

Electronic States of F- and OH-Apatite Studied by a DV-X α Method

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Abstract

The electronic states of fluorapatite(FAp) and hydroxyapatite(HAp) were calculated by a DV-X α method. A cluster used was $\text{Ca}_9\text{Ca}_2(\text{PO}_4)_9\text{X}_9$ (X=OH, F) with symmetry of C_3 and C_{3h} , respectively. The DV-X α calculation converged for FAp, but not for HAp. The lowering of symmetry for HAp due to the displacement of OH ions was essential for its electronic state. Density of state calculated for FAp was compared with X-ray photoelectron spectroscopy measured for HAp; both were in good accordance. On the basis of the electronic states, the chemical property of the apatites was discussed.

1. Introduction

Inorganic and organic substances constitute a bone. In the bone, the size of an organic substance (collagen) is 30nm and that of an inorganic crystal (hydroxyapatite: HAp) is several nanometers. The bone is consequently a typical organic-inorganic nanocomposite. On the other hand, HAp is industrially used as an adsorbent material, since this material has a special adsorption property for proteins and amino acids. Therefore, a combination of HAp with organic substances[1] is important to develop new artificial bone and adsorbent materials. The affinity of HAp for organic substances is related to its chemical bonding state and surface state.

In the present study, molecular orbital (MO) calculations were performed on HAp and fluorapatite (FAp) in order to elucidate their chemical properties. The electronic states calculated were compared with experimental results of X-ray photoelectron spectroscopy (XPS).

2. Calculation and Experiment

A discrete-variational(DV)-X α method was applied to molecular orbital calculations. A cluster used was $\text{Ca}_9\text{Ca}_2(\text{PO}_4)_9\text{X}_9$; here, X is OH or F. Figure 1 shows a cluster model for FAp whose symmetry is C_{3h} . 337 charged ions were put around the cluster.

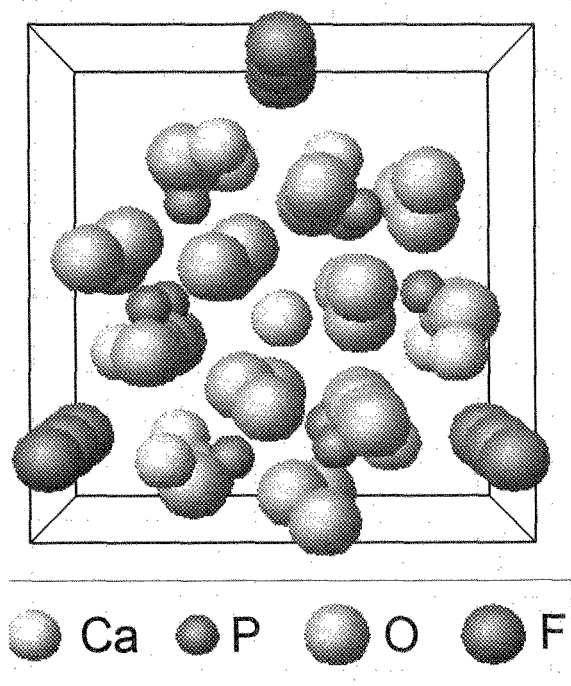


Fig.1 A cluster of fluorapatite.

Although the symmetry of HAp is lower than C_3 due to the displacement of OH ions[2], the calculation of electronic state for HAp was done on the basis of C_3 symmetry because of a limitation of the current computer's performance.

XPS was measured on sintered materials of HAp. The sintered materials were fractured in the vacuum of 10^{-8} Pa and measured immediately afterward to avoid surface pollution.

Results and Discussion

1. Density of State and XPS spectra

Figure 2 shows the energy diagrams calculated for (a) FAp and (b) HAp. The left-end column in each figure indicates whole molecular orbitals, and the other columns indicate partial density of state (pDOS) of each ion: the length of the bar is

proportional to pDOS.

