

USING COMPUTER SIMULATIONS TO ENHANCE TEACHING THE STRUCTURE OF MATERIALS

N. I. Papanearchou, Th. Leventouri

ABSTRACT

We discuss computer programs for drawing and analyzing the structure of several types of materials at the atomic level. We begin with simple examples of structure addressed to middle and high school-level students using the ATOMS program. We continue with the program for phase identification from x-ray powder diffraction data and then we go to the graduate and post-graduate levels to discuss crystal structure analysis by using computer programs based on the Rietveld refinement method.

KEYWORDS

Program ATOMS, Rietveld refinement, computer simulation

INTRODUCTION

Computer technology and on-line teaching has been part of modern learning process. One of the most difficult subjects to teach and visualize is related to the way the atoms are put together to construct the materials of our world. Structure of materials is a fundamental, broad, interdisciplinary topic that may be addressed at all levels of education and research from K-12 to graduate school to current research projects.

LEVEL K-12

First we will simulate the structure of the well-known common salt (also called table salt, rock salt, or sea salt). The official chemical name of this material is sodium chloride. It consists of repeated units of one atom of sodium (chemical element Na) and one atom of chlorine (Cl). The chemical formula of the compound is NaCl with a molecular weight 58.46 (Na 39.34%, Cl 60.66 %). It is produced by mining (rock salt), by evaporation of brine from underground salt deposits, and from seawater by evaporation, (Stecher, Finkel, Siegmund, and Szagmund, (1960)).

In order to visualize how these two types of atoms are put together to make the salt, we need to discuss the crystal structure of the compound. Imagine the atoms as balls and put them together according to the crystal system in which they belong. Sodium chloride belongs to the cubic system. By using the ATOMS program (Dowty, (1999)), put one of the two types of atoms in the corners (Cl) of a cube and the other (Na) in the middle of the distance between the Cl atoms, as in Figure 1.

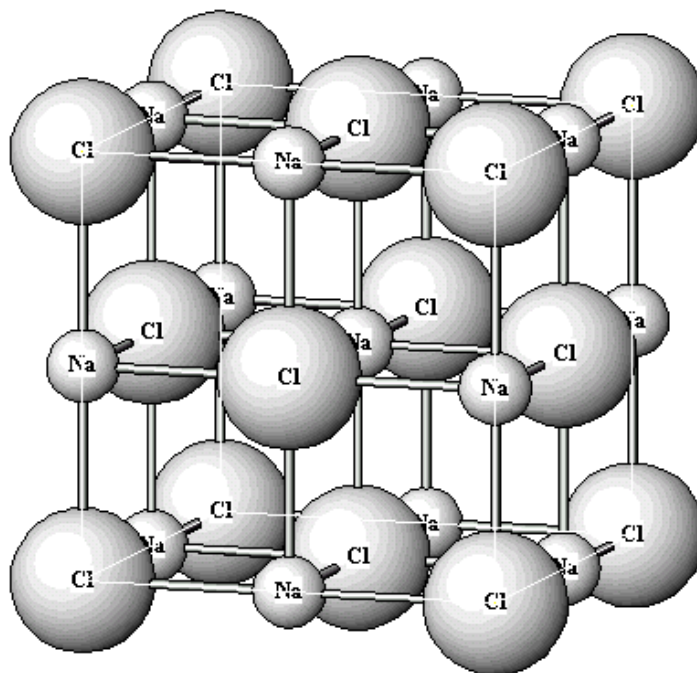
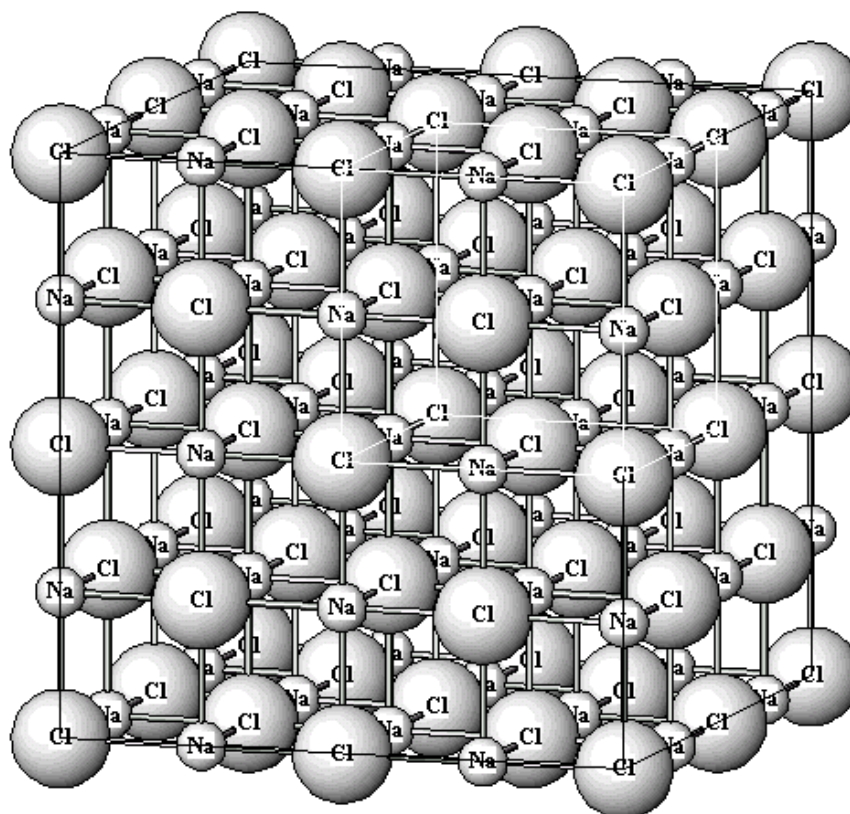


