Dynamical Effect Study of a Stable Trapped Hydrogen Atom by ESR Spectroscopy

Kouichi Nakashima*[1,#] and Jun Yamauchi[2]
[1]*Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501*
[2]*Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502*

(Received April 17, 2006; CL-060458; E-mail: kouichi@tagen.tohoku.ac.jp)

Effective spin Hamiltonian parameters of a stable trapped hydrogen atom (H atom) in X-ray-irradiated β-tricalcium phosphate (β-$Ca_3(PO_4)_2$, β-TCP) were estimated by high frequency ESR (Q-band). The dynamical effect of the H atom was investigated at various temperatures by CW-ESR (X-band) spectroscopy.

ESR studies of an H atom have continuously much attention for long time.[1–3] The attractiveness of the H atom is due to its fascinating physical and chemical properties. In particular, ESR makes an attractive method for obtaining information of dynamical effect of the H atom. There are only a few examples of the H atom observable at room temperature up to now.[2] In our previous paper,[3] some results were reported such as:

1. We succeeded in detecting the stable trapped H atom at room temperature in X-ray-irradiated β-TCP and revealed that the charge clouds of the H atom and the two phosphorus atoms in X-ray-irradiated β-TCP were overlapping.
2. At room temperature, the observations of electron spin echo (ESE) and electron spin echo envelope modulation (ESEEM), and the estimations of the relaxation times (phase memory time T_M, spin-lattice relaxation time T_1) for the H atom were carried out for the first time.
3. The short T_M below 20 K was explained by the quantum tunneling effect of the H atom.
4. 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. The stable H atom was trapped between two PO_4 groups in the B column in β-TCP and interacted with the two phosphorus atoms.

In the present work, effective spin Hamiltonian parameters of a stable trapped H atom were estimated by high frequency ESR (Q-band). Furthermore, the dynamical effect of the H atom was investigated at various temperatures by CW-ESR (X-band) spectroscopy.

Figure 1 shows Q-band ESR spectra of a stable trapped H atom in X-ray-irradiated β-TCP. The doublet splitting is attributable to the ^{1}H of a nuclear spin $I = 1/2$ with a natural abundance of 99.985%. The two components of the doublet

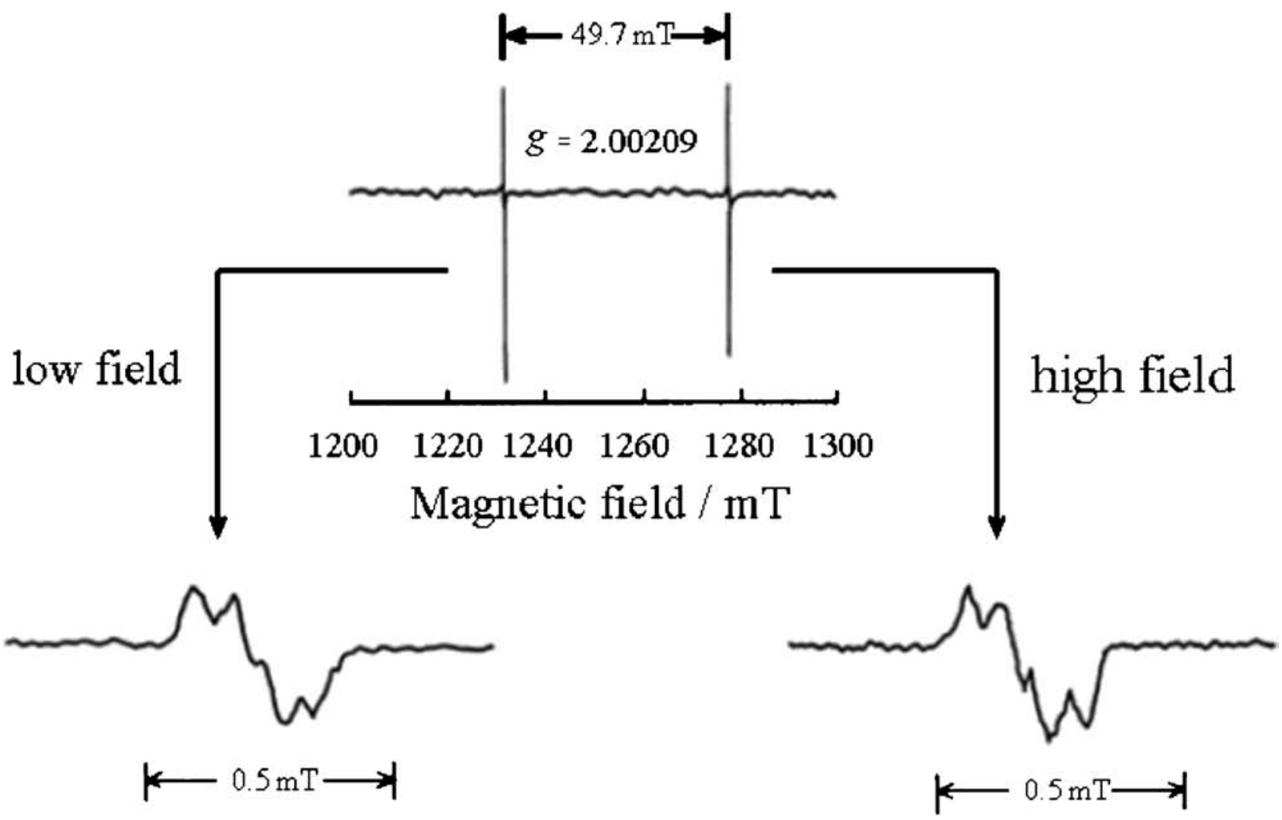

Figure 1. Q-band ESR spectra of the stable trapped H atom in X-ray-irradiated β-TCP at room temperature.

