Improvement in sensitivity of FT-ESR measurements by using a gyrotron as high-power millimeter wave source

S. Mitsudo, K. Dono, K. Hayashi, Y. Ishikawa, Y. Fujii

Research Center for Development of Far-Infrared Region, University of Fukui, Fukui, Bunkyou 3-9-1 Japan

***Abstract*—Pulsed ESR spectroscopy system was developed using the high-power millimeter wave of gyrotron. The FID signal of stable radicals of BDPA diluted with polystyrene was successfully observed by the quadrature detection method. By Fourier transforming of these FID signals, high resolution FT-ESR spectrum of BDPA was successfully obtained. An attempt was made to improve the sensitivity by averaging the obtained spectra. It was found that there was an $\sqrt{n}$-fold relationship between the number of averagings n and the S/N ratio.**

I. INTRODUCTION

THE electron spin resonance (ESR) spectroscopy is one of the most important methods to investigate microscopic properties in substances [1]. Furthermore, a pulsed ESR method has advantage of measuring relaxation times of electron spins as compared to CW ESR method. One of the most popular pulsed methods is spin echo method, in which subsequent two pulses ($\pi/2$ and π pulses) with a delay time τ are applied to a sample and the echo signal is obtained after another time τ from the end of the second pulse. In general, a pulsed ESR spectroscopy requires a certain pulse duration $\Delta\tau$, then it determines the required strength of the microwave P_{RF} as $\Delta\tau \sim P_{RF}^{-1}$. The higher power means the shorter $\Delta\tau$, which extends the applicability of pulsed ESR methods. To date, the commercial pulsed ESR systems at X-band have been used extensively by researchers. The system with millimeter and/or submillimeter wave region is thought to be more useful. However, its development includes many difficulties in the treatment and development of high-power radiation sources. Gyrotron is a high-power radiation source in the submillimeter wave region [2-4], which is suitable for the radiation source of a short-pulsed ESR system. The radiation of several kW from a high power gyrotron allows the pulse duration in nanosecond-order. Such system has a potential to develop materials sciences, especially in the subject of substance with short relaxation time.

II. RESULTS

Development of a pulsed ESR spectrometer has been promoted by using the high frequency and high-power millimeter wave of the gyrotron. At the beginning, measurement of FID (Free Induction Decay) signal of BDPA radical was carried out. BDPA radical is an interesting stable radical used for DNP-NMR.

The sample to be subjected to the pulsed ESR often has a low spin density. This is because the spin relaxation time becomes short if the distance between the spins is not long. Therefore, improvement in sensitivity is required. The magnetic moment of the nuclear spin is much smaller than the electron spin, so the signal is weak. Nevertheless, NMR is generally measured by FT spectrum. This is because the S/N ratio can be improved by averaging. In NMR, electromagnetic waves having a frequency in the MHz band are handled, so that the phase and amplitude can be completely controlled by an electronic circuit. Therefore, averaging is possible by directly adding the FID signals. In this system, high-power millimeter-wave pulses of several nano-seconds required for pulsed ESR are achieved using light controlled semiconductor shutters [5]. The pulse of the Nd-YAG laser used for switching has a jitter of 1 nsec and has a problem that complete control including a phase cannot be performed. The phase of each FID measurement becomes random, and the signal becomes zero by simple addition of the FID signal. Therefore, in this system, the sensitivity was improved by digitally processing the sampled FID signal and averaging the spectrum from which unnecessary signals were removed by several Fourier transforms.

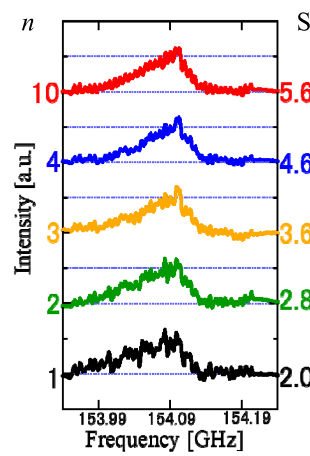

Fig. 1. Obtained FT-ESR spectrum of BDPA averaged n times and its S/N ratio.

Fig. 1 shows how the S/N ratio is improved by averaging. It was found that by performing averaging n times, the S/N ratio was improved by $\sqrt{n}$ times. This indicates that the noise included in this spectrum is due to random factors. It also shows that higher sensitivity measurement is possible by increasing the number of times of averaging. Even higher sensitivity can be expected.

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