Figure 1. One unit cell of salt (NaCl).

Such arrangement of the atoms forms a unit cell of the sodium chloride (salt). This is the smallest unit of the compound that contains all the structural information of the material. The dimensions of this unit cell are so small that the human eye cannot see them when we look at the salt. However, we can visualize the submicroscopic scale of the salt by using this type of computer program, and we can decide how many unit cells we wish to see.

Figure 2 presents 4 unit cells of the salt that were created by changing the boundaries in the data file of Figure 1 in the same program.

By using computer programs we are able to visualize atoms, their positions, distances from neighboring atoms in a given compound that would otherwise be impossible to "see", because of their very-very small size. Any two atoms in Figures 1 or 2 are apart by approximately $2.5 \times 10^{-10} \text{m}$, whereas the computer simulation can put them apart by any distance we choose in order to "see" these atoms. Of course by doing so, the relative interatomic distances are scaled correspondingly so that the real structure of the material is not altered.



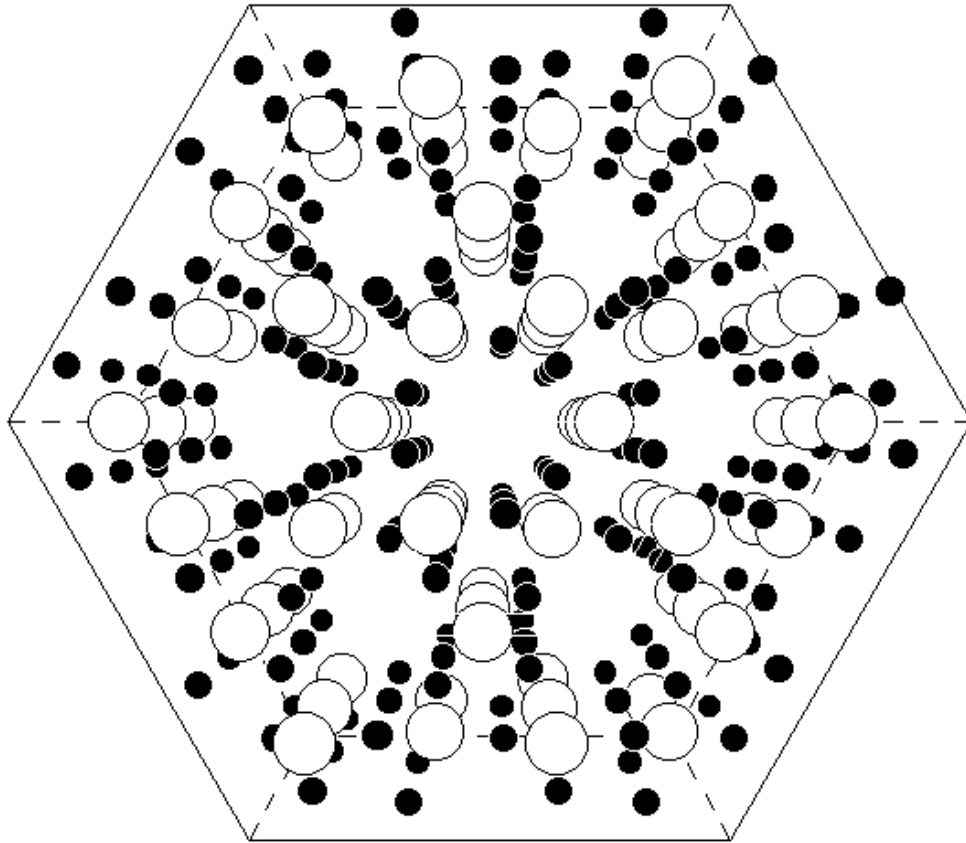
NaCl

Figure 2. Four unit cells of salt (NaCl).

There are a lot of materials that we all are familiar with but we do not see them at the atomic scale while we are able to visualize through the computer programs. We'll discuss just one more example.

