High-field ESR using SQUID magnetometer

T. Sakurai¹, R. Goto², N. Takahashi², S. Okubo³, H. Ohta²,³

¹Center for Supports to Research and Education Activities, Kobe University, Rokkodai 1-1, Nada, Kobe 657-8501, Japan
²Graduate School of Science, Kobe University, Rokkodai 1-1, Nada, Kobe 657-8501, Japan
³Molecular Photoscience Research Center, Kobe University, Rokkodai 1-1, Nada, Kobe 657-8501, Japan
E-mail: tsakurai@kobe-u.ac.jp

Abstract. We have developed high-field ESR system using commercially available SQUID magnetometer equipped with the superconducting magnet up to 5 T. This is a longitudinal magnetization detection type ESR. The minimum detectable spin number is evaluated as \(2 \times 10^{13}\) spins/G for 105 GHz. The most advantageous points as compared with other high-field ESR are that high-field ESR can be done very easily and both microscopic and macroscopic magnetic properties can be obtained at once. Moreover, the transmission technique without using cavity enables us to make multi-frequency ESR measurement in the wide frequency region. We have succeeded in observing ESR from 70 to 315 GHz.

1. Introduction

High-field electron spin resonance (ESR) is a very powerful means to clarify local spin states of magnetic semiconductors. It has several advantages as compared with commercial X-band (∼9.5 GHz) ESR spectrometer equipped with a water-cooled electromagnet whose magnetic field is generally limited up to about 1 T. For instance, the high-field ESR can obtain a spectrum with high resolution and observe ESR across the large energy splitting. And these advantages give us microscopic information about the magnetic center of material in detail, which can not be revealed by X-band ESR measurement. However, the high-field ESR equipments usually need large and complicated setups and its measurement can not be made so easily. Here, we demonstrate a very simple high-field ESR system using commercially available superconducting quantum interference device (SQUID) magnetometer equipped with a superconducting magnet (SQUID-ESR). This is a longitudinal magnetization detection type ESR. In this technique, the resonance is observed as the change of the longitudinal magnetization parallel to the external magnetic field. When the resonance condition is satisfied under the irradiation of the electromagnetic wave, spins are excited with the change of \(|\Delta S_z| = 1\). The magnetization changes correspondingly and it is detected by the SQUID magnetometer. The advantageous points as compared with other high-field ESR system are that the high-field ESR measurement can be made much more easily and the macroscopic magnetization measurement can also be made if only the irradiation of the electromagnetic wave is stopped. The SQUID-ESR technique was first reported by Cage et al. [1]. In this study, we have improved the sensitivity and extended the frequency region as compared with Cage’s system, as is described below in detail. We demonstrate our high-field SQUID-ESR system and several results obtained by this system.
These results will show that the SQUID-ESR is an easy but very useful tool to study magnetic properties of semiconductors.

2. Outline of the SQUID-ESR system
Our SQUID-ESR system is schematically drawn in Fig. 1. We use Magnetic Property Measurement System (MPMS) XL equipped with a superconducting magnet (Quantum Design Co. Ltd.) as the SQUID magnetometer. The magnetic field is available up to 5 T. The Gunn oscillator and its multiplier are used as the light source and the available frequency region is from 70 to 315 GHz. The sample holder rod is also used as the light pipe and the electromagnetic wave is irradiated from the top of the rod. A sample set in a straw is simply attached at the end of the rod. The other measurement procedure is the same with that of the MPMS measurement.

The ESR system using commercially available SQUID magnetometer was first reported by Cage et al. [1]. In Cage’s system, a waveguide matched for TE$_{11}$ mode for the frequency around 100 GHz with inner and outer diameter of 2.54 $\phi$ and 3.175 $\phi$ is used as the light pipe, while an oversized waveguide with inner and outer diameter of 5.4 $\phi$ and 6.0 $\phi$ is used in our system. In both SQUID-ESR systems, the cavity is not used and the transmission technique is adopted. Therefore, the use of a waveguide matched for the fundamental mode rather causes the loss of energy of the electromagnetic wave. As is shown later, the use of an oversized waveguide is proven to improve the sensitivity greatly. Another difference is that Gunn oscillator is used as the electromagnetic wave source in this study and it can be operated much easier than klystron which is employed in previous experiment [1]. Although its output power is generally lower than that of klystron, we have succeeded in observing ESR in the wide frequency region from 70 to 315 GHz, as is also shown later.

