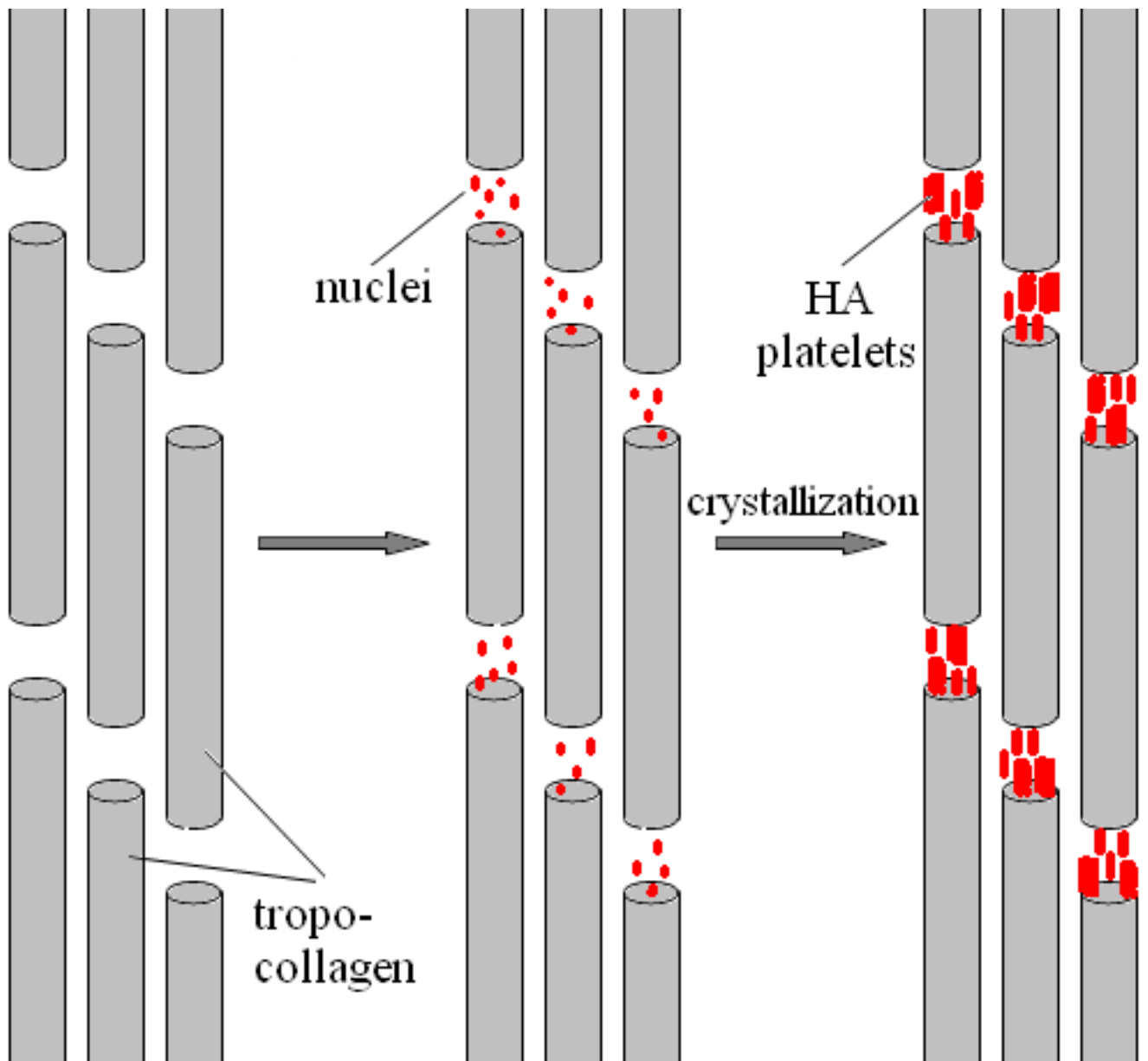
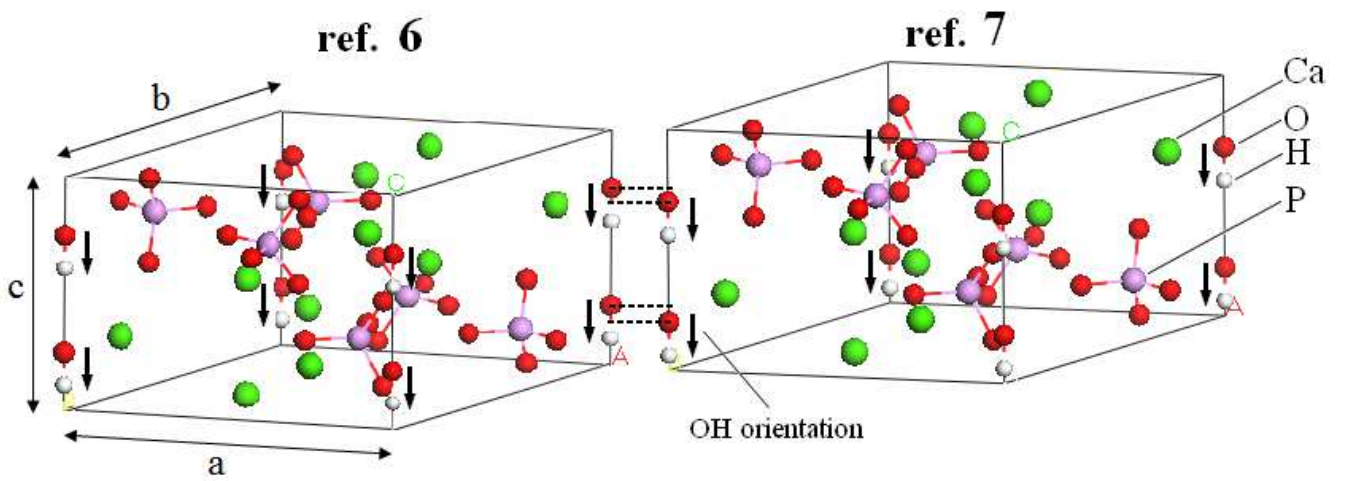