SIMULATING THE STRUCTURE OF THE SAND

Consider the sand on the beach. A major component of the sand is silicon oxide (SiO_2) or quartz under its common name. Silicon (Si) and oxygen (O) atoms are put together in a periodic special arrangement to make up the whole material. The crystal system of quartz is hexagonal. Imagine the silicon atoms as white balls and the oxygen atoms as black balls. We take the crystallographic information from a data bank that is called International Crystallographic Standards (ICSD) and enter the information as an input file in the ATOMS program. Figure 3 shows a clinographic view of this hexagonal structure.



QUARTZ SiO₂

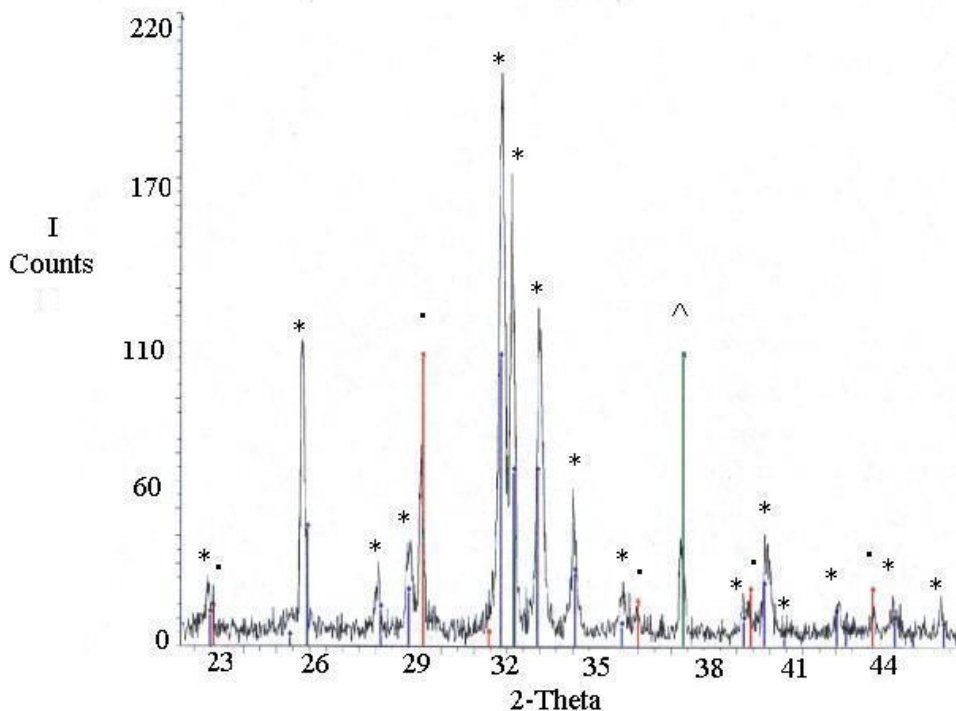
Figure 3. The structure of Silicon dioxide SiO₂.

Quartz has a molecular weight of 60.06, with weight percentages of the two types of atoms Si 46.72 % and O 53.35 %. It occurs in nature as quartz, sand, flint, chalcedony, opal, or agate. It appears either as crystalline, colorless, transparent, tasteless, or as a white, amorphous powder. It can be melted to a glass phase. Silica has the lowest coefficient of expansion by heat of any known substance. It is insoluble in water or acids, except for the hydrofluoric acid in which it readily dissolves forming the gas silicon tetrafluoride.

