First principles NMR study of fluorapatite under pressure

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ABSTRACT

NMR is the technique of election to probe the local properties of materials. Herein we present the results of density functional theory (DFT) ab initio calculations of the NMR parameters for fluorapatite (FAp), a calcium orthophosphate mineral belonging to the apatite family, by using the GIPAW method (Pickard and Mauri, 2001). Understanding the local effects of pressure on apatites is particularly relevant because of their important role in many solid state and biomedical applications. Apatites are open structures, which can undergo complex anisotropic deformations, and the response of NMR can elucidate the microscopic changes induced by an applied pressure. The computed NMR parameters proved to be in good agreement with the available experimental data. The structural evaluation of the material behavior under hydrostatic pressure (from -5 to $+100$ kbar) indicated a shrinkage of the diameter of the apatitic channel, and a strong correlation between NMR shielding and pressure, proving the sensitivity of this technique to even small changes in the chemical environment around the nuclei. This theoretical approach allows the exploration of all the different nuclei composing the material, thus providing a very useful guidance in the interpretation of experimental results, particularly valuable for the more challenging nuclei such as ^{43}Ca and ^{17}O.

1. Introduction

Calcium orthophosphates, and in particular apatites (general formula $Ca_5(PO_4)_3X$ (X=F,Cl,OH)), are extensively studied because of their significance in many fields, from geology and materials science to medicine. Apatites, with various degrees of substitutions and defects, are commonly found in the Earth's crust and are considered one of the most abundant sources of phosphorous in the marine environment, acting as phosphorous "sinks" [1]. Apatites are also attracting a great interest in the field of biomaterials due to their intrinsic biocompatibility and bioactivity. Calcium phosphates, such as synthetic hydroxyapatite (HAp), fluorapatite (FAp), α and β-tricalcium phosphate (α-TCP, β-TCP), displayed intrinsic osteoinductive properties, namely the capacity of promoting bone formation without presence of oesteogenic factors, as well as osteoconductive properties (the capacity of supporting and guiding the growth of newly forming bone). Apatite bioceramics are used in bone repair and augmentation, as bone cements, as coatings for bio-inert prostheses, and for bone scaffolding [2,3]. The study of natural apatites is complicated by the fact that the apatite crystal structure can

readily accept substitution(s) from a large variety of ions. For example, fluoride ions are found to readily substitute in human enamel, due to their presence in drinking water as a result of soil erosion or added on purpose for caries prevention policies [4]. This capability of accepting various substitutions and incorporating even bulky ions, such as Cd(II) and Cu(II), as well as U(IV), is making this class of materials also attractive for nuclear waste management and water remediation [5,6].

Fluorapatite (FAp) is one of the most well-characterized members of the apatite family, and in materials science it has found interesting applications as a host for solid state diode lasers when doped with rare-earth elements, such as praseodymium or ytterbium [7]. It can be also used as a phosphor for fluorescent lamps or plasma display panels, exploiting its photoluminescent properties when doped with Sr, or rare-earth elements [8,9].

Good knowledge of the local structural properties and the response of FAp to external stimuli is of paramount importance to gain understanding of this material and, due to its structural similarity, the study of FAp can be considered as a reference for the other members of the apatite family. Solubility, crystallization, dissolution, and ion exchange have been intensively studied [10,11], but relatively few studies explored the behavior of FAp under pressure and they were mainly focused on the bulk properties of the material, studied by using vibrational spectroscopic techniques and X-ray diffraction [12–15].

In the present work we aim to explore the effects of pressure at the local level, by first principles calculations of the NMR parameters response. NMR is the technique of election for studying the local structure of materials since it is very sensitive to changes in the atomic environment. A deformation occurring around a nucleus will in fact affect its shielding, thus providing information on the deformation itself. In particular, our theoretical approach allows us to obtain unambiguously all the components of the shielding tensor and therefore to have a clear three dimensional picture of the effects of pressure on each nucleus in the material.

The *ab initio* modeling of apatites is demanding from a computational point of view and was performed only in few cases in the past [16–27]. The published works have been mainly focused on structural and electronic features: a first principles study of fluorapatite and hydroxyapatite has been recently published by Rulis et al. [25] where the authors computed electronic structure, charge distribution and X-ray absorption spectra on a supercell slab along the (001) surface. Some theoretical NMR studies are available in the literature, but they are mainly focused on hydroxyapatite [28–30]. First principles calculations of NMR parameters have been available for molecules and clusters since the 1970s [31–35] while their application to periodic/crystalline systems was implemented at a later time [36] due to the difficulty of including a macroscopic magnetic field, requiring a non-periodic vector potential. In 2001, Pickard and Mauri implemented the Gauge Including Projector Augmented Wave (GIPAW) method [37] in the plane-wave pseudopotential (PWPP) framework, based on linear-response, aimed at calculations of periodic systems. In the GIPAW method, the key to an accurate evaluation of NMR chemical shifts is the reconstruction of the all-electron wavefunction from a pseudopotential calculation, by a modified PAW transformation, in order to describe the nodal structure of the wavefunction close to the nuclei. Hence the GIPAW method retains the accuracy of all-electron calculations at the much lower cost of pseudopotential calculations, i.e. explicit treatment of valence electrons. The availability of this methodology allowed the study of a growing number of extended systems, where NMR parameters could be reliably computed at (relatively) modest computational costs. An overview of the different GIPAW/NMR applications has been recently published by Charpentier et al. [38].