Figure 1

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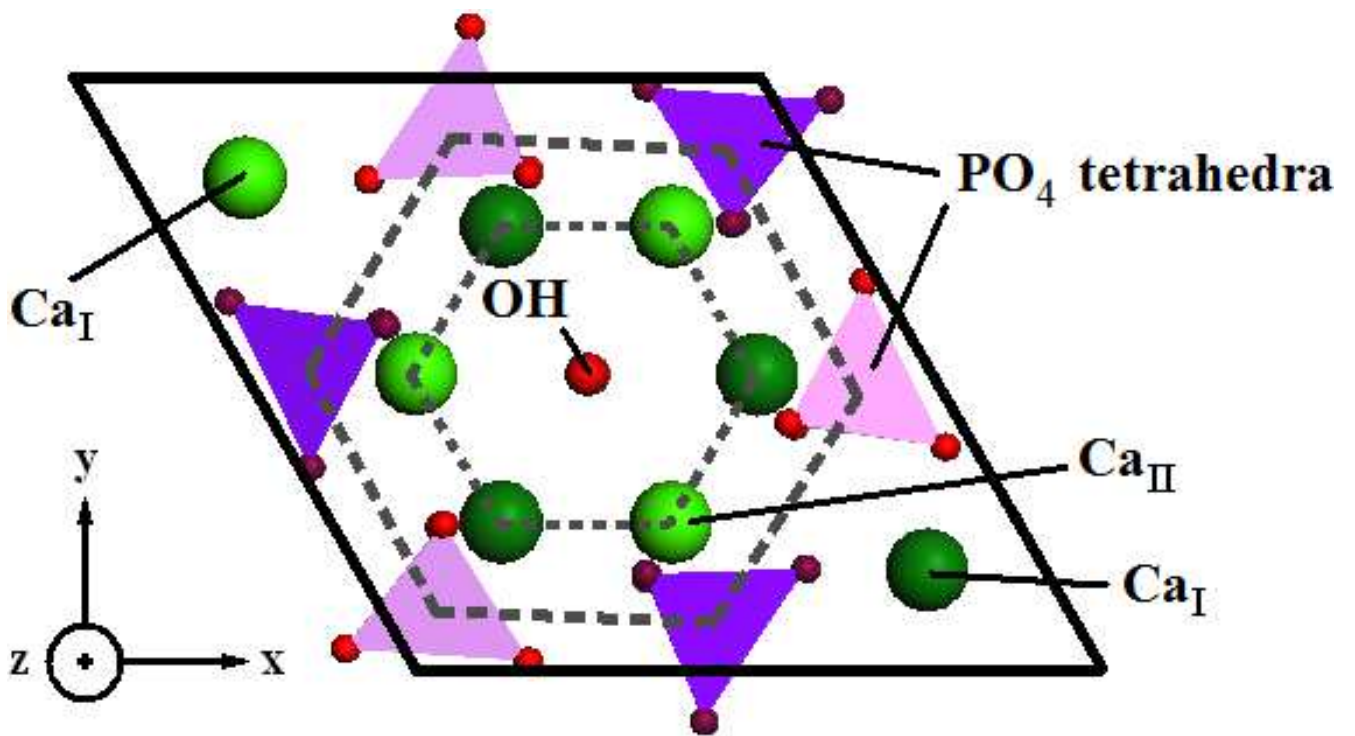