UNDERGRADUATE AND GRADUATE SCHOOL LEVEL

We'll discuss first the common question of identifying the phases in a given or prepared specimen. How many and what type of phases are present in a given sample of material of research interest? X-ray powder diffraction data, updated data banks and sophisticated computer codes are used for the qualitative analysis of any given specimen. First you prepare and measure the powder diffraction pattern of the specimen. Figure 4 presents an example from a sample of carbonate hydroxyapatite that was prepared in our laboratory, (Leventouri, Moghaddam, Papanearchou, Bunaciu, Levinson, and Martinez (2000), Leventouri, Chakoumakos, Papanearchou, and Perdikatsis, (2001), and Leventouri, Chakoumakos, Papanearchou, Moghaddam, and V. Perdikatsis, (2001)). The diffraction pattern was measured with a Siemens D5000 powder diffractometer equipped with a diffracted beam graphite monochromator, and CuK α radiation (wavelength $\lambda = 1.5406 \text{ \AA}$). Part of the measured diffraction pattern with the major peaks is shown in this Figure.

Phase identification was performed by using the DiffracPlus program version 6.0 IC, and the ICDD (International Center for Diffraction Data) data bank, (web page from the ICDD).




 275MbD – File: 275MbD.RAW - Type:2Th/Th locked-Start: 10.000° - End: 90.000 – Step: 0.020° - Step time: 2.0s –Temp.: 25.0°C (Room) – Time Started: 2 s – 2 –Theta: 10.000° -Theta: 5.000°-Phi: Operations: Import
 ^ 37-1497 (*) – Lime, syn – Cao – Y: 50.00 % - d x by: 1. – WL: 1.54056 – Cubic -
 * 09-0432 (I) – Hydroxyapatite, syn – Ca₅(PO₄)₃(OH) – Y: 50.00 % - x by: 1.000 – WL: 1.54056-Hexagonal
 • 05-0586 (*) – Calcite, syn – CaCO₃ – Y:50.00 % - d x by: 1.000 – WL: 1.54056-Rhombohedral – I/Ic PDF 2.

Figure 4. Phase identification of the room-temperature x-ray diffraction pattern of the synthetic CHAp275M in the angle range 22° to 45°. The major phase is hydroxyapatite (marked with *), followed by CaCO₃ (marked with •). CaO also develops as a third phase (shown with ^).

Three phases were identified: Hydroxyapatite, calcium carbonate and calcium oxide. This type of computer-aided studies and computer programs also provides a quantitative measure of the developing phases in a given specimen through the relative intensities of the peaks that identify each one of the phases.

SIMULATING THE CRYSTAL STRUCTURE OF THE MAIN FACE IN OUR BONES AND TEETH: STRUCTURE OF CARBONATE HYDROXYAPATITE Ca₅(CO₃)_x(PO₄)_{3-x}(OH) CRYSTAL STRUCTURE ANALYSIS USING THE RIETVELD REFINEMENT METHOD

Here we present an example of using major equipment and computer programs in a National Laboratory in order to investigate the crystal structure properties of carbonate hydroxyapatite that is the major component of our bone a teeth (~70 % wt).

Neutron powder diffraction data were collected with the HB-4 high-resolution powder diffractometer (wavelength $\lambda = 1.0918 \text{ \AA}$) at the High Flux Isotope Reactor of the Oak Ridge National Laboratory. The HB-4 powder diffractometer has an array of 32 detectors and available 2θ scattering angles between 11° and 135° . Then the diffraction data were refined in the hexagonal system, space group P6₃/m with anisotropic atomic displacement parameters.

Figure 5 shows an example of a Rietveld refinement fit (Young, (1993)), using the GSAS refinement program, (Larson and Von Dreele, (1986)). The experimental diffraction pattern is shown with crosses, and a continuous line is used for the calculated pattern. The difference between the two that follows the refinement computation is the lower trace.

A crystallographic model of the phase identified in the actual specimen is needed in order to start the refinement process. The ICSD (International Crystallographic Standards) data bank provides the input to construct the file for the calculated diffraction pattern.

Table I shows the type of all the atoms in the hydroxyapatite crystal structure, the refined positional parameters, fraction (site occupancy) and atomic displacement parameters, along with the lattice parameters and quality factors of the Rietveld refinement. The standard deviations of each refined quantity is in parenthesis.