In the present work, the structural properties of FAp will be evaluated when hydrostatic pressure is applied in the range from −5 to +100 kbar, and particular focus will be dedicated to the response of the NMR shielding. For the nuclei with spin $I > 1/2$ the quadrupolar coupling constant (C_q) and the asymmetry parameter (η_q) will also be provided. This paper is organized as follows: in Sections 2 and 3 we discuss the methodology and the structural data, in Sections 4 and 5 we present and discuss our NMR calculations results, and conclusions are in Section 6.

2. Computational methods

The calculations of fluorapatite (FAp) have been performed by using *ab initio* density functional theory (DFT) [39] as implemented in the Quantum-ESPRESSO package [40], with the PBE exchange-correlation functional [41]. Well converged plane wave basis sets were employed for all the presented calculations, using norm-conserving GIPAW pseudopotentials with a kinetic energy cut-off chosen at $E_{cut} = 80$ Ry. The convergence criteria for the total energy was set in all cases at 10^{-8} Ry. The **k**-points sampling in the Brillouin zone (BZ) used a Monkhorst–Pack grid with a converged mesh of $2 \times 2 \times 2$.

The FAp structure used for comparing the computed NMR parameters with the experimental data was constructed using the experimental lattice parameters (Ref. [42]) and fully relaxed

internal degrees of freedoms. The structures used for the evaluation of the NMR response under an applied pressure were obtained by imposing a target pressure (from −5 to 100 ± 1 kbar), and relaxing not only the atomic positions, but also the lattice parameters (Wentzcovitch damped dynamic algorithm, Ref. [43]). The only constraint imposed on these relaxations was the conservation of symmetry, under the assumption that no phase transition would occur at small enough pressures. This variable cell relaxation approach well simulates hydrostatic pressure for bulk systems.

NMR shieldings critically depend on the electronic wavefunctions in proximity of the nucleus. However, those are explicitly neglected in the pseudopotential approach, where the electronic wavefunctions are described by smooth functions and thus their correct nodal structure is lost. In the present work, specially designed norm-conserving GIPAW pseudopotentials were used[1] which allowed the calculation of the NMR shieldings. We also used a modified calcium pseudopotential, constructed with a rigid shift of the 3d orbitals by $+3.2$ eV, for the calculation of Ca and O NMR shieldings. The choice of using this pseudopotential was based on the observation by Profeta et al. [44] that in calcium oxides and calcium aluminosilicates the Ca PBE functional tends to overestimate the degree of covalency of the Ca–O bonds, thus causing the shielding on both Ca and O to be too small. However, this correction on the Ca pseudopotential had a negative influence on the computed equilibrium volumes and the computed phonon frequencies. Therefore in the present work, the structural relaxations and the NMR shieldings of F and P were obtained by using unit cells computed with the unshifted Ca pseudopotential, while the use of the shifted pseudopotential was limited to the calculation of Ca and O NMR parameters, assuming that the underprediction of the NMR shielding was a problem limited to Ca–O interactions, and that this effect was not relevant when calcium was present in different atomic environments.

The NMR absolute chemical shielding tensor ($\overleftrightarrow{\sigma}$) is defined as $\mathbf{B^{ind}} = -\overleftrightarrow{\sigma}(\mathbf{r}) \cdot \mathbf{B^{ext}}$, where $\mathbf{B^{ext}}$ is the externally applied uniform magnetic field. $\mathbf{B^{ext}}$ generates a local current at the nucleus, which in turn induces a local magnetic field $\mathbf{B^{ind}}$ so that the total magnetic field experienced by the nucleus is $\mathbf{B} = \mathbf{B^{ext}} + \mathbf{B^{ind}}$.

Several different conventions for notation are in current use: in the present work the "Haeberlen notation" is used [45]. We report the isotropic NMR shielding (σ_{iso}) as the average of the principal components of the shielding tensor ($\overleftrightarrow{\sigma}$), expressed in a suitable set of axes X, Y, and Z:

$$\sigma_{iso} = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})$$

where the three principal components are related as follows:

$$|\sigma_{ZZ} - \sigma_{iso}| \geq |\sigma_{XX} - \sigma_{iso}| \geq |\sigma_{YY} - \sigma_{iso}|$$

To fully describe the local symmetry around the nucleus, the shielding anisotropy (ζ) is also reported as

$$\zeta = \sigma_{ZZ} - \sigma_{iso}$$

as well as the asymmetry parameter (η) as

$$\eta = \frac{\sigma_{YY} - \sigma_{XX}}{\zeta}$$

Finally, for the nuclei with $I > 1/2$ (^{17}O and ^{43}Ca), the quadrupolar interactions are described by their quadrupolar coupling

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[1] We used standard Martins–Troullier pseudization. For oxygen and fluorine, the local channel is p and cutoff radii are 1.3 and 1.4 atomic units, respectively. For phosphorous, the local channel is d and cutoff radius is 1.9. For calcium, the local potential is derived from the d channel, and cutoff radii are 1.45, 2.00, 1.45 for the s, p, and d channel respectively.