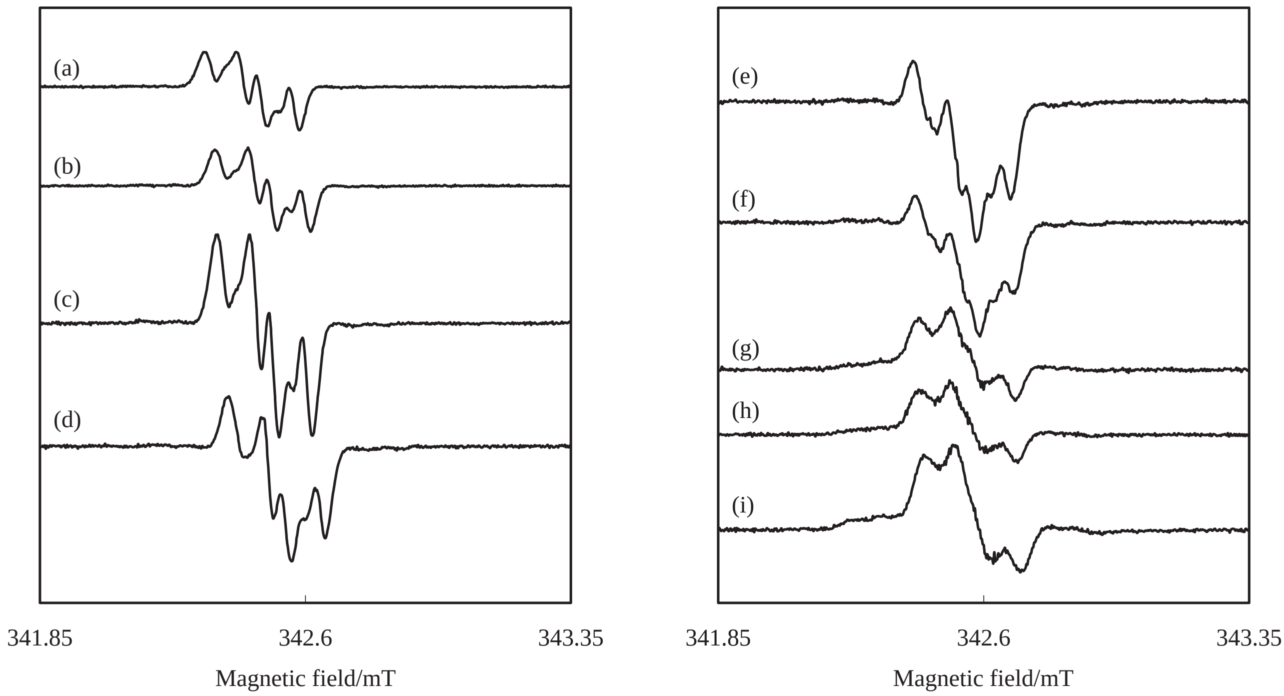

Figure 2. ESR spectra of the trapped H atom (high field) in X-ray-irradiated β-TCP at various temperatures. Power: 0.005 mW, sweep time: 8 min, time constant: 0.1 s, amplitude, (a) and (b) 500, (c) and (d) 250, (e)–(i) 500, modulation: 0.01 mT, frequency: 8.953 GHz, temperature/K, (a) 154, (b) 100, (c) 80, (d) 50, (e) 40, (f) 30, (g) 20, (h) 10, and (i) 4.

splitting consist of four lines which are attributable to the superhyperfine splitting on the basis of ^{31}P of a nuclear spin $I = 1/2$ with a natural abundance of 100%. The Zeeman splitting factor (g-value) and the hyperfine splitting constant, A, of the H atom was obtained from the strict calculations.[4] The results are $g = 2.00209$ and $A = 1390.72$ MHz (49.63 mT). Compared with the previous report of X-band ESR spectra ($g = 2.00219$, $A = 1390.61$ MHz (49.6 mT)), there are only small differences in the parameters. The reason why the g-value is a little small is that high frequency ESR (Q-band) enhances the sensitivity.

Figure 2 shows ESR spectra of a stable trapped H atom (high field) in X-ray-irradiated β-$Ca_3(PO_4)_2$ at various temperatures. The line shape of ESR spectra above 50 K was similar to that at room temperature. The ESR spectra, however, were broad below 50 K. Therefore, it is assumed that spin–spin relaxation time T_2 becomes short at low temperature. As a matter of fact, T_M of the H atom was short at low temperature.[3] Accordingly, our previous result of T_M at low temperature demonstrated that the CW-ESR spectra were broad. It is remarkable that the ESR spectra become broader below 20 K further. It is explained by the quantum tunneling effect of the H atom.

Judging from these experimental findings, the ESR spectra data correspond to pulse-ESR data. Relaxation phenomena which are found by CW-ESR and pulse-ESR spectroscopy are very important to study the dynamical effect of the H atom.

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Present address: Institute of Multidisciplinary Research for advanced Materials, Tohoku University, Aoba-ku, Sendai 980-8577.

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