

# Surface properties of inorganic materials

## SPECTRAL AND QUANTUM-MECHANICAL STUDY OF ELECTRONIC STRUCTURE OF ULTRADISPERSED CALCIUM HYDROXYAPATITE

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### Abstract

The regularities of electronic structure of calcium hydroxyapatite samples of different genealogy were investigated by X-ray, IR spectroscopy methods and by quantum-mechanical calculations -  $X_\alpha$  and LMTO (methods of the band theory). The evolution of valence band and charge states of atoms is described. It was established that distribution of p- and d-electronic states of calcium in samples of calcium hydroxyapatite of different origin is practically identical. Beside a high ionic component, covalent and hydrogen bonds are present in calcium hydroxyapatite. The indirect metal-metal interaction is observed in a metal sublattice. It was shown that a sublattice of the phosphatic tetrahedra determines the shape and main features of a valence band of calcium hydroxyapatite. The lack of a part of calcium ions in the nonstoichiometric samples results in weakening of P-O bond within a mirror plane. An influence of the crystal-ultradispersed state transition on the shaping of X-ray emission spectra was first investigated. Considerable localisation of metal d-states is observed in the ultradispersed hydroxyapatite samples.

### Introduction

Calcium hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (HAP) attracts attention of the researchers because of its use in quantum electronics, instrument making, medicine, biology and household chemistry.

HAP belongs to the group of compounds with the structure relating basically to hexagonal space group  $P6_3/m$  and chemical structure  $M_5(\text{ZO}_4)_3\text{X}$  (for example,  $M=\text{Ca}, \text{Sr}, \text{Pb}$ ;  $Z=\text{P}, \text{As}, \text{V}, \text{Si}, \text{Cr}$ ;  $\text{X}=\text{OH}, \text{F}, \text{Cl}$ ). The crystallographic data are given in [1]. There are two non-equivalent crystallographic positions for Ca, namely -  $\text{Ca}_{(1)}$  (Ca in a column) at  $z=0$  and  $3/4$ , and  $\text{Ca}_{(2)}$  (Ca screw axis) at  $z=1/4$  and  $3/4$ . Each  $\text{Ca}_{(1)}$  ion is surrounded by 9 atoms of oxygen from 6  $\text{PO}_4$ -groups, and  $\text{Ca}_{(2)}$  ion - with 7 atoms of oxygen from 5  $\text{PO}_4$ -groups and 1 OH group. Thus, the apatite structure can be expressed as  $[\text{Ca}_{(1)}]_4[\text{Ca}_{(2)}]_6(\text{PO}_4)_6(\text{OH})_2$ .

The HAP crystalline structure practically remains unchangeable within a wide range of structure deviations from stoichiometry ( $\text{Ca}/\text{P}=1.66$ ), and the  $\text{OH}^-$  ions are stable even at rather high temperatures (under  $1350^\circ\text{C}$ ). The property of "friability" of crystal structure allows one to occur the isomorphous substitutions in wide range of element concentrations that can be useful in an electronic structure investigation. It is known that  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Pb}^{+2}$  and other mono-, bi- and trivalent metals can substitute calcium.

Remarkable feature of the biological HAP is a fine crystallinity. It is known that

dimensions of ultradispersed crystals of a native bone do not exceed  $500 \times 80 \times 80$  Å. Such crystal has a specific surface area of more than  $400 \text{ m}^2/\text{g}$ . This fact is extremely interesting for X-ray spectral investigations since the ratio of surface/volume atomic concentration increases considerably. In such crystals more than 25% of atoms are in the surface positions.

So, the alteration of physical-chemical properties of non-stoichiometric samples in many cases is determined by their electronic structure. The main aim of these researches was a systematization of the HAP electronic structure data obtained from samples of various origin and preparation procedures with use of XPS, X-ray and IR-spectroscopy, and quantum-mechanical calculations as well.

## **Experimental**

### *Samples preparation*

HAP Samples in the area of homogeneity ( $1.58 < \text{Ca/P} < 1.72$ ) were synthesized from water solutions of calcium nitrate and ammonium phosphate (“wet” chemical synthesis) with subsequent annealing at various temperatures in the range of 110-1300°C. The chemical composition and the structure of samples obtained were determined by chemical and X-ray phase analysis methods.

The synthesis of samples in anhydrous annealing atmosphere resulted in the formation of oxyapatites  $\text{Ca}_{10}(\text{PO}_4)_6\text{O}\square$  -samples of pink colour (“pink” samples,  $\square$ - vacancy). All “pink” samples had a lack of calcium ( $\text{Ca/P}=1.61$ -1.63). The amorphous calcium phosphate (ACP) and ultradispersed samples were produced by the method described in [1].

### *X-ray emission spectral techniques*

The investigations were carried out by a secondary fluorescent method, which guaranteed an invariability of phase and chemical structure of samples during the experiment. The electronic spectrometer DEE-15, modernized spectrograph DRS-2M, X-ray spectrometer SARF-1, and also X-ray spectrometer-monochromator RSM-500 were used.

The X-ray spectra were obtained by the standard method described in [2, 3]. All spectra are shown after addition and averaging of several scans results. Because of optical luminescence of samples the time of exposition of calcium K-spectra has reached to about 250 hours in the investigated compounds.