Table 1. Refined structural parameters for the carbonate hydroxyapatite (sample CHAp15M) at room temperature.

$a = 9.3958(3) \text{ \AA}, c = 6.8951(4) \text{ \AA}, \chi^2 = 1.2, R_{WP} = 6\%$.							
Atom	Site symmetry		x	y	z	Fraction	U_{eq} $100 \times \text{\AA}^2$
Ca1	4f	3	1/3	2/3	0.002(1)	0.94(2)	0.93
Ca2	6h	<i>m.</i>	0.245(1)	0.991(1)	1/4	0.96(1)	0.59
P	6h	<i>m.</i>	0.400(1)	0.373(1)	1/4	0.97(1)	0.90
O1	6h	<i>m.</i>	0.3265(4)	0.4819(4)	1/4	1.0	0.73
O2	6h	<i>m.</i>	0.5843(3)	0.4662(4)	1/4	1.0	1.48
O3	12i	1	0.3435(7)	0.2592(7)	0.0716(2)	1.0	2.48
O(D)	2a	-6	0	0	0.208(3)	0.5	3.55
D	2a	-6	0	0	0.096(2)	0.5	4.00

Figure 5 shows the whole range for the measured, (marked with crosses), calculated (solid line), and difference patterns (lower trace). The calculated Bragg peak positions are shown with vertical lines.

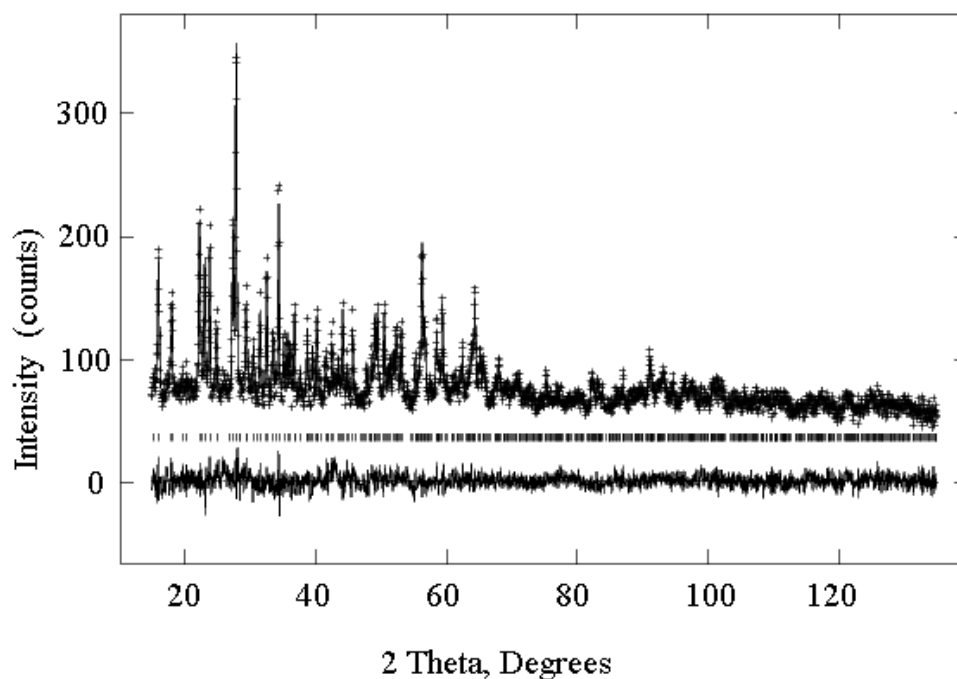


Figure 5. A Rietveld refinement fit of the room temperature neutron powder diffraction data ($\lambda = 1.0918$ Å) from the synthetic hydroxyapatite (sample CHAp 15M). The crosses show the observed data (experimental pattern), and the solid line is the calculated diffraction pattern. The vertical black lines mark the positions of the calculated Bragg peaks and the lower trace is the difference between the observed and calculated patterns.

The results of the refinement are listed in special files of the program. From these results a number of crystal structure parameters can be calculated using files of the same program. To mention a few, distances between the atoms in the unit cell of the compound (bond lengths), angles between the bonds and parameters related to the atomic vibrations (atomic displacement parameters).

