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To cite this article: F Murzakhanov *et al* 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **155** 012006

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# Conventional electron paramagnetic resonance of $Mn^{2+}$ in synthetic hydroxyapatite at different concentrations of the doped manganese

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**Abstract.** Powders of synthetic hydroxyapatite doped with  $Mn^{2+}$  ions in concentrations from 0.05 till 5 wt. % were investigated by conventional electron paramagnetic resonance (EPR). The parameters of the spin-Hamiltonian are derived. Partially resolved hyperfine structure in the magnetic fields corresponding to  $g \approx 4.3$  and  $g \approx 9.4$  is observed. The narrowing of the central peak with concentration is reported. A possibility to use the linewidth and intensity of the central peak for concentration measurements are discussed. The results could be used for the identification and qualification of  $Mn^{2+}$  in oil, mining and ore formations.

## 1. Introduction

Calcium phosphates (CaP) are the materials of the scientific and application interest due to their abundance in the nature and presence in the living organism. In nature, different calcium phosphate minerals are produced within a wide range of environments by geological (igneous apatite), geochemical and/or geomicrobiological (phosphorite), and biological (biological apatite) processes. Igneous apatite minerals nucleate and crystallize from molten, phosphate-rich rock, forming crystalline fluorapatite ( $Ca_5[PO_4]_3F$ ), chlorapatite ( $Ca_5[PO_4]_3Cl$ ), or hydroxyapatite ( $Ca_{10}[PO_4]_6[OH]_2$ , HAp or HA) [1]. The experimental results indicate that HAp/ $MnO_2$  composite may be an effective adsorbent for the removal of lead ions from aqueous solutions [2], while the HAp supported manganese could serve as precursor for the oxide catalysts [3].

Manganese is essential impurity element in CaP. Oil containing formation – rock, sands or bitumen very often possess impurity manganese [4]. One of the powerful experimental methods for identification of manganese, especially in 2+ state ( $Mn^{2+}$ ) in different types of materials (including apatites) and characterization of structure of their complexes is electron paramagnetic resonance (EPR) [4-16]. Despite the large number of the studies performed, many important problems relating to anionic and cationic substitutions in HAp are not sufficiently investigated. Moreover, data of different studies are contradictive. The most contradictive information is associated with the sites of the ions localization in biomineral, synthetic and nanosized samples.



In this work we investigate  $\text{Mn}^{2+}$  doped synthetic HAp with the nominal concentrations of manganese in the range of 0.05 wt % - 5 wt % by using conventional EPR approaches at X-band range (9 GHz) aimed to show some additional (or not well-known) abilities of the established technique for characterizing CaP:Mn systems.

## 2. Materials and Methods

$\text{Mn}^{2+}$ -containing HAp samples with the chemical formula  $\text{Ca}_{10-x}\text{Mn}_x(\text{PO}_4)_6(\text{OH})_2$  (Mn-HAp) were synthesized by the wet precipitation technique. Calcium nitrate monohydrate  $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (235 g) was dissolved in 420 ml of 20%  $\text{NH}_4\text{OH}$  (Solution A) while  $(\text{NH}_4)_2\text{HPO}_4$  (72.2 g) was dissolved in 380 ml of deionized water (Solution B). After the  $(\text{NH}_4)_2\text{HPO}_4$  was completely dissolved, 30 ml of 20%  $\text{NH}_4\text{OH}$  was added. Mn-containing reagent ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) was dissolved in 100 ml of deionized water and then added to the A solution. The B solution was then added to the Mn-containing A solution and mixed by a magnetic stirrer for 24 h. After mixing, the precipitate was allowed to age for 48 h. Subsequently, the supernatant was decanted and then washed with 2.5 l of deionized water three times to remove the excess of  $\text{NH}_4\text{OH}$  and  $\text{NO}_3^-$ . The washing procedure was repeated three times. After washing, the Mn-HAp precipitate was separated from the liquid by filtering through Buhner funnel. A part of the Mn-HAp precipitate was heated at  $900^\circ\text{C}$  for 3 h to remove residual  $\text{NH}_4\text{NO}_3$  and improve sample crystallinity. In this work we investigate four samples with the nominal concentrations of 0.05; 0.1; 1 and 5 wt %.