### *Techniques of vibration spectra obtaining*

A powder of the substance studied is mixed up with a potassium bromide (with a weight part of the researched substance of 1-3%) to obtain IR-spectra on spectrometer Specord M-80. Then the tablets with diameter of 3 mm and thickness of  $\sim 1$  mm were pressed. The tablet in the holder was located in cuvette section of IR-spectrometer with transparency geometry. The measurements were carried out in the range of KBr transparency ( $4000$ - $400 \text{ cm}^{-1}$ ).

### *Techniques of electronic spectra registration*

The absorption of samples was measured in UV range with the use of electronic spectrometer Specord M-40. Since the research of samples in UV and visible regions of spectrum in the transparency geometry is not practically possible, the diffuse reflectance method with the use of focusing sphere was applied. The spectra were recorded in the range from  $50000 \text{ cm}^{-1}$  up to  $30000 \text{ cm}^{-1}$ .

### *Quantum-mechanical calculations*

The experience shows that the best agreement of theoretical and experimental data in researching metal phosphates is achieved with use of LMTO or  $X_\alpha$ -SW methods. Quantum-mechanical calculations of the HAP electronic structure were carried out by the LMTO method with the use of data about the atoms position in an unit cell [1]. Also the  $[\text{PO}_4]^{3-}$  cluster calculations were carried out by  $X_\alpha$ -SW method.

The self-consistent calculation of electronic structure, total and partial densities of

states were carried out by a linear method of MT-orbitals (LMTO) with taking combined corrections into account [4-6]. The procedure of the self-coordination included charge density of core states. The Bart-Hedin approximation [7] was used for the exchange-correlation part of potential. The detailed description of calculation method one can find elsewhere [8, 9], therefore we point only some details out here. The calculations were carried out in so-called scalar-relativistic approximation, i.e. all relativistic effects (dependence of mass on speed, the Darwin term) except for spin-orbital interaction were considered. In the expansion of wave function s, p, d-harmonics for both metals and non-metals were taken into account. The integration in Brillouin zone was carried out by the improved tetrahedron method [10] on a grid of 650 points.

## Results and discussion

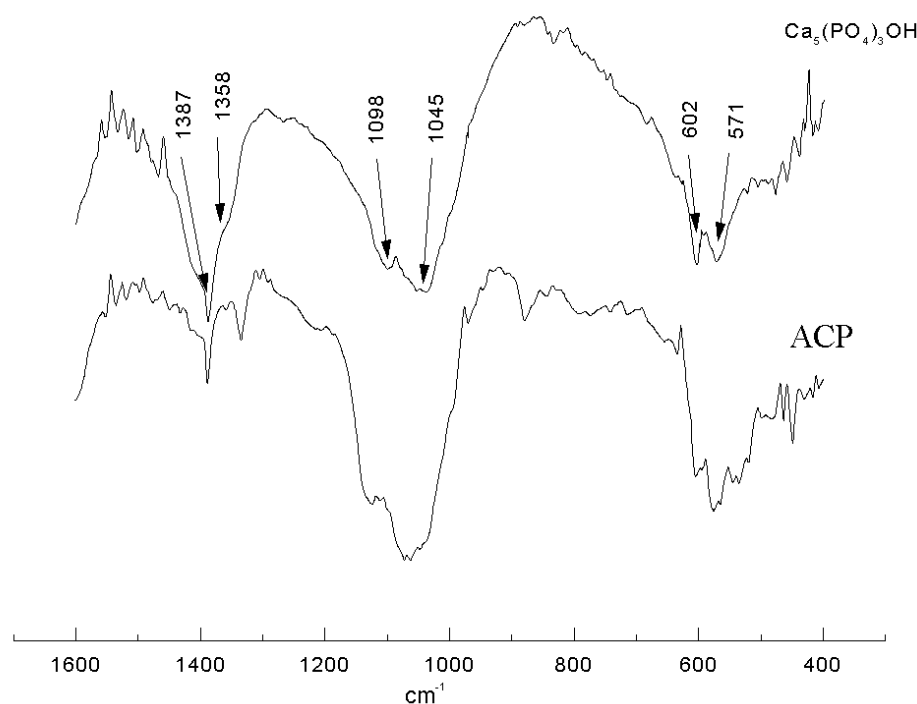
### *Researches of vibration and electronic spectra*