Such type of crystallographic information from polycrystalline data was simply unimaginable prior to the wide development and use of computers and the corresponding programs. During the last twenty years it has succeeded in giving rebirth of several research areas and has opened new horizons in the materials science.

Figure 6 shows part of the same refined diffraction pattern in the angle range 14 to 44 degrees for the reader's convenience.

The powplot subroutine of the GSAS code is used for all the refined diffraction patterns.

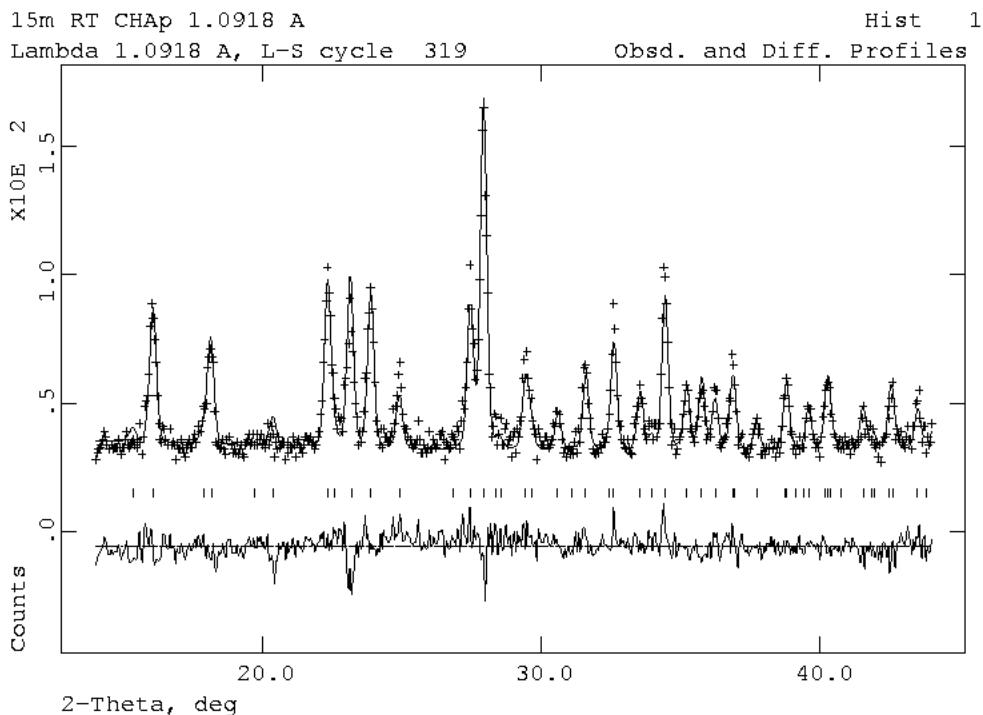


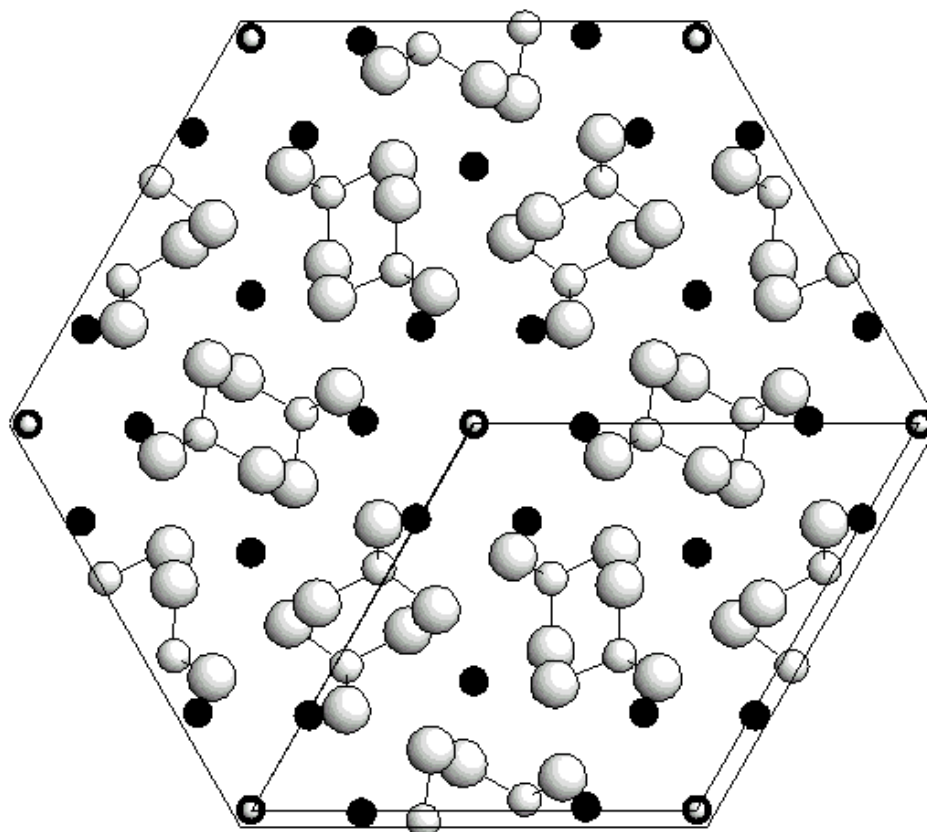
Figure 6. Part of the Rietveld refinement fit of Figure 5 from the room temperature neutron powder diffraction data ($\lambda = 1.0918 \text{ \AA}$) from the synthetic hydroxyapatite (sample CHAp 15M). The crosses show the observed data (experimental pattern) and the solid line is the calculated diffraction pattern. The small vertical lines mark the positions of the calculated Bragg peaks and the lower trace is the difference between the observed and calculated patterns.