X-ray diffraction (XRD) analysis (D2 Phaser diffractometer, Bruker) shows that all the samples contain only one phase with the parameters of the unit cell typical for the bulk crystals of the hydroxyapatite. The micromorphology of the powders was examined by scanning and transmission electron microscopy (JEM-2000FX II, JEOL, operated at 200 kV; and FESEM LEO SUPRA 50VP, Carl Zeiss, 5 kV). The chemical content of the powders was defined by EDS (INCA Energy+, Oxford Instruments, attached to LEO SUPRA 50 VP), ICP-MS (ELAN - DRC II, Perkin Elmer) and X-ray fluorescence analysis with total external reflection (S2 Picofox, Bruker).

Continuous wave EPR measurements were done at room temperature using X-band (9 GHz) Varian E-12, Bruker ESP-300, Elexsys 580 and table top LABRADOR (Ekaterinburg, Russia) spectrometers to compare the results obtained at different equipment and test limitations of each of them.

## 3. Results and Discussion

EPR spectra for the investigated samples are presented in Figure 1. One of the remarkable features of EPR (in addition to the facts that it is a non-destructive method with the high selective sensitivity to  $\text{Mn}^{2+}$  complexes) that its parameters are sensitive to the interaction of paramagnetic centers with the magnetic moments of the own and neighbouring nuclei (hyperfine and super-hyperfine interaction). Because the nuclear spin  $I = 5/2$  for  $^{55}\text{Mn}$ , six lines ( $2I + 1 = 6$ ) of partially resolved hyperfine (HF) structure of  $\text{Mn}^{2+}$  with the isotropic HF constant  $A_{\text{iso}} \approx 90(2)$  G are to obtain at top of the central one corresponding to  $g = 2.01$  (Figure 1 A). To make a transition from the magnetic field values to the frequency  $\nu$  and to the dimensionless  $g$ -factor, a standard EPR equation for the Zeeman interaction with the magnetic field:

$$h\nu = g\beta B, \quad (1)$$

where  $h$  is a Planck constant,  $\beta$  is an electronic Bohr magneton,  $B$  is a magnetic field strength is used.

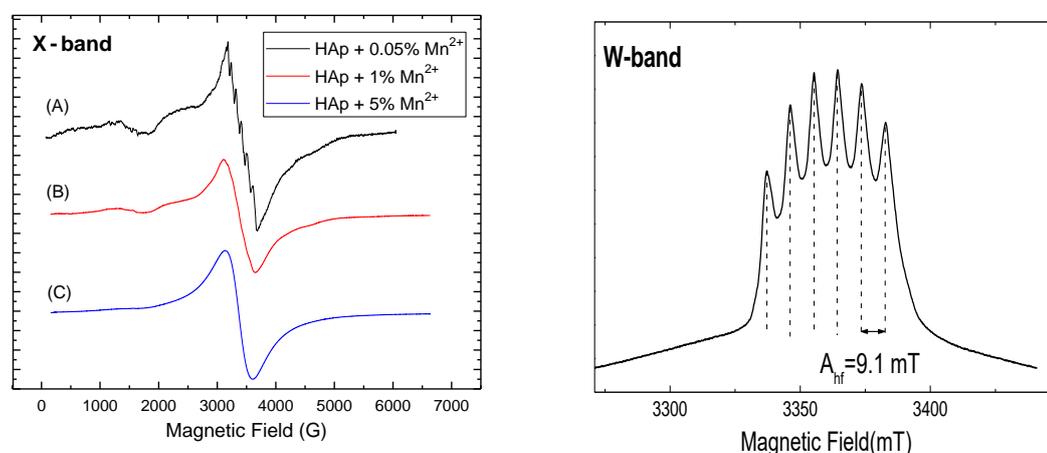
The investigated system could be described by the spin-Hamiltonian:

$$\hat{H} = g\beta\mathbf{B}\mathbf{S} + D^*[S_z^2 - S^*(S+1)/3] + E^*(S_x^2 - S_y^2) + \text{ASL}, \quad (2)$$

where  $S_{x,y,z}$  are the projections of the electronic spin  $S = 5/2$  on the principal direction of  $D$ ,  $D$  and  $E$  are the commonly used (axial and orthorhombic, correspondingly) parameters for zero-field interaction (interaction with the crystal field), other parameters are defined above in the text. For simplicity we assume that the main axes of  $g$ ,  $A$  and  $D$  tensors coincide. To describe the powder spectra function *pepper* of the EasySpin program was used [17]. It gives  $g = 2.01$ ,  $D = 530(40)$  G,

$E = 145(25)$  G,  $A_{\text{iso}} = 90 \pm 2$  G. It follows that  $E/D \approx 0.27$ , i.e. the system is quite anisotropic like glass [18]. Nevertheless, the  $g$  and  $A$  tensors could be taken isotropic and XRD analysis (within its accuracy) does not reveal any traces of the amorphous phases.

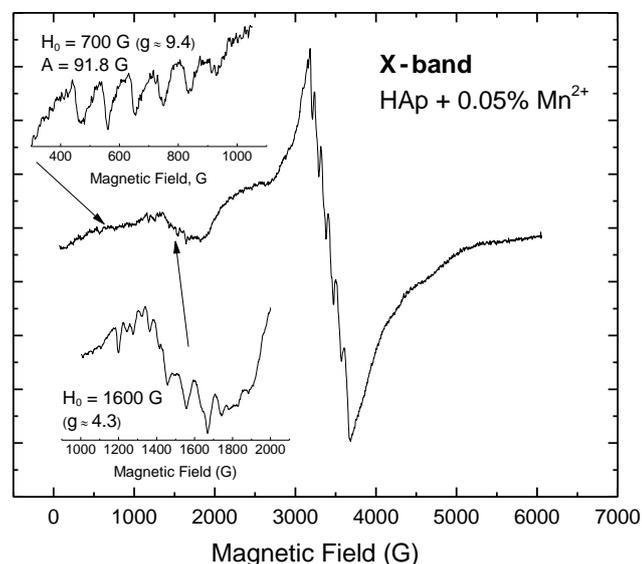
The presented in Figure 1 result is not trivial. Very often the observation and interpretation of the HF structure (HFS) is a rather complicated task. Even in the perfect crystals the resolution of the HFS spectra, the number of the components of the structure, their relative intensities strongly depend on the concentration of PC, orientation of the applied magnetic field and the EPR frequency [8-10, 19]. That is why, for example, the resolved HFS of  $\text{Mn}^{2+}$  is rarely observed at X-band in the disordered systems (powders, ceramics, glasses, nanosized samples, inhomogeneous samples of biogenic origin, samples containing non-crystal amorphous phase, etc) and a transition to the higher frequencies are necessary to interpret the EPR spectra correctly (Figure 1, ref. [8-10, 15]).



**Figure 1.** Left panel: comparison of EPR spectra of the manganese doped HAp at 9 GHz and  $T = 300$  K for (A) 0.05%; (B) 1 % and (C) 5 %. Six lines of the partially resolved hyperfine structure due to the  $I = 5/2$  for  $^{55}\text{Mn}$  nuclei is to observe for 0.05%  $\text{Mn}^{2+}$ . The signal amplitudes (vertical axes) are normalized for visibility. Right panel: W-band (95 GHz) field-swept electron spin echo EPR spectrum of 0.1% Mn-HAp detected at room temperature. The components of electron-nuclear hyperfine splitting are marked.