All samples were investigated in the IR range of wavelengths from 2.5 up to 25 microns. The optical absorption in HAP is the result of the vibrations of phosphate and hydroxyl ions. The IR absorption spectrum of stoichiometric HAP is given in Fig. 1. It is known that free  $\text{PO}_4^{3-}$ -tetrahedron has active vibrational modes such as  $\nu_1=980\text{ cm}^{-1}$ ,  $\nu_2=363\text{ cm}^{-1}$  and  $\nu_3=1082\text{ cm}^{-1}$ ,  $\nu_4=515\text{ cm}^{-1}$ . Since the symmetry is usually lowered in a crystal, the spectra are split into peaks with more complex structure. The symmetry of phosphate group (6/m) results in nine IR-active vibrational modes in HAP structure. Six of these ( $\nu_1$ ,  $\nu_{2a}$ ,  $\nu_{3a}$ ,  $\nu_{3b}$ ,  $\nu_{4a}$ ,  $\nu_{4b}$ ) are vibrations belonging to  $E_{1u}$  notion, in which the movements of atoms are symmetric to the mirror plane. Other three vibrations ( $\nu_{2b}$ ,  $\nu_{3c}$ ,  $\nu_{4c}$ ) belong to the symmetry  $A_u$ , movements of these atoms are antisymmetric with respect to the mirror plane. The hydrogen bond is reflected in IR absorption of  $\text{OH}^-$  groups. The absorption bands observed at  $631\text{ cm}^{-1}$  and  $3573\text{ cm}^{-1}$  (is not given) corresponds to libration and stretching modes. OH-stretching band, which becomes apparent as a weak peak, shows weakness of hydrogen bonds of  $\text{OH}^-$  groups. The only atoms capable to form such bonds in HAP structure are those of oxygen from neighbouring OH and  $\text{PO}_4$ -groups. In HAP, the O-O distance between the neighbouring OH-groups is  $3.44\text{ \AA}$  and too large to form of hydrogen bond, while the distance between oxygen atom of phosphate group and that of OH-group is  $3.05\text{ \AA}$ . Hence, the hydrogen bond between -OH and  $\text{PO}_4^{3-}$  can exist as  $\text{O}-\text{H}\cdots\text{OPO}_3$  and thus it is directed along hexagonal axis of crystal that can be an important factor for a crystal growth.

The bands in the area of  $1400\text{ cm}^{-1}$  should be attributed to stretching and librational vibrations of OH group. In crystalline HAP this band has the large intensity and besides an its splitting occurs because of the influence of internal crystal field. The insignificant intensity of this band in ACP testifies to extreme difficulty of the preparation of OH-groups of free ACP samples. However, taking into account the forms of spectra (Fig. 1) and practically identical positions of peaks, it is necessary to note that in amorphous phosphate the environment of phosphorus remains practically the same. Thus, it is possible to approve that samples ACP are characterized by the near order and can have a polycluster structure.

As the result of calcium atoms absence in points of lattice of non-stoichiometric HAP samples there is a further downturn of  $\text{PO}_4$ -tetrahedron symmetry, that entails decrease or increase of phosphorus-oxygen distance for the corresponding points reflected in the change of the position of the corresponding bands of IR spectra (Table 1). So the deviation HAP structure from stoichiometric one results in a drop of line position close to  $473\text{ cm}^{-1}$ . These vibrations characterize a displacement of  $\text{O}^{2-}$  ions within the mirror symmetry plane. Thus, the absence of the certain share of calcium ions results in weakening of some P-O bonds within the mirror symmetry plane. As it was mentioned above, the line of absorption about  $630\text{ cm}^{-1}$  is attributed to the librational vibrations  $\text{OH}^-$  ions. These vibrations are vibrations of

OH-groups in the perpendicular direction of a crystal axis what corresponds to the assumption of hydrogen atom swinging relatively to the oxygen atom or the centre of system weights.



**Fig. 1.** IR absorption spectra of HAP and ACP.

**Table 1.** Spectral positions of IR absorption bands of the various HAP samples.

Sample	Bands, cm <sup>-1</sup>							
HAP, Ca/P=1.66	965	473	1098	1045	602	570	3573	632
HAP, Ca/P=1.58								
synthesized at 180°C	965	470	1100	1060	603	567	3563	630
at 700°C	962	470	1094	1039	600	563	3563	630
at 1300°C	966	470	1087	1040	602	565	–	630
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> O□ (“pink”, N <sub>2</sub> )	963	465	1095	1047	602	567	–	–
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	957	442	1100	1055	607	565	–	–
Volcanic HAP								
(The peninsula Kamchatka)		470	1090	1040	600	572	3530	–
Bone mineral	965	465	1100	1040	610	565	3510	625
Ultradispersed HAP								
(ashes of bone)	965	477	1094	1052	603	566	3510	633

*Note:* an error of the measurements is  $\pm 3$  cm<sup>-1</sup>

The intensity of the observed band is determined by hydroxyl amount in researched samples and it correlated well with the results of NMR studies [10]. For all samples the band position coincides within the limits of accuracy of experiment, except for a mineral of the

bone, where the nature of displacement is not precisely established. In IR-spectra absorption of “pink” samples there are no bands of librational vibrations of OH<sup>-</sup> groups but there are bands close to 440 and 460 cm<sup>-1</sup>, characteristic of TCP. The reason of occurrence of these phenomena can be connected with an absence of oxygen ions in the corresponding points of lattice. The shortage of oxygen ions can also result in formation of additional levels in the energy-band structure (so-called “colour centres”) in ionic crystals. The lines of optical absorption in such “pink” samples are really established, they are about 2.4 eV. The similar lines of absorption close to 2400 cm<sup>-1</sup> are established in reflection spectra of ultradispersed HAP samples of the human bones. The increase of intensity of optical reflection in a yellow-red part of spectrum causes the corresponding bone colour.