Figure 3 BG12027 27SEP2011

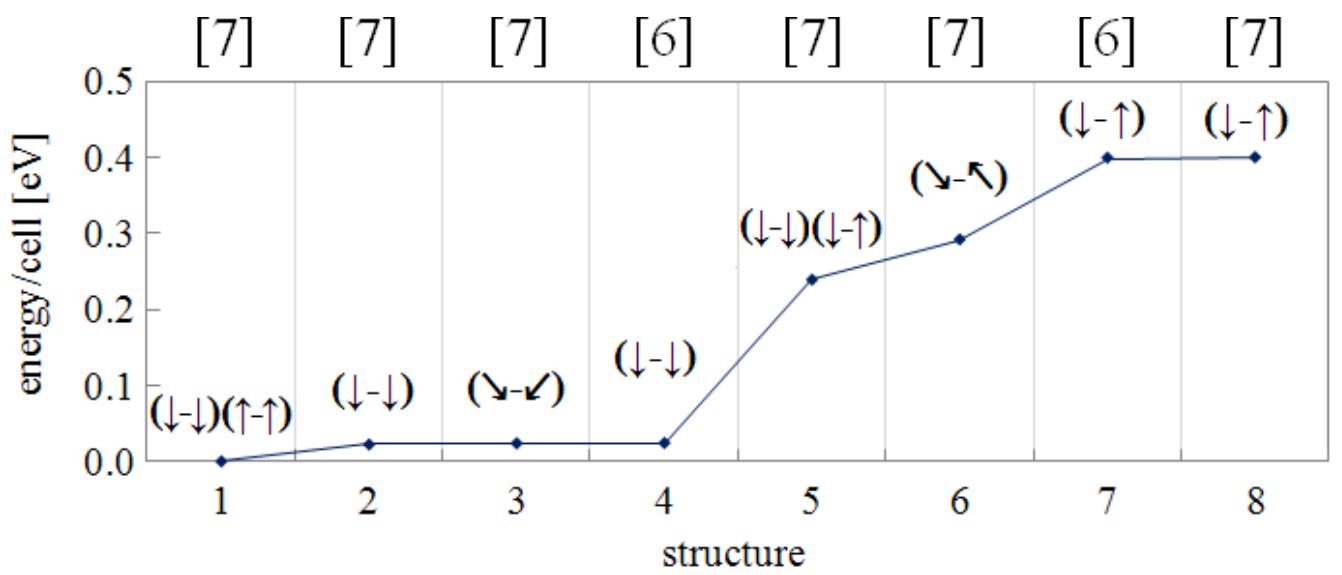
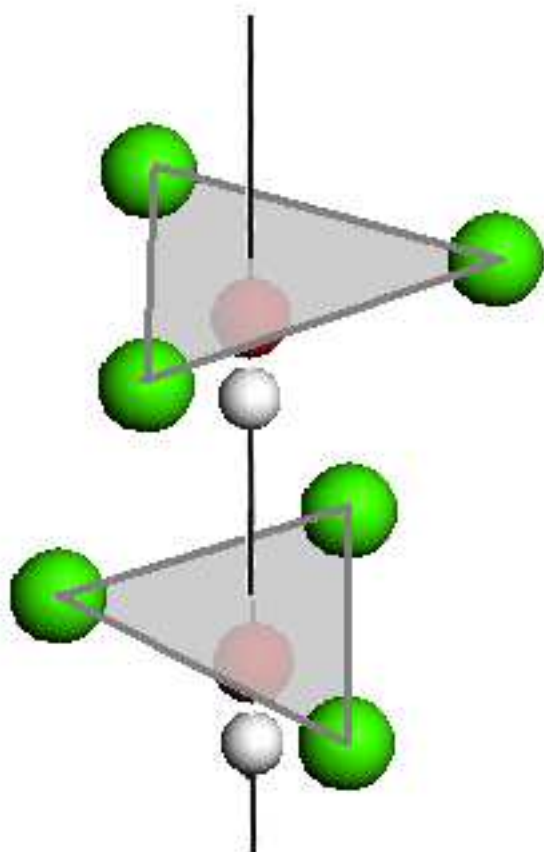
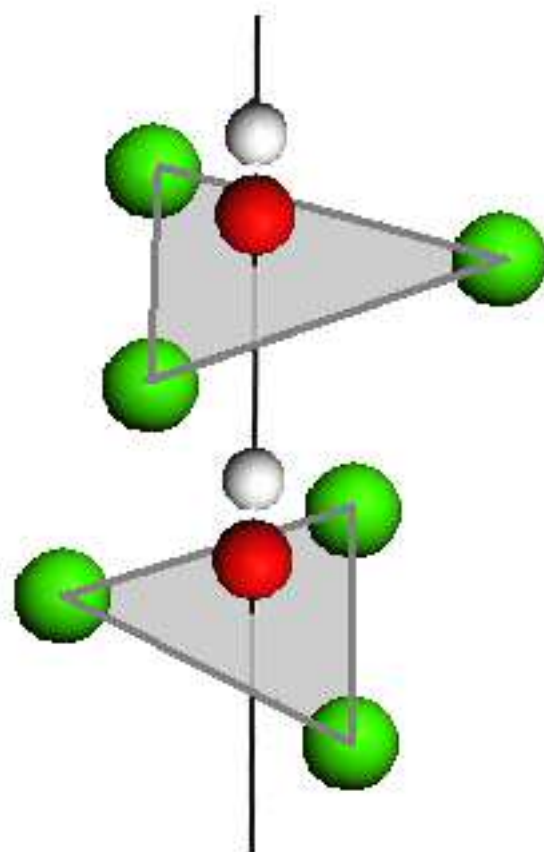