In these calculations, energy levels for FAp smoothly converged, whereas those for HAp did not sufficiently converge. The calculation of HAp was very sensitive to an initial condition. In fact, midgap states are found in Fig.2(b). The midgap states result from the C_3 symmetry of the cluster used, since a real structure of HAp has no symmetric operation as mentioned above. Thus, this behavior of the calculation inversely supports that the arrangement of OH in HAp is staggered in the direction of (110)[2].

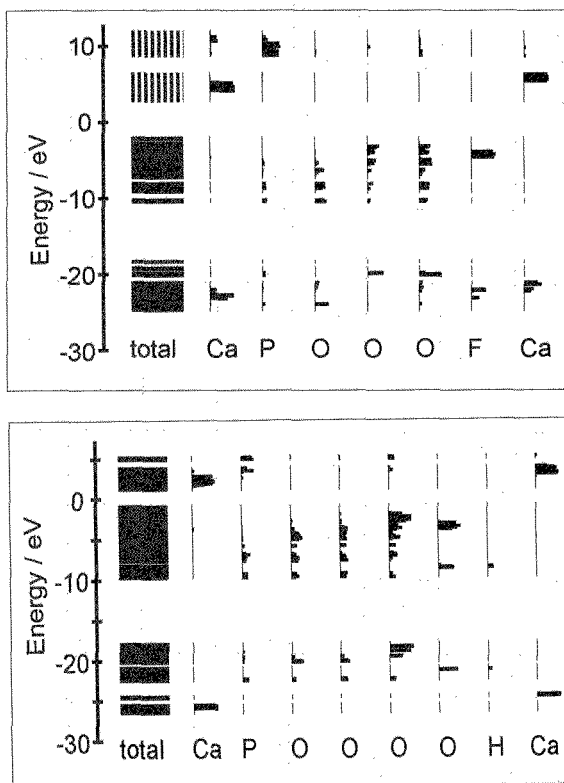


Fig.2 Energy diagrams calculated for FAp (a: above) and HAp(b: blow).

An electronic state of the apatites was discussed on the basis of the result calculated for FAp.

Total density of state (DOS) was estimated from the energy diagram of Fig2(a). The result is shown in Fig.3. In general, DOS is approximately correspondent to an XPS spectrum.

Figure 4 shows the XPS spectrum measured for HAp. A charge-up effect took place as samples used were electric insulators. The energy deviation due to the charge-up effect was about 6eV, which is compensated in Fig.4.

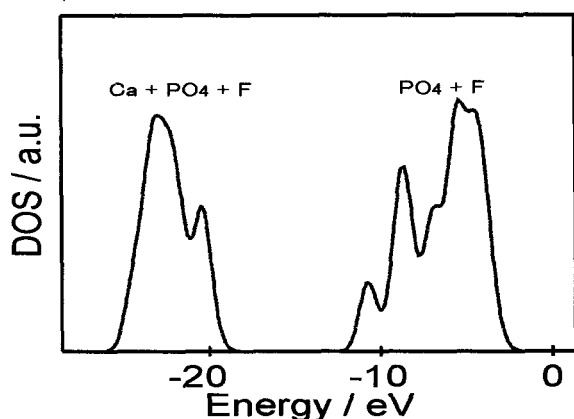


Fig.3 Density of state of FAp calculated.

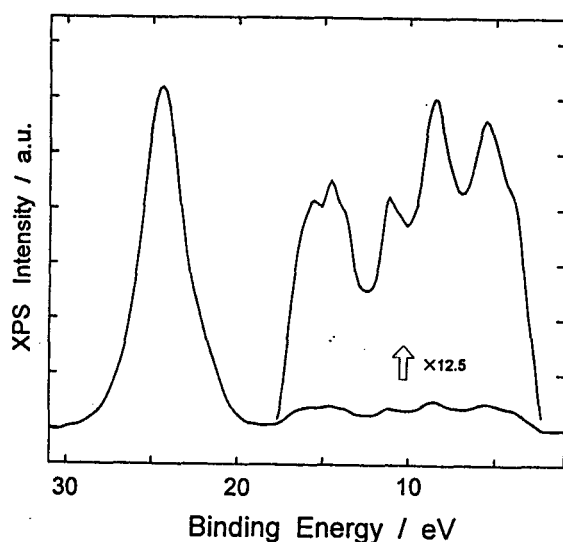


Fig.4 XPS spectrum observed for HAp.