The active vibrational modes describing PO<sub>4</sub><sup>3-</sup> tetrahedron in a number of compounds (Table 1) get small changes except for TCP where they are caused by an absence of hydroxyl groups. It is possible to explain the significant changes observable for stretching band of OH-group in a number of researched samples in such a way: during the transition from stoichiometric HAP to samples of other origin the essential changes in structure are observed only lengthways the hexagonal axis of a crystal. So, in HAP samples of a volcanic origin natural temperature annealing results in the formation of (HPO<sub>4</sub>)<sup>2-</sup> ions in HAP structure, initiating the weakening of hydrogen bond directed lengthways hexagonal axis of a crystal. For ultradispersed HAP crystals of the bone and its ashes, because of their large specific surface area, there is an interaction of superficial atoms with their environment resulting in weakening of bonds of OH-groups (Table 1). According to the data of samples absorption in UV region it was established that the width of the HAP forbidden band of stoichiometric structure makes 5.59 eV. In biological HAP samples as well as in stoichiometric one the width of a band has a significant energy extent (about 5.52 eV) what determines their dielectric properties. The dependence of a width of the forbidden band for non-stoichiometric HAP samples on contents of OH-groups is observed.

*X-ray spectral and quantum-mechanical researches*

As a rule, only experimental methods are not enough for the complete description of an electronic structure of compound. So we apply a technique of comparison calculated and experimental data. It is clear from the Fig. 2-4 that the calculation data have been shown to have a good conformity to the experimental ones. The experimental features of an electronic structure of investigated compound are considered on the basis of the analysis of X-ray spectra combined in one energy scale by a standard procedure [2, 3]. The X-ray photoelectron spectra of valence band are not given because of their small informational ability for the given compounds. The matching is carried out in accordance with the binding energy of the core levels (Table 2).

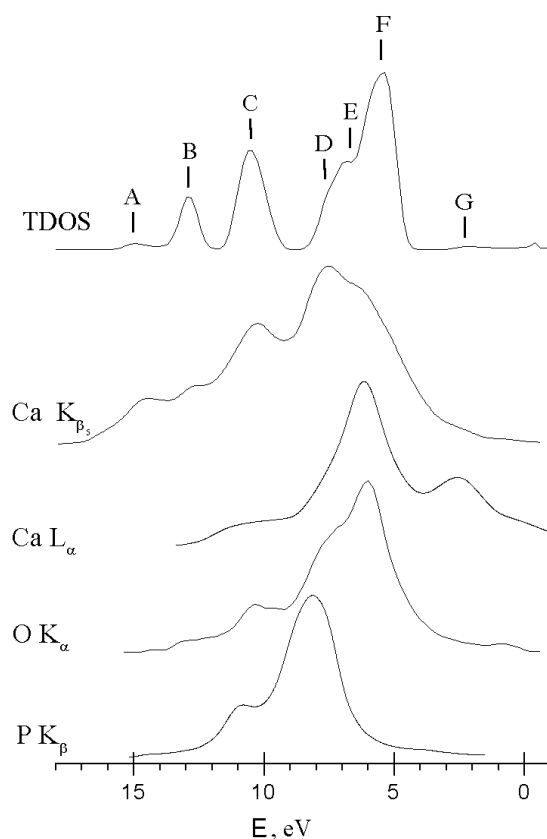
**Table 2.** The binding energy of the core electrons in HAP

Substance	Ca 2p <sub>1/2</sub>	Ca 2p <sub>3/2</sub>	P 2p	O 1s
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>	351.2	347.5	133.6	532.4

The space orientation of PO<sub>4</sub>-groups causes more complex form of the calcium HAP valence bands in comparison with CaCO<sub>3</sub>, where CO<sub>3</sub>-group has a plane orientation [11].

It follows from the comparative analysis of X-ray emission spectra that in HAP crystals strong polarized Coulomb interactions prevail. The displacement of inner emission lines of calcium and phosphorus testifies to significant charge transfer from calcium to PO<sub>4</sub><sup>3-</sup> ions, and inside of PO<sub>4</sub><sup>3-</sup> - from phosphorus to oxygen. The form of the curve of total density

of states (TDOS) also characterizes compound with a large part of ionic bond (Fig. 2).



**Fig. 2.** X-ray spectra and curve of total density of states (TDOS, band calculation), combined in one energy scale, for the hydroxyapatite sample.