Figure 4

($\downarrow\downarrow$) configuration



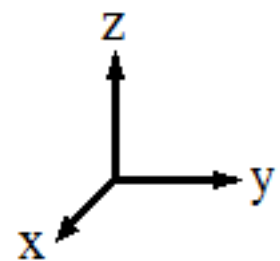
($\uparrow\uparrow$) configuration



H moves along z



H rotates around O



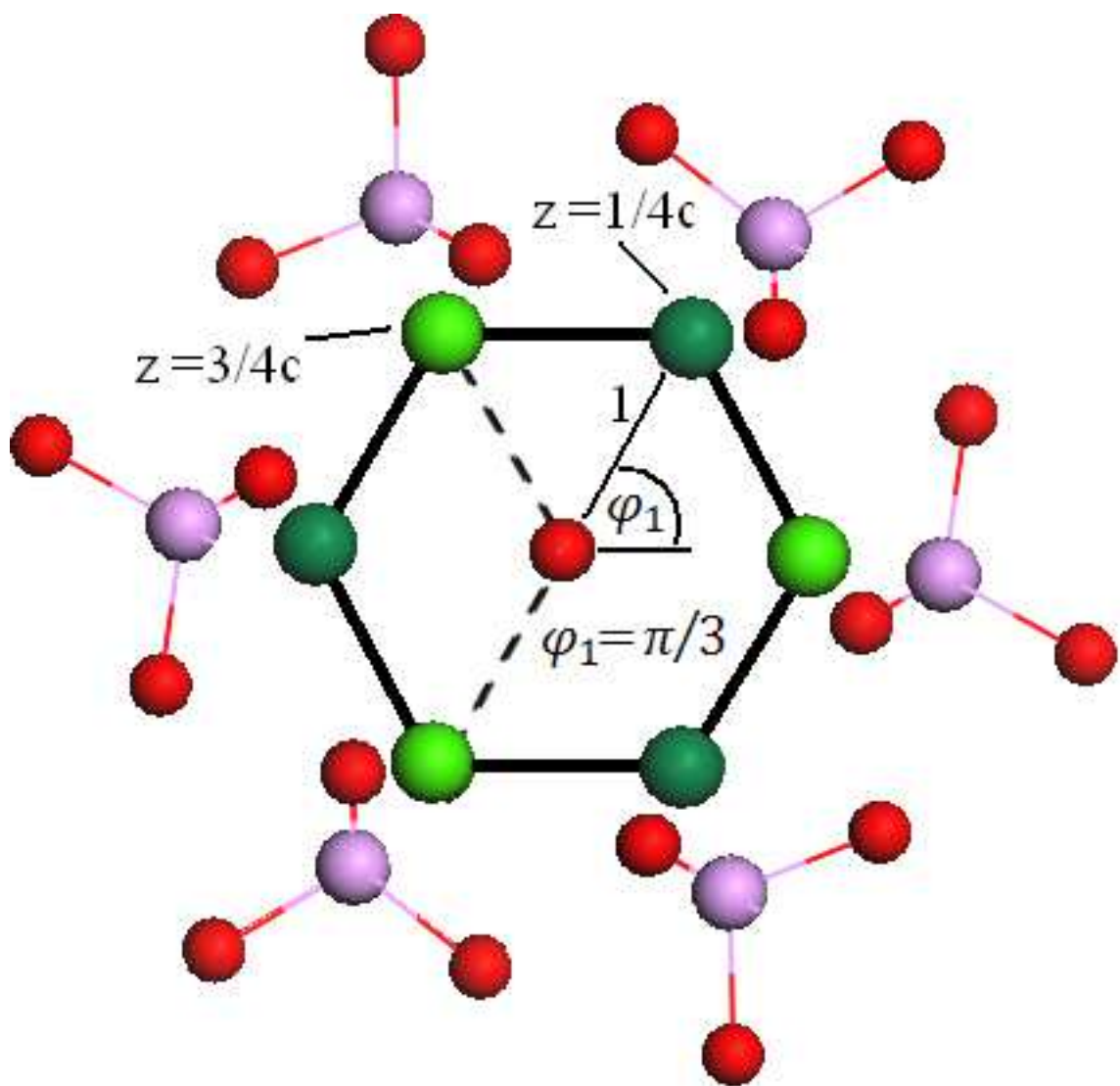


Figure 6

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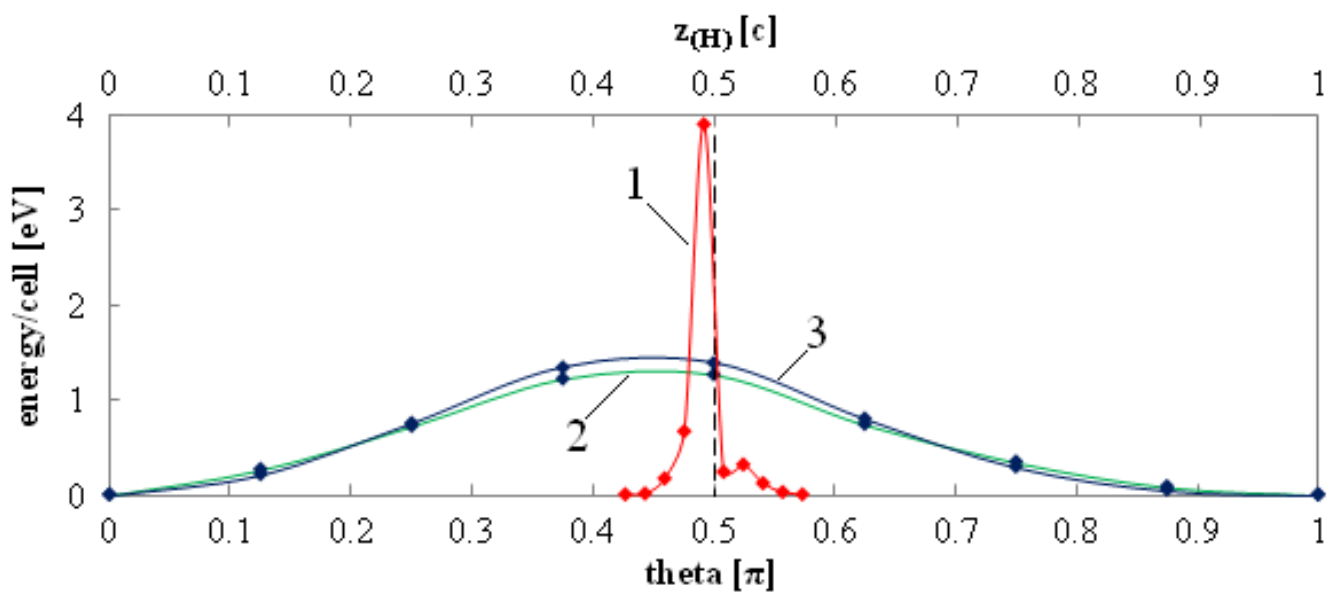


