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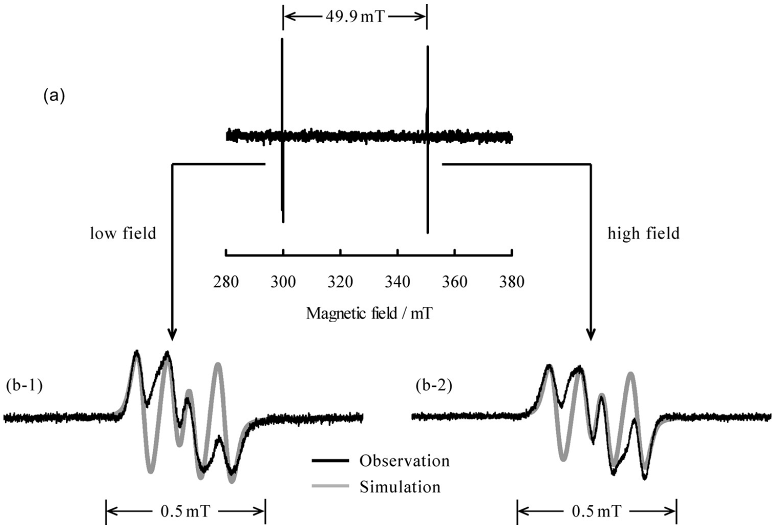

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ESR Investigation of a Stable Trapped Hydrogen Atom in X-ray-Irradiated β-Tricalcium Phosphate at Room Temperature

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The hydrogen atom (H atom) with a single 1s electron is a relatively stable paramagnetic species in a wide variety of substances when the temperature is sufficiently low.[1,2] Under these conditions, its paramagnetism is very similar to that of a free atom. However, the wave function of the H atom is somewhat modified from the atomic 1s wave function by a crystalline field, that is, by its environment. In general, it is difficult to trap the H atom at room temperature because, in addition to being the smallest of all the elements, it is highly active. Electron spin resonance (ESR) investigations of a H atom have continuously attracted attention for a long time.[1−9] The research of the trapped H atom was carried out by means of ESR spectroscopy from the latter half of the 1950s. Up to now, there are only a few examples of the H atom observable at ambient temperature.[1,3] Regarding relaxation phenomena of the H atom, Sasamori et al. estimated relaxation times (phase memory time $T_M = 0.87\ \mu$s, spin−lattice relaxation time $T_1 = 13\ \mu$s) of the H atom by electron spin−echo (ESE). In this case, measurement was performed for degassed sample at 77 K. Echo signals, however, were not obtained at room temperature because of the fairly small relaxation times. Analysis of relaxation phenomena of a H atom at room temperature is not examined in detail now.

β-Tricalcium phosphate (β-$Ca_3(PO_4)_2$, β-TCP) has been found to be an attractive new functional material[10] as a biomaterial,[11] a high-temperature humidity sensor,[12] and thermoluminescence phosphor.[13] Our previous article presented photoluminescence and thermoluminescence phenomena of dysprosium-doped β-tricalcium phosphate (β-$Ca_3(PO_4)_2$:Dy, β-TCP:Dy) phosphor. Investigating the thermoluminescence mechanism of β-TCP:Dy phosphor with ESR spectroscopy,[14,15] we discovered a stable H atom trapped in X-ray-irradiated β-TCP at room temperature for several months. In the present work, behavior of the H atom in X-ray-irradiated β-TCP was investigated by means of continuous wave ESR (CW-ESR) and pulse-ESR spectroscopy. Furthermore, based on the CW-ESR spectra and electron spin−echo envelope modulation (ESEEM), we discuss the site of the stable H atom in the X-ray-irradiated β-TCP.