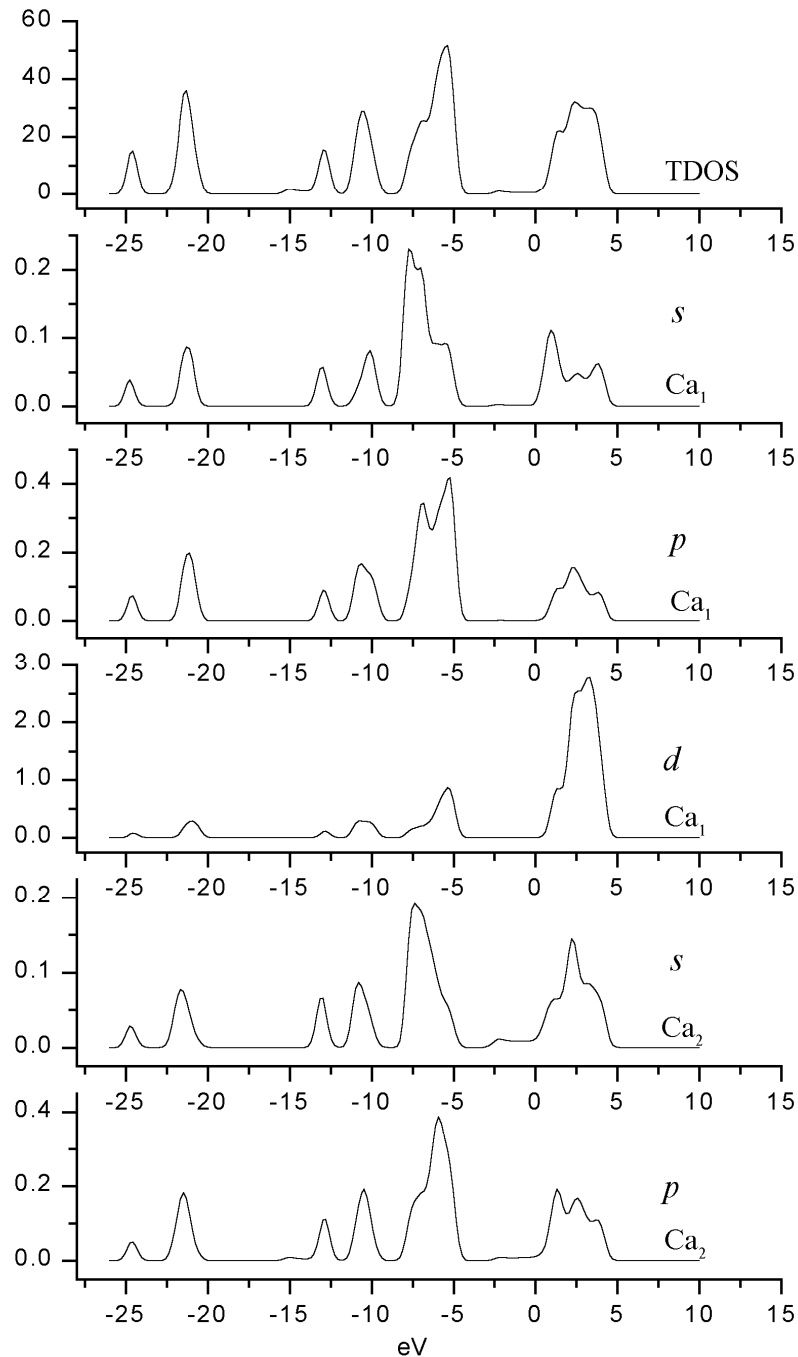
Two features determine basically a form of the main maximum of calcium K-spectra. D feature is formed by d- and p- states of calcium and short-wave maximum F, related mainly with display of p-states of oxygen and d-states of calcium. Also the p-states of phosphorus and oxygen contribute to feature D of TDOS. E feature is basically formed due to hybridization of p-, d-states of calcium and p-states of phosphorus and oxygen. The observed splitting of the main maximum of a Ca K-band in hydroxyapatites in comparison with TCP [11] is related, as it was mentioned above, with existence of two various structural calcium positions.

As was established earlier in [11, 12], atomic effects play a significant role in the formation of calcium  $L_{\alpha}$ -spectra form of such compounds. So the presence of Ca d-states in the bond is levelled by its significant localization.

The position of G feature in Ca  $L_{\alpha}$ -spectrum corresponds to position of the main maxima of K- and L-spectra in metal [12], and thus reflects metal-metal interaction having in HAP, by absence of feature in calcium K-spectrum, mainly s-s character.

As the direct interaction between Ca atoms is excluded by a atomic structure [1], such interaction occurs with a certain part of the influence of atoms of oxygen Ca-O-Ca. As it shown from Fig. 3 and 4, the features corresponding to G are observed on calcium density curve of both  $Ca_1(s)$  crystallographic positions,  $Ca_1(p)$ ,  $Ca_2(s)$ ,  $Ca_2(p)$  and oxygen  $O_4(s)$  from hydroxyl group and  $O_3(p)$  from phosphate of group. The features in  $Ca_1(s)$ ,  $Ca_1(p)$  and  $O_3(p)$  have considerably smaller intensity in comparison with  $Ca_2(s)$ ,  $Ca_2(p)$  and  $O_4(s)$ , that can

testify to the much greater participation of Ca<sub>2</sub> atoms in bond. The metal-metal interaction with the participation of calcium atoms in Ca<sub>1</sub> positions is realized with contribution of p-density of oxygen from PO<sub>4</sub>-group, in contrast to an interaction, which is executed via s-density.



**Fig. 3.** Densities of states for Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>.

As it seems the interaction between calcium atoms in the Ca<sub>1</sub>-position either does not exist or is weakly expressed. The presence of the feature on s-density of hydrogen curve in the examined area can testify that the indirect interaction metal-metal occurs with participation of hydrogen s-density. From above-stated it is possible to conclude that the interaction in sublattice of metal exists mainly between atoms in Ca<sub>2</sub> positions with participation of atoms

of oxygen from hydroxyl group, thus the channel of  $\text{Ca}_2\text{-O}_3\text{-Ca}_1$  interaction through atoms of oxygen from  $\text{PO}_4$ -groups is less expressed.

$\text{K}\beta_1$ -emissional band of phosphorus reflects 3p-states of  $\text{PO}_4^{3-}$  ion. One double (coupled) and three single (uncoupled) bonds connect phosphorus with ions of oxygen that corresponds to valence 5. Direct bond P-Ca in hydroxyapatite is not observed, and the bond with Ca ions can be realized only through oxygen P-O-Ca. Common feature observed in Ca K-, O K- and P K-spectra can testify to such a bond.