Figure 7 BG12027 27SEP2011

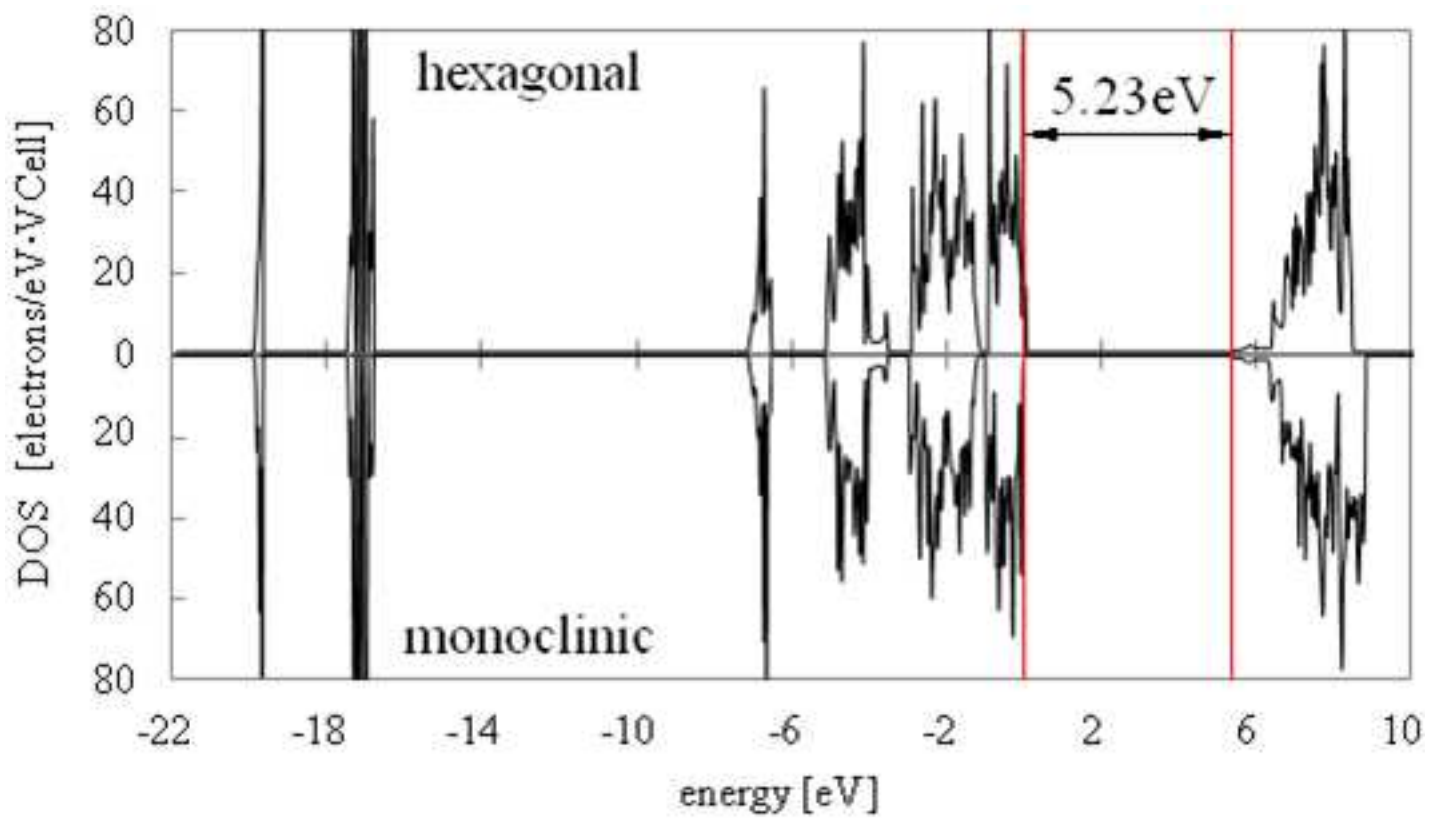


Figure 8a

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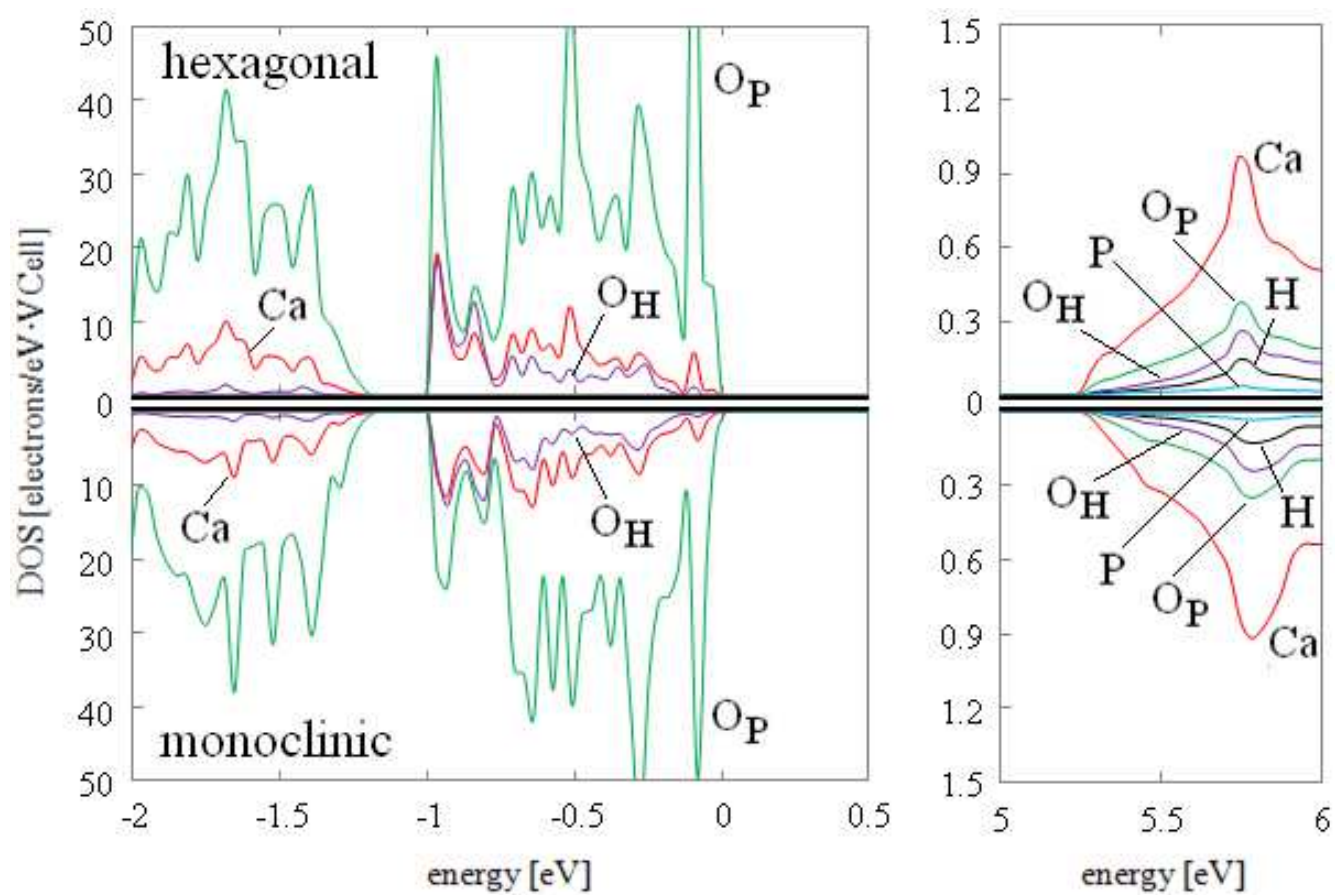