3. Results and discussions
We tried high-field SQUID-ESR measurement by a stainless light pipe with inner and outer diameter of 2.6 $\phi$ and 3.0 $\phi$ first for several compounds. Here we show a result of cobalt Tutton salt (NH$_4$)$_2$Co(SO$_4$)$_2$·6H$_2$O as an example. A single crystal with a mass of 19.2 mg is used. The magnetic ion is Co$^{2+}$ (3d$^7$) and it is often explained as fictitious spin 1/2 with anisotropic g-value
Figure 2. SQUID-ESR spectra of cobalt Tutton salt obtained at 4.0 K. $M_0$ is defined as $M_0 = \frac{N}{2} (g_1 + g_2) \mu_B S$ and $\Delta M$ is the difference of the magnetizations with or without irradiation.

Figure 3. Magnetization curve of cobalt Tutton salt at 4.0 K. The broken and solid lines are equation (1) and the second term of equation (1), respectively. The inset shows SQUID-ESR spectra obtained at 130 GHz.

when it is in nearly cubic symmetry [2]. Cobalt Tutton salt is known to have two inequivalent CoO$_6$ octahedra, namely two $g$ sites [3]. The magnetic field is applied nearly parallel to the most anisotropic $g$ principle axis for one site (site I). The measurements were done by “DC measurement” with or without irradiation of the electromagnetic wave. The magnetic field was swept by 0.3 T for one frequency with a step of 0.01 T. The magnetization was obtained by scanning 3 cm length (24 points) and by averaging two scans at each field point. Figure 2 shows the SQUID-ESR spectra of the cobalt Tutton salt at 4.0 K. The spectra are obtained by subtracting the magnetization curve obtained without irradiation of electromagnetic wave from that obtained under irradiation. We have succeeded in observing ESR in the wide frequency region form 80 to 315 GHz as shown in Fig. 2. The measurements above 140 GHz have never been done before and this is the first measurement at the higher frequency for SQUID-ESR. The signal intensity depends on the output power of the oscillator mainly. The output power tends to decrease as the frequency increases. It is 36 mW for 120 GHz and 1.5 mW for 315 GHz, for instance. A shoulder-like structure was observed for each absorption line and this is probably due to twinned crystal. From the linear fitting to the plot of frequency versus resonance field, the $g$-value is obtained to be $g_1 = 6.34$ for site I. And another $g$-value for site II is obtained to be $g_2 = 3.17$ as shown in the inset of Fig. 3. These $g$-values are consistent with the known values [3]. With these $g$-values, we can draw the magnetization curve as

$$M = \frac{N}{2} \mu_B S (g_1 \tanh x_1 + g_2 \tanh x_2) + \alpha H,$$

where the first term is the Brillouin function with $S = 1/2$, the second term is the correction term with a fitting parameter $\alpha$, $x_i = g_i \mu_B S H / (k_B T)$, $N$ is number of magnetic ion, $\mu_B$ is Bohr magneton, $k_B$ is Boltzmann factor, $H$ is magnetic field and $T$ is temperature. As shown in Fig. 3, the calculated line completely coincides with the raw data with a suitable fitting parameter $\alpha$ ($\alpha = -3.65 \times 10^{-8} M_0$ emu/G). Thus, it is clearly shown that the SQUID-ESR has proven to
be a powerful tool to obtain both magnetic macroscopic and microscopic properties.

In order to improve the sensitivity, we tried an oversized waveguide by a stainless pipe with inner and outer diameter of 5.4 φ and 6.0 φ with a handmade slide seal assembly. The results are shown in Fig. 4 with the results obtained by 3 φ light pipe for comparison. An organic free radical compound DPPH (1, 1-diphenyl-2-picrylhydrazyl) is used as a sample. A powder with a mass of 13 mg is used. The magnetic field was swept by 80 mT for one frequency with a step of 2 mT. As clearly seen in Fig. 4, the sensitivity improves greatly. The signal intensity increases by more than one order of magnitude for 80 GHz. Moreover, we observed ESR at 70 GHz at which ESR was hardly observed with 3 φ light pipe. The minimum detectable spin number is evaluated as $2 \times 10^{13}$ spins/G at 105 GHz (output 52.5 mW) at 1.8 K. Thus, it is found that the oversized wave guide is very effective to improve the sensitivity for SQUID-ESR.

4. Summary

We have developed high-field ESR system using commercially available SQUID magnetometer equipped with a superconducting magnet up to 5 T. It was confirmed that the available frequency region is from 70 to 315 GHz. The minimum detectable spin number was obtained as $2 \times 10^{13}$ spins/G for 105 GHz (52.5 mW) at 1.8 K by using an oversized waveguide. We found that the SQUID-ESR is a very powerful means to study magnetic properties from the macroscopic and microscopic point of view at once.

Acknowledgments

This research was partially supported by Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Creative Scientific Research (No.19GS1209), Scientific Research (C) (No. 60379477).

References

[1] Cage B and Russek S (2004) Rev. Sci. Instrum. 75 4401
[2] Abragam A and Pryce M H L (1951) A206 173.
[3] Kuroda A, Motokawa M and Date M (1978) J. Phys. Soc. Jpn. 44 1797