Furthermore, we observed HFS not only on the central line but also in the magnetic fields corresponding to  $g \approx 4.3$  and  $g \approx 9.4$  (Figure 2) in samples with the lowest concentration of  $\text{Mn}^{2+}$ . Such features were rarely reported in the literature (especially for  $g \approx 9.4$ ) [20]. Conventionally, the appearance of the EPR signals at low magnetic fields in glasses is ascribed to the large values of  $D$  and  $E$  parameters, while the possibility to obtain the resolved HF in low magnetic fields is speculated to be due to the two definite positions in the matrix with the distinct but quite specified values of  $D$  and  $E$  [18]. Following this line of reasoning, our experimental results confirm that manganese at already low concentrations occupies both of the two different calcium positions in HAp [12].

From the application point of view, the obtained feature could help to interpret the results of CaP inspection by EPR. Indeed, the detection of EPR signals at  $g \approx 2$ ,  $g \approx 4.3$  and sometimes at  $g \approx 9$  in geological and biological samples is conventionally ascribed to the  $\text{Fe}^{3+}$  ions [11]. But the most abundant stable isotopes of Fe either have  $I = 0$  ( $^{56}\text{Fe}$  and  $^{58}\text{Fe}$ ) or  $I = 1/2$  ( $^{57}\text{Fe}$ ) and could not give six line HF pattern.



**Figure 2.** EPR of 0.05 %  $\text{Mn}^{2+}$  with the amplified parts corresponding to  $g \approx 4.3$  and  $g \approx 9.4$ .

At higher concentrations electron-electron spin-spin interaction leads to the broadening of the EPR lines, HFS disappears, the lines in the vicinities of  $g \approx 4.3$  and  $g \approx 9.4$  flatten, only central peak which mainly corresponds to the allowed transition (with  $\Delta M_s = -1/2 \leftrightarrow +1/2$  around  $g \approx 2.0$ ) remains dominate. Analysis of its lineshape shows that for 5 %  $\text{Mn}^{2+}$  it is well fitted by the only Lorentzian curve while at the lower concentrations small Gaussian contribution appears. The central peak narrows with concentration from 1190 G down to 920 G for the halfwidth on the half peak,  $\Delta H_{1/2}$  that could be used for the rough estimation of  $\text{Mn}^{2+}$  concentration or its change during the release - adsorption processes in catalytic processes, for example. The observed narrowing in paper [8] was connected with the exchange interaction through the oxygen bridges. Exact analytical equation for describing the obtained behavior is still not developed.

Excellent coincidence between intensity of only the central EPR peak (after double integration) with ICP-MS data (Table 1) confirms that this simple way of estimation of  $\text{Mn}^{2+}$  concentration is applicable at least for the investigated concentration range. This is of particular importance for the specialists who use small - type EPR spectrometers like LABRADOR or Bruker e-scan: they are able to sweep the magnetic field only in the narrow field range (as a rule around  $g \approx 2$ ). As we show even that is enough to estimate the concentration of  $\text{Mn}^{2+}$  in HAp correctly.

**Table 1.** Comparison of ICP-MS data with the relative intensity of the central EPR line after the double integration.

Nominal concentration, wt. %	$M_{\text{Mn}}/M_{\text{Ca}}$ from ICP-MS (relative values)	Relative integral intensity of the central EPR line
0.05 %	1	1
0.1 %	1.86(6)	1.8(1)
1%	18.53(4)	19(1)
5%	99.69(5)	96(3)

#### 4. Conclusion and Perspectives

In this paper we have shown that the possibility of even conventional EPR approaches for investigation and analysis of Mn doped HA are still not fully exploited and many mechanisms of the spin-spin interaction in HA (like exchange interaction) are not described in details. We hope that our paper would encourage the specialists in different scientific and industrial branches to use different EPR approaches in their studies and routine analyses.

#### Acknowledgements

This work was supported by Russian Foundation for Basic Research under Grant # 18-42-160015 p\_a. E.K and V.P. acknowledge partial support from Lomonosov Moscow State University Program of Development.

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