Polycrystalline β-TCP (lattice constants (hexagonal setting) $a = b = 1.0424$ nm, $c = 3.7341$ nm) was characterized by means of ESR spectroscopy. No ESR signals were shown for β-TCP before X-ray irradiation. The ESR spectrum, however, was observed after β-TCP was X-ray-irradiated (Figure 1a). The largest separation in the magnetic field allows ΔMs = 1 lines in the hyperfine splitting constant 49.9 mT. This doublet splitting is attributable to the ^{1}H of a nuclear spin $I = {}^1/_2$ with a natural abundance of 99.985%. Rather sizable hyperfine splitting with the 1s electron of the H atom arises from the Fermi contact interaction.[16] The Hamiltonian describing the lowest four states of the free H atom in a magnetic field is given by $\mathscr{H} = g\beta\mathbf{H}\cdot S + A\mathbf{S}\cdot\mathbf{I} - g_n\beta_n H\cdot I$, where β, $\mathbf{H}$, $\mathbf{S}$, $\mathbf{I}$, g_n, and β_n are described as the Bohr magneton, the magnetic field, the electron spin vector operator, the nuclear spin vector operator, the nuclear g factor, and the nuclear magneton, respectively. The Zeeman splitting factor (g-value) and the hyperfine splitting constants, A, of the H atom were obtained from strict calculations.[17] The results are $g = 2.00219$ and $A = 1390.61$ MHz (49.6 mT). There is only a small difference in the parameter from the free-atom values ($g = 2.00226$, $A = 1420.41$ MHz (50.7 mT)), perhaps due to the van der Waals effect.[4,5] Many articles reported various g-values and hyperfine splitting constants, A, of the H atom.[2] In particular, Weil et al. discussed g-values and hyperfine interactions in detail.[18−20] As compared with their data, A in the present system is small.

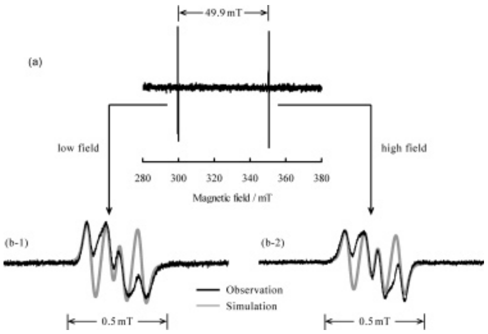

Figure 1. ESR spectra of H atom in X-ray-irradiated β-TCP at room temperature.

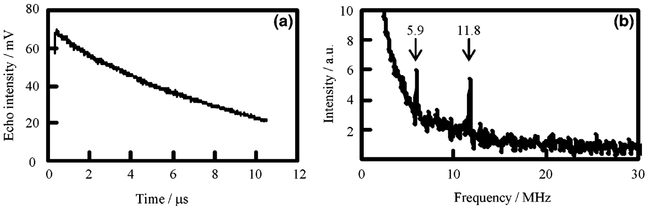

Figure 2. (a) ESEEM time decay of the primary spin−echo intensity observed in Figure 1, part b-2. (b) Fourier transformation spectrum of (a).

The two components of the doublet splitting consist of four lines (Figure 1, b-1 and b-2). These four lines are attributable to the superhyperfine splitting on the basis of ^{31}P with a nuclear spin I of ${}^1/_2$ with a natural abundance of 100%. This superhyperfine interaction indicates the overlapping of the wave functions of the H atom with the two phosphorus (P) atoms.

The ESEEM spectrum of the primary echo intensity observed in Figure 1, part b-2, is shown in Figure 2a. The nuclear modulated echo decay could be obtained at room temperature. The ESEEM time decay provided information concerning the relaxation times, that is, the phase memory time T_M from the primary spin−echoes and the spin−lattice relaxation time T_1 from the stimulated spin−echoes. At room temperature, the relaxation times were very long

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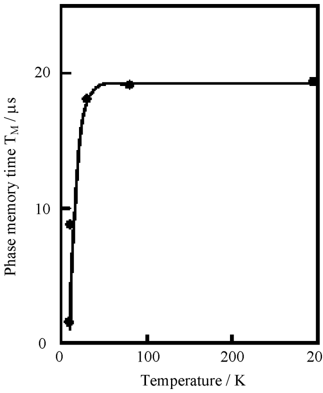

Figure 3. Temperature dependence of the phase memory time T_M of the H atom in X-ray-irradiated β-$Ca_3(PO_4)_2$.

