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ACTUAL PROBLEMS OF MAGNETIC RESONANCE AND ITS APPLICATION

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Nitrogen-containing species in the structure of hydroxyapatite nanocrystals: a combined multifrequency EPR/ENDOR and DFT study

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Nanosized hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; nano-HAp) is considered to be a promising biomaterial [1]. It is known that the structure of hydroxyapatite is highly labile for the different types of ionic substitutions. These impurities can affect physicochemical properties of nano-HAp and its biocompatibility. Previously we have shown the abilities of high-frequency electron paramagnetic resonance (EPR) spectroscopy for studying paramagnetic impurities both in the synthetic and biogenous HAp [2, 3].

In the present work the combination of X- (10 GHz) and W-band (94 GHz) EPR and electron-nuclear double resonance (ENDOR) pulsed techniques with density functional theory (DFT) based calculations has been employed to investigate the distribution of nitrate impurity in the structure of nano-HAp produced via wet synthesis process.

We have observed the EPR signal of radiation induced paramagnetic center which is supposed to be a stable NO_3^{2-} radical allocated in nano-HAp structure and produced from NO_3^- anionic impurity. X- and W-band field-swept spin-echo spectra and their simulations are presented on fig.1. The concentration of the radical was estimated to be of $4 \cdot 10^{18}$ spins per gram. We assume that the nitrate anions incorporate in the structure of the nano-HAp during the synthesis process from the reagents (by-products).

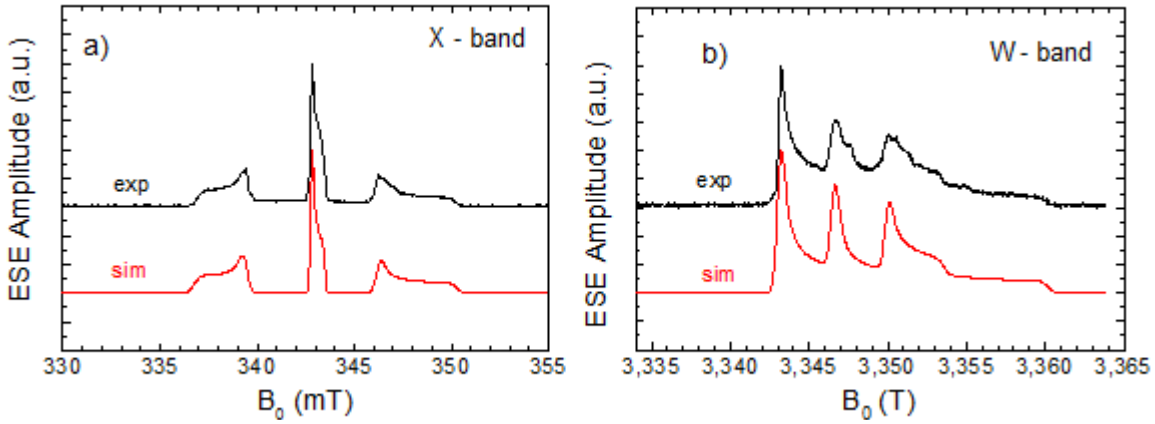

Fig.1. Field swept echo detected EPR spectra (exp) of nano-HAp: (a) X-band (9.6 GHz), T = 300 K; (b) W-band (94.1 GHz), T = 50 K and their corresponding simulations (sim).

To specify the coordination of the obtained paramagnetic centers ENDOR experiments were carried out. Fig.2 presents the Mims-ENDOR spectra in the vicinity of phosphorous (^{31}P) and hydrogen (^{1}H) Larmor frequencies. The interpretation of the ENDOR results suggests two possible crystallographic sites of NO_3^{2-} radical localization, namely the site of OH group and the position of PO_4.

Ab-initio calculations have been carried out within the framework of the plane-wave