Figure 8b

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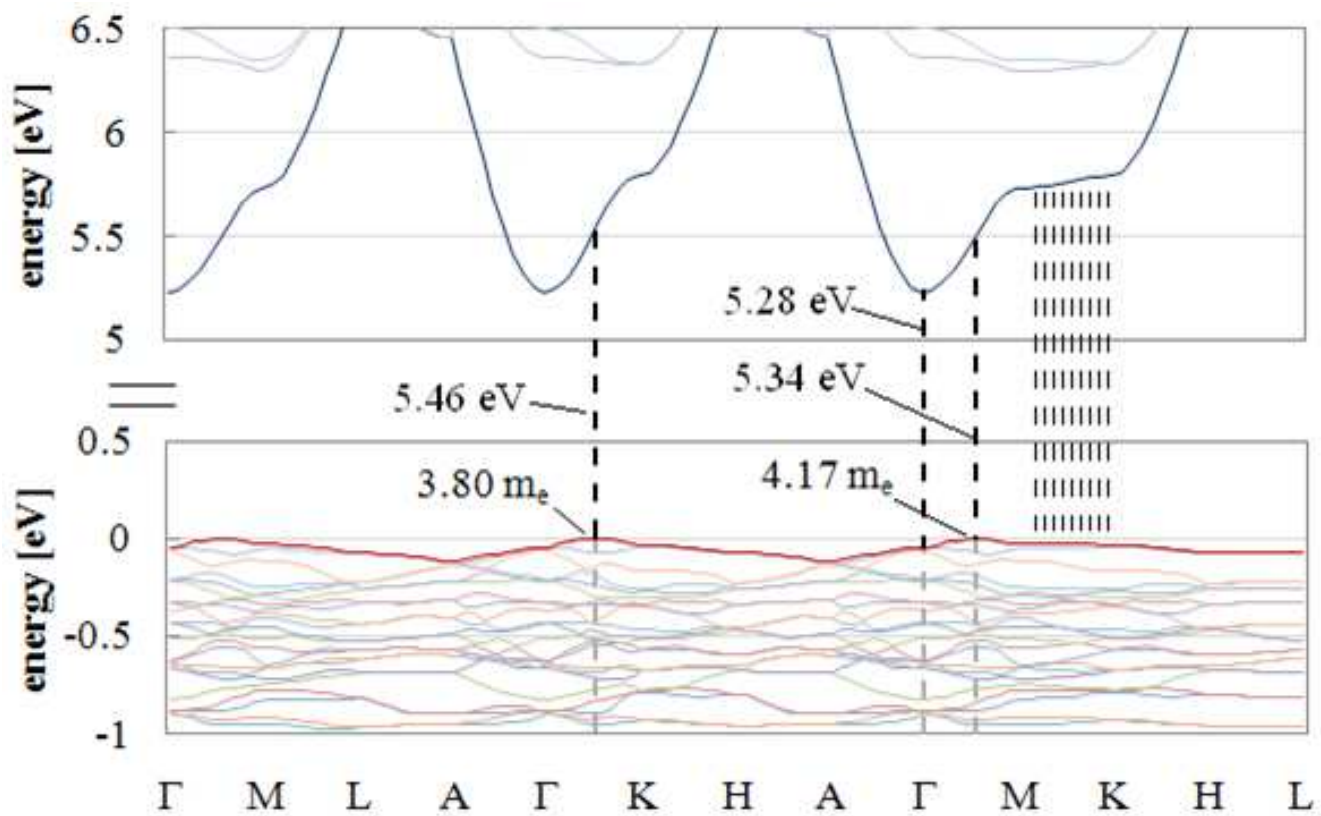


Figure 9

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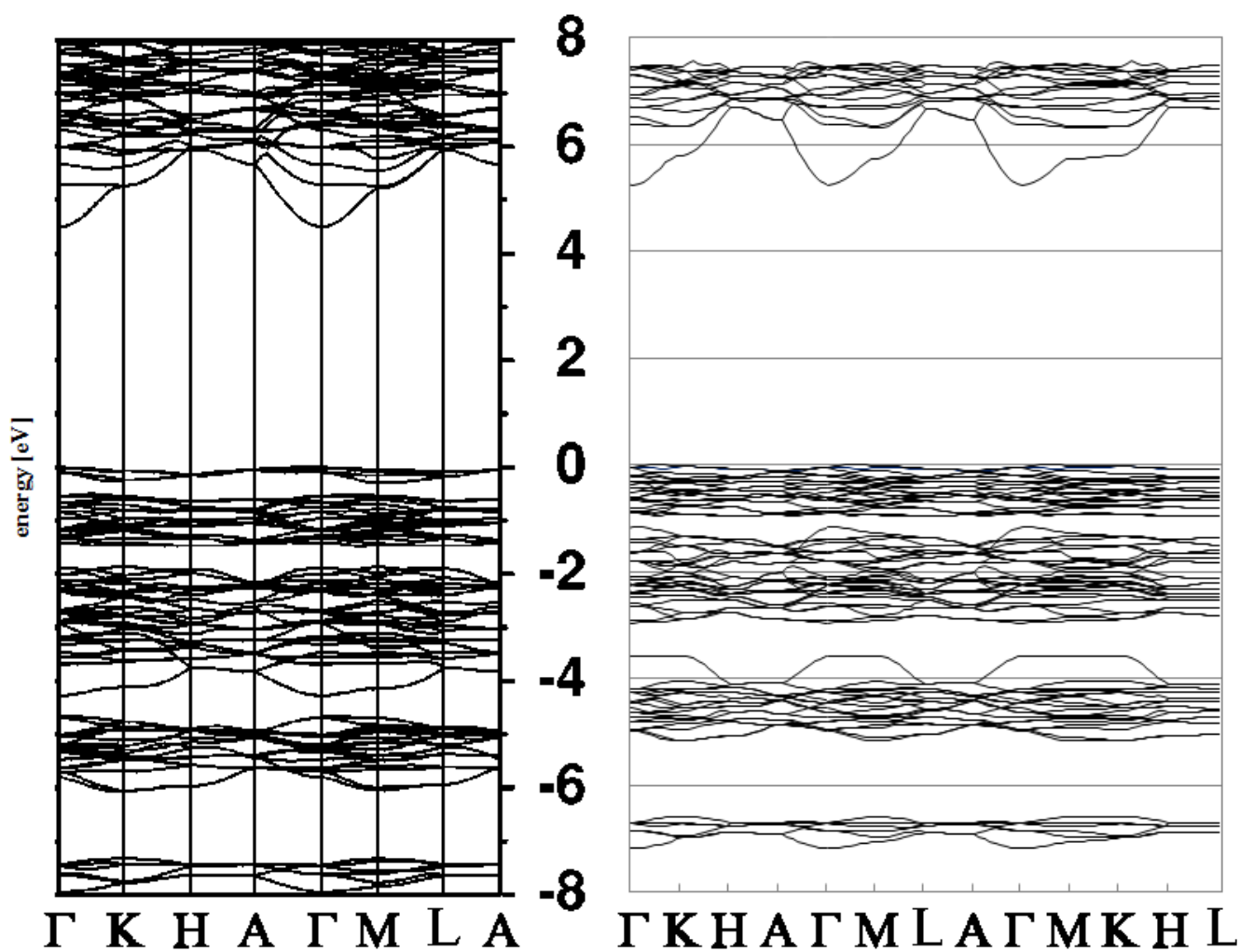