The maxima A and B of TDOS in the range of 12÷15 eV completely coincide with long-wave features of Ca K-bands and are generated from that part of 2p electronic density of oxygen, which occurs in chemical bond with phosphorus. The peaks in the area of bottom of valence band in the range of 20÷25 eV are basically formed by s-states of oxygen (Fig. 3, 4).

Comparative researches of calculation data of the occupied part of valence band of  $[\text{PO}_4]^{3-}$ -cluster ( $X_\alpha$ -RW cluster calculation and TDOS of HAP cell-band LMTO calculation) revealed the common tendencies in formation of structure of a valence band.

The identical regularities of a cluster and crystal valence band features as in area of bottom valence band and its middle part (Fig. 5) are practically observed. The identical quantity of features on cluster and crystal TDOS curves, except for feature on 15 eV, determined by presence of hydroxyl group, is also observed. The discrepancy of energy positions of the features of valence band of a cluster and crystal in the area of its top can be related to the peculiarities of a cluster calculation method.

Whereas the energy position of hybridized s-, p-states of hydroxyl cannot be determined unequivocally on X-ray emission spectra data, the contributions to TDOS from  $\text{PO}_4$  sublattice of calcium and hydroxyl groups were appreciated. It is shown (Fig. 5) that the largest contribution to TDOS is made by  $\text{PO}_4$ -groups.

The contribution of metal sublattice is much less, and contribution of sublattice groups is levelled by an insignificant part, mainly in the range of energies up to 10 eV. Thus, it is necessary to note that the hydroxyl electronic states, as it seems from the calculated data, form exactly the top of valence band - feature at 2.5 eV reflecting, as it was mentioned above, indirect interaction of metal ions.

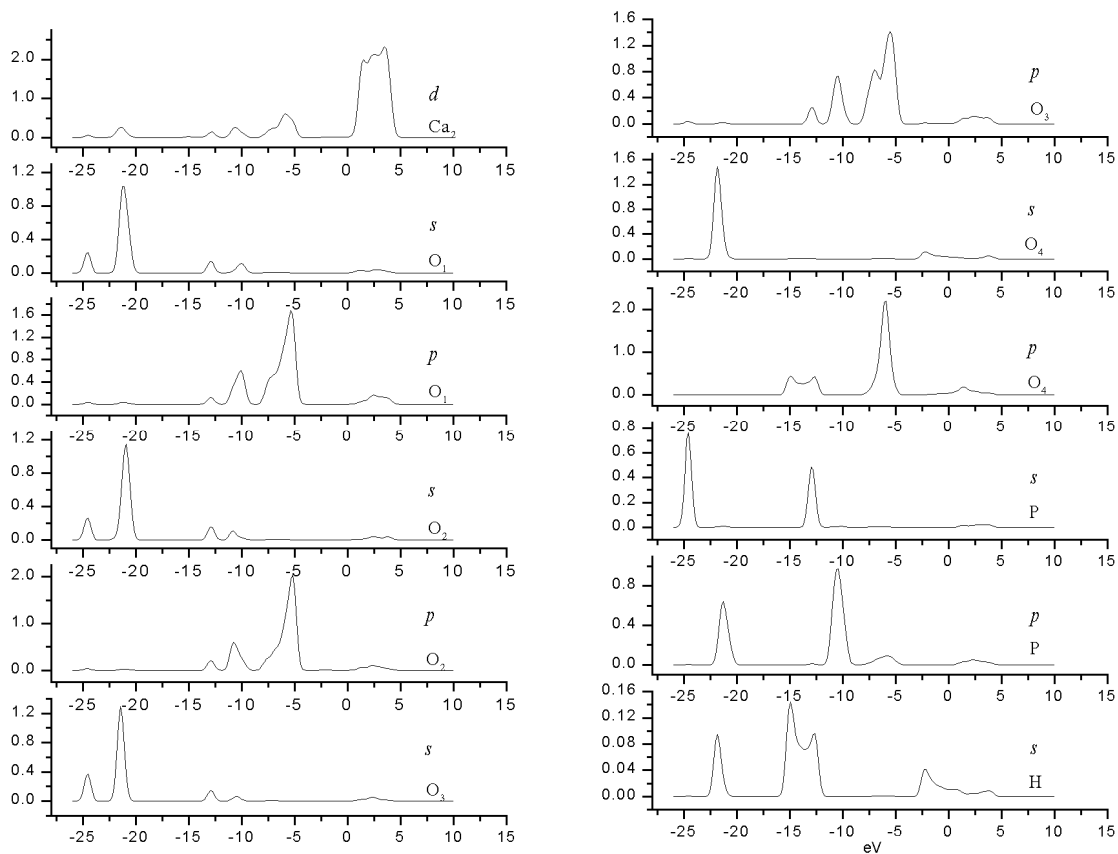
Comparing the obtained data with the results of researches [11] (where for ultradispersed samples a lot of features in low energy area O  $\text{K}\alpha$ -, P  $\text{K}\beta$ - and Ca  $\text{K}\beta_5$ - bands were found) it is possible to draw conclusion that apatite structure changes, related with OH-groups, determine these features.