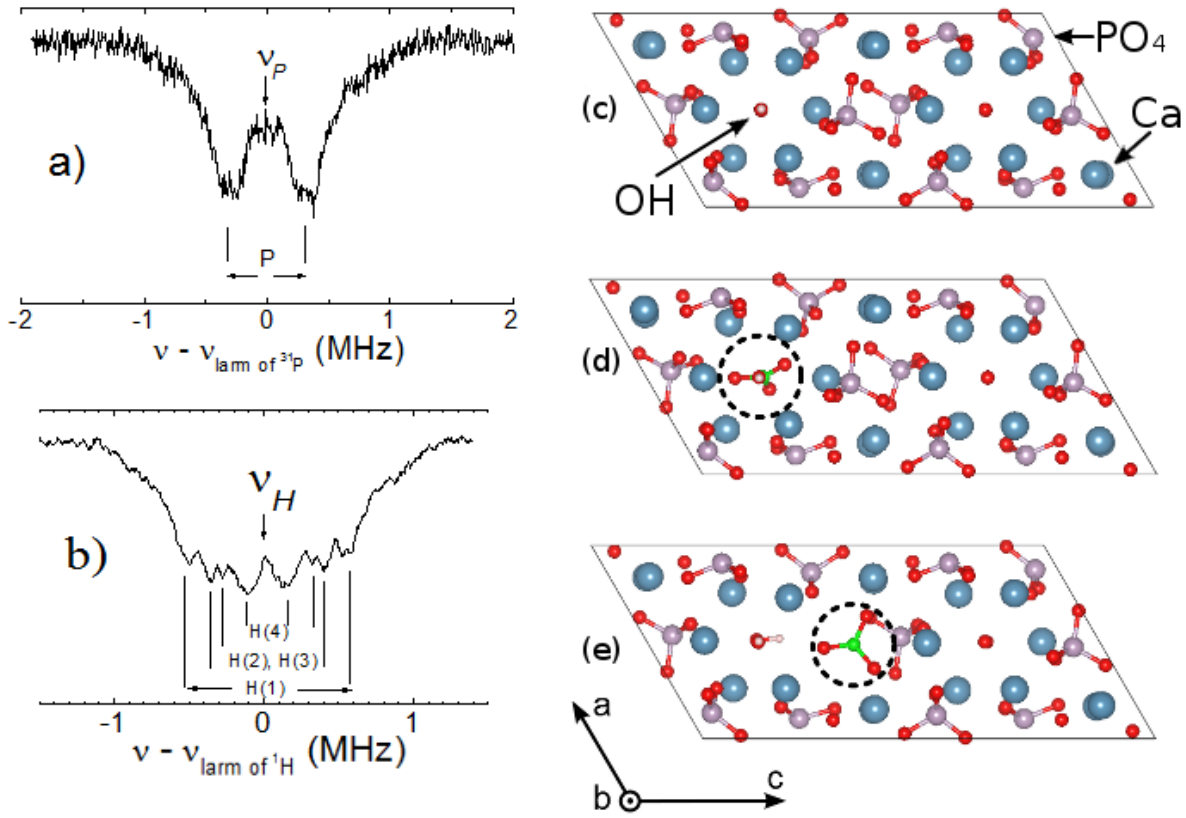

Fig.2. ENDOR spectra of the nano-HAp in the vicinity of (a) phosphorous and (b) hydrogen Larmor frequencies obtained in W-band at T = 300 K and the structures of (c) pure HAp, and HAp with nitrate localized (d) in OH-site and (e) in the position of PO_4. The dashed circles in (d-e) show the positions of the impurity.

pseudopotential DFT using the Quantum ESPRESSO package [4]. Spectroscopic parameters (hyperfine coupling constants and *g*-tensors) of the NO_3^{2-} radical were obtained by using the gauge-including projector augmented wave (GIPAW) approach [5]. Two models of nitrate incorporation were considered (as suggested by ENDOR; cf. fig.2): A-type (OH-site) and B-type (PO_4-site). After the preliminary structural optimization the spectroscopic parameters were calculated. From the excellent correspondence of the calculated hyperfine coupling constants with the experimental ones (Table 1), it can be concluded that the obtained EPR and ENDOR spectra originate from the B-site located radicals only.

Table 1. DFT calculated ^{14}N hyperfine components for the A- and B-types of substitution compared to those derived from experimental EPR spectra (in mT)

	A_{xx}	A_{yy}	A_{zz}
A-type	2.485	2.478	5.183
B-type	3.277	3.273	6.413
experiment	3.35(4)	3.35(4)	6.65(4)

To summarize, we have shown that due to the high sensitivity of the pulsed multifrequency EPR and ENDOR methods we were able to detect the radiation-induced NO_3^{2-} impurity center presented in the structure of nano-HAp in trace concentration. The combination of ENDOR with DFT calculations was found to be helpful for the investigation of the localization of the impurity. All these, finally, could be used for the design of the HAp-

based materials with desired physico-chemical properties.

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