Figure 10

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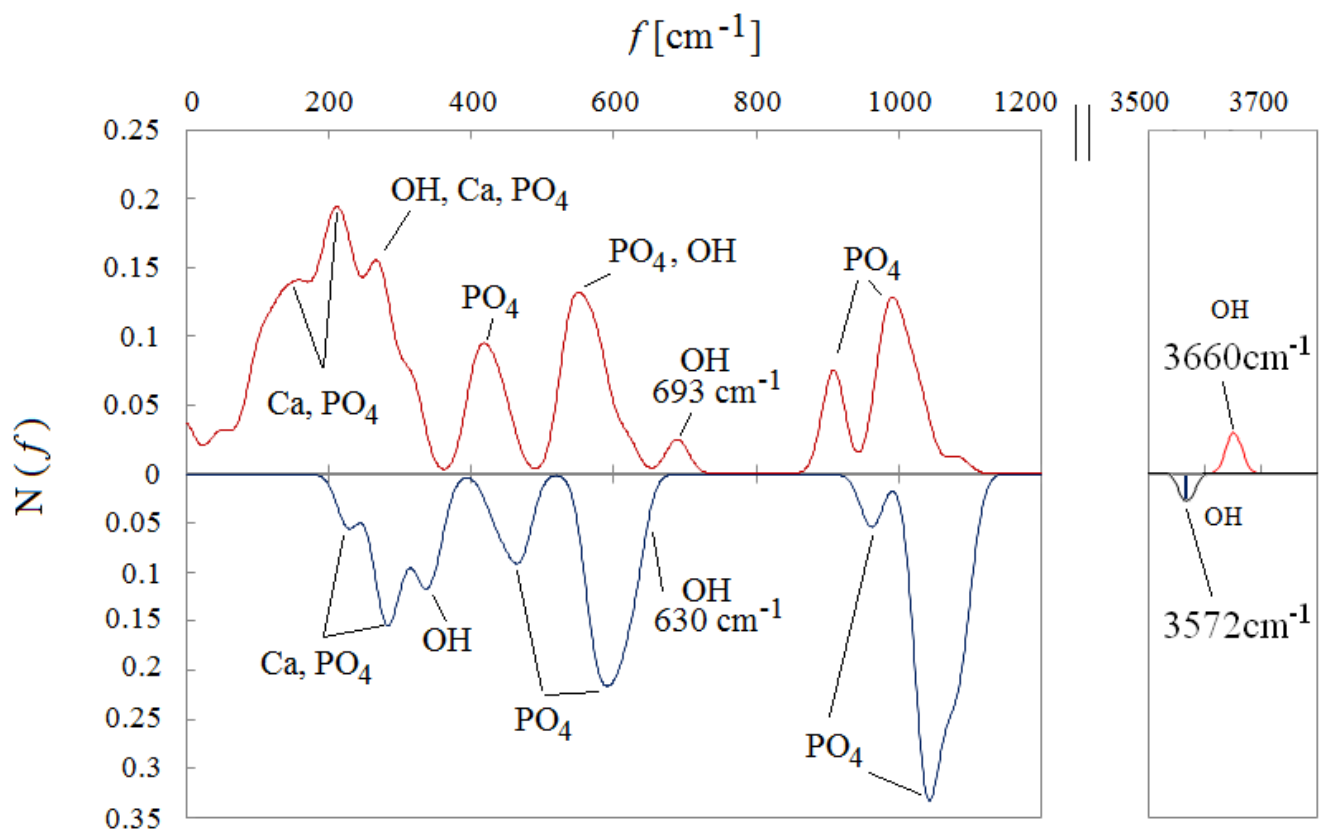