#### *X-ray spectroscopy researches of samples with non-stoichiometric structure*

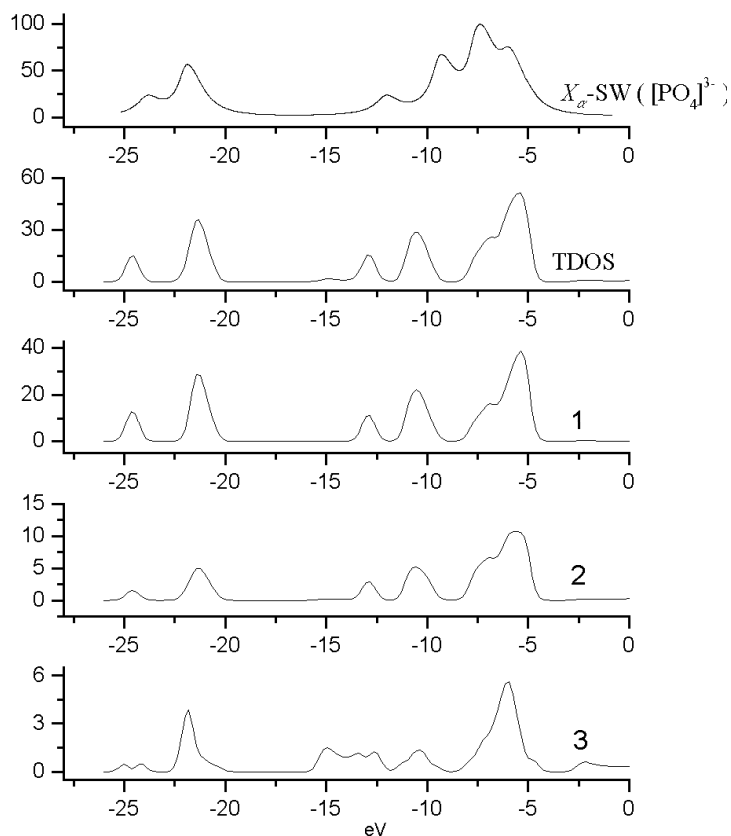
A unique characteristic of HAP is non-stoichiometry of the composition. The concentration ratio, Ca/P, is used as an index non-stoichiometry. Most HAP powders synthesized by a “wet” chemical procedure are non-stoichiometric. We investigated this peculiarity in details by calcium  $\text{K}\beta$ -bands. As it is seen from Fig. 6 with increase of Ca/P ratio from 1.58 value up to stoichiometric one and higher widening of A, B, C peaks, related with the display of phosphorus 3p-state and 2p-state of oxygen, with conservation of absolute values of their intensities in relation to the main peak is above-observed. In Ca K-band spectrum of the sample with Ca/P ratio 1.58 the A, B and C peaks has more marked character, that can testify to the greater part of ionic bond, and thus about more atom-like character of hybridized orbitals.

The discrepancy of A, B, C peaks of D-35 sample and “pink” samples (Fig. 6), and the researches carried out by NMR- and IR-spectroscopy methods can testify that the temporary factor results in evolution of ultradispersed bone crystals of a dinosaur with formation of a mineral containing combined water, instead of replacement hydroxyl by oxygen.

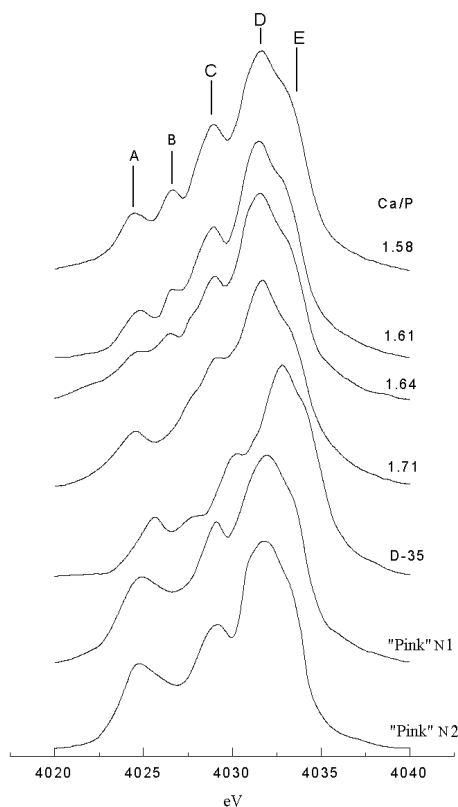




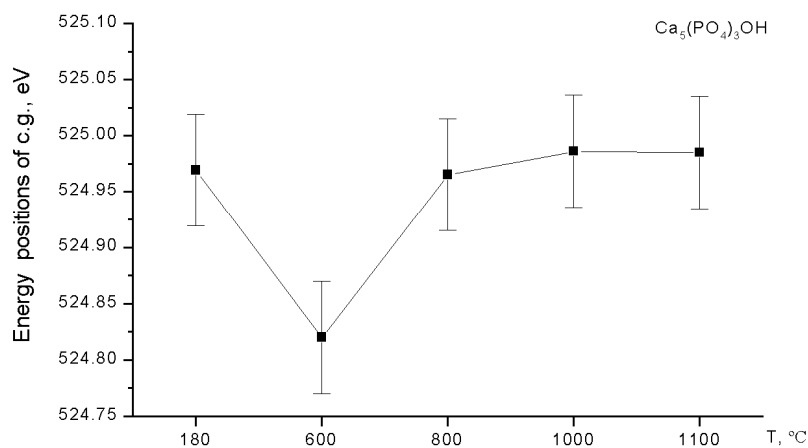
**Fig.4.** Partial densities of states of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$