($T_M = 19.4$ µs, $T_1 = 75.8$ µs) compared with those of general paramagnetic species. Both of these appropriate values of the relaxation times permitted easy detection of the spin−echoes even at room temperature. Information regarding the P atom is indicated from the Fourier transformation of the ESEEM (FT-ESEEM) of Figure 2b. The peaks of 5.87 and 11.83 MHz corresponded to the P atom and its multiple components, respectively, at the magnetic field of this ESR observation for the nuclear frequency. In this region, there was no peak of the H atom because the hyperfine splitting constant of the H atom was too large (1390.61 MHz). The ESE was obtained from room temperature to 9 K. The temperature dependence of the T_M is shown in Figure 3. The T_M was kept constant from room temperature to 20 K. The T_M decreased abruptly below 20 K. The T_1 was measured for the temperature dependence as a matter of course. The correct T_1, however, was not obtained at low temperature because the ESE decay time was too long. The short relaxation time T_M below 20 K might be explained by the quantum tunneling effect of the H atom. More relaxation data for the trapped H atom will be necessary.

The present background of experimental work on the trapped H atom provides a fairly good qualitative picture of the site at which the H atom is trapped. It appears that the H atom can be trapped at either substitutional or interstitial sites in various matrixes.[2] In the present work, we suggest that the H atom in β-TCP is located around the core between two PO_4 groups, that is, the H atom can be trapped at the interstitial site. In the structure of β-TCP,[21,22] illustrated in Figure 4a, emphasis is given to columns of ions of the form ···PO_4 Ca Ca Ca PO_4 ··· (B column) that can be identified running parallel to the *c*-axis. We suggest that the H atom is trapped between two PO_4 groups in this B column. The PO_4 group has a tetrahedral structure, and it is assumed that the distances from the H atom to the nearest P are R_1 and R_2 (Figure 4b). The two lines of the CW-ESR spectra would have split into three lines if R_1 and R_2 represented the same distances. However, in the present investigation, each pair of lines split into four lines, respectively (Figure 1, parts b-1 and b-2). This result indicates that R_1 and R_2 represent different distances.

In conclusion, in this research, we succeeded in detecting a stable trapped H atom at room temperature in X-ray-irradiated β-TCP and characterized it by CW-ESR and pulse-ESR spectroscopy. ESR spectroscopy revealed the hyperfine structure of the H atom and the superhyperfine structure of the two P atoms, resulting in the overlapping of the charge clouds of the H atom and the two P atoms in the X-ray-irradiated β-TCP. The most important facts are the detections of ESE and ESEEM at room temperature. At room temperature, the observations of ESE and ESEEM and the estimations of the relaxation times (T_M, T_1) for the H atom were carried out for the first time until now. The site of the H atom in the X-ray-irradiated β-TCP was determined on the basis of the CW-ESR and pulse-ESR analyses.

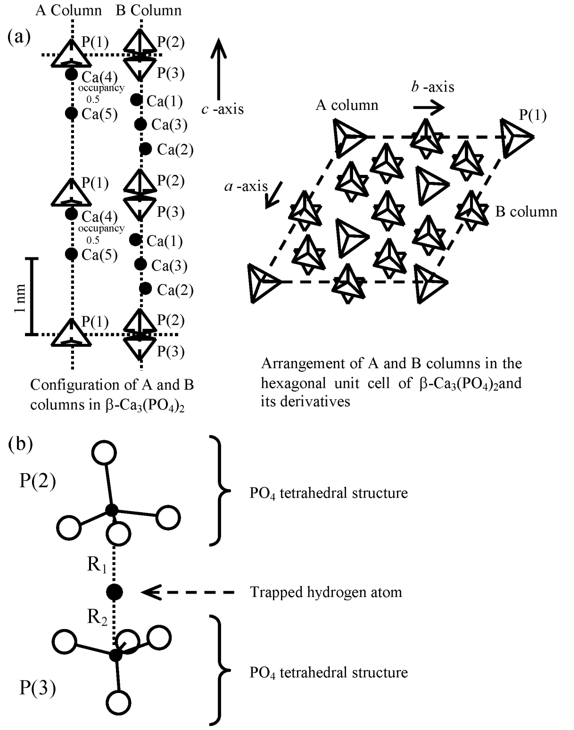

Figure 4. (a) Structure of β-$Ca_3(PO_4)_2$. (b) Trapped H atom site in X-ray-irradiated β-$Ca_3(PO_4)_2$.

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