RESULTS OF THE RIETVELD REFINEMENT CRYSTAL STRUCTURE ANALYSIS AS INPUT FILE TO THE ATOMS PROGRAM

The results of the refined diffraction pattern through the GSAS program are used to calculate crystal structure parameters such as lattice parameters, interatomic distances, angles and parameters related to the vibrations of the atom around their equilibrium position. These parameters are imported in the ATOMS program in order to visualize the crystal structure of the atoms to form one or more unit cells.

As an example, Figure 7 shows a plot of a c-axis projection of three unit cells of a carbonate hydroxyapatite using the ATOMS program. The crystal structure parameters of the input file are the refined values listed in TABLE 1.

For simplicity, in this plot we choose to simulate the atomic vibrations as isotropic, although the actual refined values of the atomic displacement parameters are anisotropic.



Bioapatite $\text{Ca}_5(\text{PO}_4)(\text{CO}_3)(\text{OH})$ Crystal Structure SG P 3 6/m

Figure 7. A c-axis projection for 3 unit cells from the room-temperature refined data of the carbonate hydroxyapatite sample CHAp15M with isotropic temperature factors. Only the P-O bonds of the phosphate tetrahedron are plotted. Small white balls are used for the P atoms, black for the Ca atoms, and large white balls for the oxygen atoms. The two atoms of the hydroxyl are plotted at the corners of the hexagon (c-crystallographic axis or channel positions), black for the O and white for the H.

CONCLUSIONS

The purpose of this presentation was to illustrate the teaching effectiveness of some modern computer codes. We hope that with the above examples we have given a clear picture of how computers and computer programs are used today as teaching tools at all levels of education, as well as research tools.

REFERENCES

Dowty, E., (1999). ATOMS for Windows and Macintosh, Version 5.

Internet Information@ICDD.com.

Larson, A. C., and Von Dreele R. B., (1986). Los Alamos Nat. Lab. Rept. LAUR 86-748, version MS-DOS (2000).

Leventouri, Th., Moghaddam, H.Y., Papanearchou N., Bunaciu, C. E., Levinson, R. L., and Martinez, O., (2000). Mat. Res. Soc. Proc. 599, 79.

Leventouri, Th., Chakoumakos, B. C., Papanearchou, N., and Perdikatsis, V., (2001). J. Mat. Res. 16, 2600.

Leventouri, Th., Chakoumakos, B. C., Papanearchou, N., Moghaddam, H. Y., and Perdikatsis, V., (2001). Mater. Sci. Forum, 378, 517-522.

Stecher, P. G., Finkel, M. J., Siegmund, O. H., Szagmund, B. M., (1960). The Merck Index of chemicals and drugs, Merck & Co., Inc.

Young, R. A., (1993). The Rietveld Method, ed., Oxford Science Publications.

N. I. Papanearchou and Th. Leventouri
Physics Department
Florida Atlantic University
Boca Raton FL, 33431
USA.
Email: nearchos@bellsouth.net, leventou@fau.edu