As regards energy position, the figure 3 is in good agreement with Fig.4, though their peak intensities are different. The difference in the peak intensity is due to the difference in XPS transition probabilities of constituent atoms. The peaks observed around 12eV is not found in Fig.3, but it can be ascribed to the transition of Ca_{3p} excited by X-ray of Mg-K β . It is thus concluded that the results calculated are appropriate for the electronic state of the apatites.

3.2. Molecular Orbitals in Apatite

The molecular orbitals located at -25 to -15eV consist of Ca_{3p} , and P_{3s} and O_{2s} of a PO_4 ion, while those located at -10 to 0eV consist of P_{3p} and O_{2p} of the PO_4 ion, and F_{2p} .

Hybrid orbitals form in the PO_4 ion. An electron occupancy for 3s/3p/3d of P was 0.81/1.58/0.95. Therefore, the hybrid orbital in the PO_4 ion was approximately described by sp^2d . As for oxygen in the PO_4 ion, an electron occupancy for O_{2s} was 1.90+0.05, and that for O_{2p} was 5.25+0.25. Total charge of the PO_4 ion was consequently about -2.5e for the cluster used here.

-Chemical bonding between inner orbitals-

Delocalization of molecular orbitals except for PO_4 ions was also found in the deep molecular orbitals which locate between -25eV and -15eV in energy. Especially, Ca_{3p} forms chemical bonds with F_{2s} there. As this Ca ion partially combines with O_{2s} in PO_4 ions, a chemical bond between F and PO_4 ions forms through the Ca ion, i.e. F-Ca- PO_4 . This means that the F ions are stabilized by forming

chemical bonds with the Ca ions in the deep energy levels.

On the other hand, HAp has a tendency that Ca and O of OH can not form chemical bond between inner orbitals of Ca_{3p} and O_{2s} . The $2s$ orbital of hydroxyl O is mainly utilized to stabilize the OH bond by forming a sp hybrid orbital with its $2p_z$. Therefore, the $2s$ orbital can little contribute to chemical bonding between Ca and hydroxyl O($2s$). This difference in chemical bonding between FAp and HAp presumably reflects the difference in their chemical properties. Especially, FAp is very different from HAp in the viewpoint of affinity for organic substance.

-Chemical bonding between outer orbitals-

The difference in the electronic state between HAp and FAp was found in the chemical bonding between outer orbitals.

The molecular orbitals which exist between -10eV and 0eV are divided into two parts. The half of lower side mainly consists of P_{3s} and O_{2p} of the PO_4 ion, and the half of higher side is composed of

P_{3p} and O_{2p} , and F_{2p} . Frontier electrons are lone pair electrons on O of PO_4 ions. Ca_{3p} and F_{2p} are mixed in the higher orbitals which are related to the chemical property of the apatites.

4. Conclusions

A DV- $X\alpha$ method was applied for a cluster of $Ca_9Ca_2(PO_4)_9X_9$ ($X=OH, F$). The calculation smoothly converged for FAp of C_{3h} but not for HAp of C_3 . Chemical bonds form between Ca_{3p} and F_{2s} in FAp. It was suggested that the lowering of symmetry due to the displacement of OH ions was essential for electronic state of HAp. Density of state calculated for FAp was in agreement with X-ray photoelectron spectroscopy measured for HAp.

Reference

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2. J.C.Elliott, P.E.Mackie and R.A.Young, Science 180(1973)1055.