**Fig. 5.** Density of states  $[(\text{PO}_4)^{3-}]$  cluster and HAP cell (band calculation): 1 - contribution to crystal TDOS is made by  $\text{PO}_4$ -tetrahedrons; 2 - contribution to crystal TDOS is made by a sublattice of metal; 3 - contribution to TDOS is made by of hydroxyl groups.



**Fig. 6.** X-ray Ca  $K_{\beta}$ -bands of the nonstoichiometric calcium apatites - "pink" samples: "Pink" N1 - 900°C, 3 hrs; "Pink" N2 -1250°C, 5 hrs, and also in the thigh bone of a *Dinosauria Saurolophus* (D-35) (the sample was given by the State Archaeological Museum of National Academy of Sciences of Ukraine, the age is about 35 million years, territory of Mongolia).

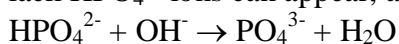


**Fig. 7.** Energy positions of gravity centre in O  $K_{\alpha}$ -spectra of hydroxyapatites obtained at various annealing temperatures.

*Spectral researches of samples prepared at various annealing temperatures*

The presence of OH<sup>-</sup> ions is confirmed by various methods in all samples in range of annealing temperature up to 1200°C. In some samples with annealing temperature 1250-1300°C these ions are practically absent. The samples produced at temperatures

~1300°C are characterized by lack of calcium. It is known [1], that in HAP crystals with Ca lack  $\text{HPO}_4^{2-}$  ions can appear, and, at high temperatures, take place transformations:



As the result of this reaction the amount of  $\text{OH}^-$  ions decreases sharply. The molecules of water evaporate partially, however, their presence was fixed in NMR spectra [10] of volcanic origin samples, and in samples with the annealing at 1300°C.

Taking into account that at temperature of annealing the main changes occur in sublattice of hydroxyl, the analysis of K-spectra of oxygen was undertaken. The energy positions of a centre of gravity (CG) of spectra of oxygen (Fig. 7) were exposed to the analysis, since the form of all obtained spectra was practically the same. As it is seen from the given figure of CG position has only one feature. Practically identical positions for samples with 180, 800, 1000, and 1100°C annealing temperature testify about the identical charge state of oxygen atoms in these samples. The decrease of CG position in a sample with annealing temperature of 600°C testifies to increase of electronic density on oxygen atoms, with can be related to the greater part of delocalization of calcium electrons.

## Conclusions

The presence of several areas is characteristic for HAP electronic structure. The structure of each area is formed by the contribution of s-, p- and d-electronic conditions of calcium, phosphorus and oxygen ions. The structure of subvalent states is totally determined by s-states of oxygen. The distribution of p- and d-electronic states of calcium in HAP samples of a various origin practically coincides. The strong ion component of chemical bond in HAP crystals ranks with hydrogen component. In sublattice of metal the indirect metal-metal interaction existing between atoms in  $\text{Ca}_{(2)}$  position with the presence of oxygen atoms from hydroxyl group is observed thus the channel of interaction  $\text{Ca}_2\text{-O}_3\text{-Ca}_1$  through atoms of oxygen from  $\text{PO}_4^-$  groups is less expressed. It is shown that sublattice of phosphate tetrahedron is the main in the forming TDOS calcium hydroxyapatite form and it's features. On the basis of the analysis of electronic spectra it is established that all investigated samples have significant extent of forbidden band. The quantity of  $\text{OH}^-$  ions in HAP samples influences on spectral position of the edge of optical absorption and width of the forbidden band. The hydrogen bond in HAP exists as  $\text{O-H}\cdots\text{OPO}_3$  and thus is directed lengthways the hexagonal axis of a crystal, that can be important factor at crystal growth. The absence of certain amount of calcium ions in the points of lattice of non-stoichiometric samples results in weakening of some P-O bonds within mirror pane. In HAP samples of a volcanic origin a natural temperature annealing initiates the weakening of hydrogen bond. In general the annealing temperature of HAP samples only at 800°C results in a certain delocalization of calcium electronic states. Transition from crystal to ultradispersed HAP does not bring considerable changes in X-ray emission metal K-band formed by nearest calcium environment mainly. Apparently, calcium occupying volume that formed by  $\text{PO}_4^{3-}$  tetrahedron and having no salient directed bonds cannot occupy surface position and thus cannot change coordination environment in case of ultradispersed crystal state. So hydroxyl group occupying its surface place results in increasing of crystal surface chemical activity. The basic binding energies in ultradispersed samples of biological origin are close to artificial crystals, in which the lack of Ca is found, and the O-H binding energy in bones is lower, that is caused by an ion exchange between liquid and solid components of bone tissue. Temporary degradation of ultradispersed HAP crystals of native bone occurs through the channel of formation of the combined water, instead of the HAP mineral formation.

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