Toward Terahertz ESR Spectroscopy Using a Microcantilever

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A new method of high-frequency electron spin resonance (ESR) using a microcantilever is reported. In our technique, ESR signal is mechanically detected while a magnetic field is swept under electromagnetic-wave irradiation. The achieved spin sensitivity was on the order of $10^9$ spins/G at 80 GHz. Using multiple light sources, ESR spectroscopy in the millimeter wave region up to 315 GHz is successfully performed.

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I. INTRODUCTION

High-frequency electron spin resonance (ESR) is a powerful technique in the study of magnetism [1]. In particular, high $g$-value resolution and multi-frequency measurement allow spectroscopic studies of spin systems, from which detailed information on the spin Hamiltonian is obtained. Recently, we successfully improved detection sensitivity of high-frequency ESR measurement using a microcantilever [2, 3]. In this system, ESR signal of a microcrystal on the order of 1 μg can be detected in the millimeter wave region.

The principle of our technique is as follows: for a spin $s=1/2$ case, ESR absorption is accompanied with a spin reversal process. In this process, spin distribution function is modified, and hence a magnetization of the system changes. In sample-on-cantilever configuration, the magnetization change can be detected as a change of force/magnetic torque acting on the cantilever. In this way, ESR signal can be mechanically detected, similar to magnetic resonance force microscopy (MRFM). A striking difference between our method and MRFM is the operating frequency. Namely, MRFM typically works in the microwave region ($\sim$10 GHz), while in our system, high-frequency light sources in the millimeter-wave region is used to attain better spectral resolution.

Furthermore, an electromagnetic wave is introduced into the sample position via an oversized waveguide, so multi-frequency ESR measurement can be easily performed. This feature enables a new kind of spectroscopy of magnetic systems. In the following, we present the current status of our cantilever ESR technique as well as underlying developments for ESR spectroscopy in terahertz region beyond 1 THz.

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TABLE I: Comparison of sensitivity parameters between pulsed-field and static-field measurements.

|                  | pulsed field (dc method) | static field (modulation method) |
|------------------|--------------------------|----------------------------------|
| S/N ratio        | ~10                      | ~3000                            |
| (80 GHz)         |                          |                                 |
| (315 GHz)        |                          |                                 |
| sample mass      | ~1 µg                    | <1 µg                            |
| detectable spin number | 4.0 × 10^{15} | 1.4 × 10^{12}                   |
| spin sensitivity (spins/G) | 3.9 × 10^{12} | 1.6 × 10^{11}                   |
| (80 GHz)         |                          |                                 |
| (315 GHz)        |                          |                                 |

III. RESULTS AND DISCUSSION

In multi-frequency ESR measurement \(f_{\text{Gunn}}=80-315\ \text{GHz}\), we found that the resonant field systematically shifted with frequency. A linear fit gives \(g=5.07\), being consistent with previous reports. The signal intensity tends to decrease with the operating frequency, since the output power decreases in the higher frequency region. For instance, the output power was 80 and 1 mW for 80 and 315 GHz, respectively. In this sense, high-power light sources are strongly desired for better sensitivity in the future. In best conditions, the signal-to-noise ratio was greater than 10 \(^{8}\), and the corresponding spin sensitivity was estimated to be \(10^{9}\) spins/G. This value is comparable to that of other quasi-optic high-field ESR techniques \([5, 6]\). We also succeeded in ESR detection in pulsed magnetic fields, and comparison of the sensitivity parameters between static-field and pulsed-field measurements is given in Table I.

Shown in Fig. 2 is a typical result of angle-dependent ESR measurement of Co Tutton salt at 4.2 K. The Gunn oscillator’s frequency was 80 GHz. Two series of ESR absorption are clearly visible, as indicated by two dotted lines. This result is consistent with the fact that there are two different Co\(^{2+}\) sites in the crystal \([7]\). It is noted that these two signals will not be distinguished so clearly for the X-band ESR system, since the line widths of Co Tutton salt are on the order of several hundreds of gauss. The sign of ESR signal depends on which direction the magnetic field is applied with respect to the principle axis of Co\(^{2+}\) ion.

In our setup, an electromagnetic wave propagates in an oversized waveguide, so there is no upper limit for operating frequency. In order to take this advantage, further extension to terahertz region is of particular interest. For this purpose, a backward traveling wave oscillator (BWO), which covers a frequency range 300-1200 GHz, will be useful. To this end, we recently started a couple of further developments toward ESR spectroscopy in terahertz region. First, 15 T superconducting magnet equipped with a vibration control is installed, and ESR probe head is now under construction. In addition, use of softer cantilevers combined with fiber-optic detection system is developed to increase the sensitivity. Customized MEMS cantilever is also fabricated to optimize cantilever structure.

As an example of a practical application of THz ESR spectroscopy, studies of metal-containing protein such as hemoglobin is of particular interest. In these systems, metal ions play important roles in their function, and knowledge on the local electronic state of metal ion is important. In this sense, ESR technique is very sensitive to coordination environment and the valence state. However, ESR detection in these systems are often very difficult due to the existence of the so-called zero-field splitting. In addition, sample size is extremely small due to the difficulties of crystallization. In our system, sample size on the order of several \(\mu\)m can be measured, and the use of high-frequency light sources allow ESR absorption beyond zero-field splitting. Thus, our cantilever ESR technique will be a promising tool in biological and chemical analysis in the future.

IV. CONCLUSION

We have shown that ESR detection using a cantilever is possible in the millimeter-wave region up to 315 GHz. In the future, high-frequency light sources such as backward traveling oscillator will be tested to achieve better spectral resolution. In addition, the sensitivity will be increased using softer cantilevers and fiber-optic detection system.
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