Figure 11 BG12027 27SEP2011

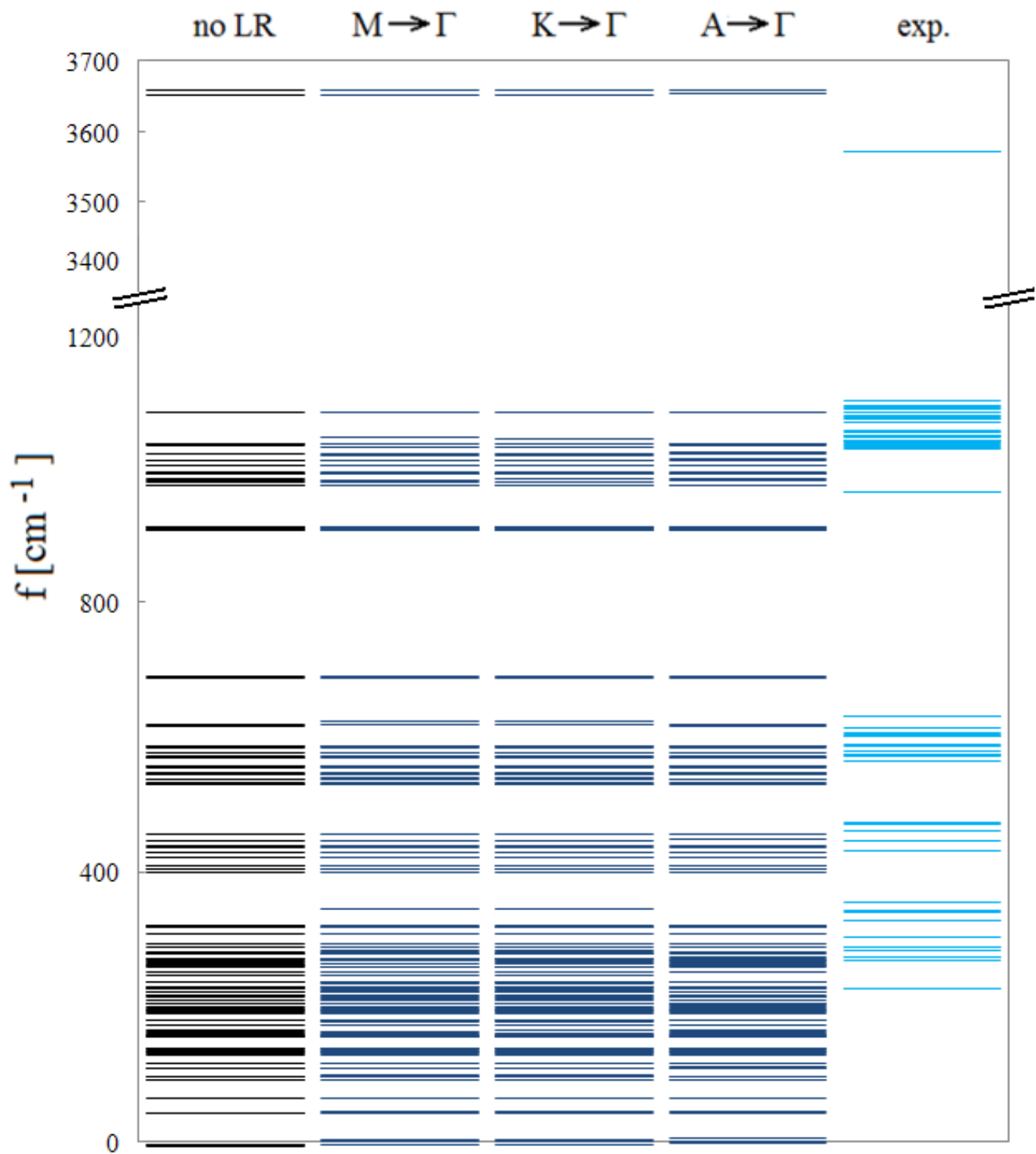


Figure 12a

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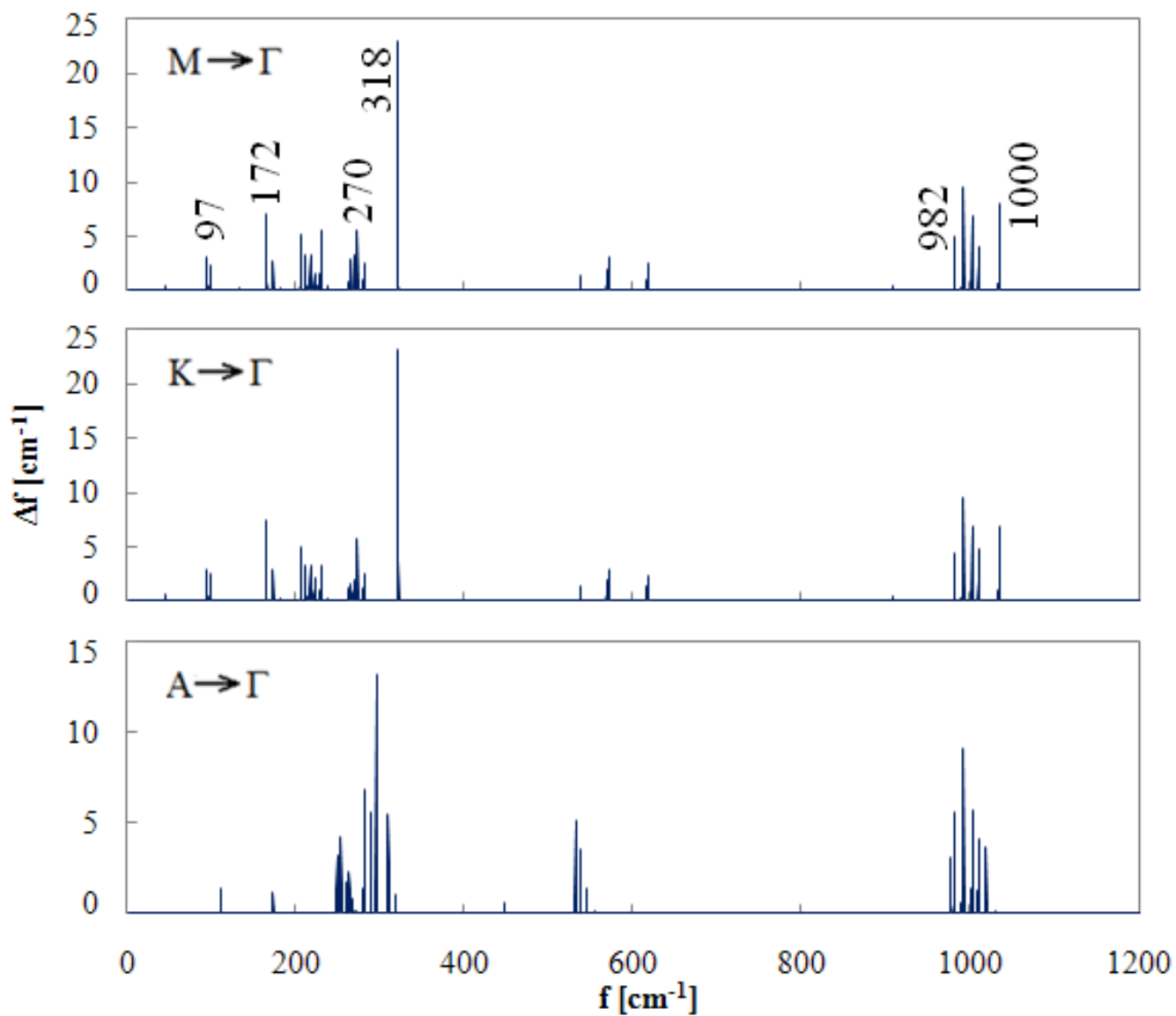


Figure 12b

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