Development of high-pressure, high-field and multi-frequency ESR apparatus and its application to quantum spin system

T. Sakurai\textsuperscript{1}, T. Horie\textsuperscript{2}, M. Tomoo\textsuperscript{2}, K. Kondo\textsuperscript{2}, N. Matsumi\textsuperscript{2}, S. Okubo\textsuperscript{3}, H. Ohta\textsuperscript{2,3}, Y. Uwatoko\textsuperscript{4}, K. Kudo\textsuperscript{5}, Y. Koike\textsuperscript{6}, H. Tanaka\textsuperscript{7}

\textsuperscript{1}Center for Supports to Research and Education Activities, Kobe University, Kobe 657-8501, Japan
\textsuperscript{2}Graduate School of Science, Kobe University, Kobe 657-8501, Japan
\textsuperscript{3}Molecular Photoscience Research Center, Kobe University, Kobe 657-8501, Japan
\textsuperscript{4}The Institute for Solid State Physics, Tokyo University, Kashiwa, Chiba 277-8581, Japan
\textsuperscript{5}Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
\textsuperscript{6}Department of Applied Physics, Tohoku University, Sendai 980-8579, Japan
\textsuperscript{7}Department of Physics, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

E-mail: tsakurai@kobe-u.ac.jp

Abstract. We have developed high-pressure, high-field and multi-frequency ESR apparatus. The pressure is available up to 14 kbar by using the clamped-type piston-cylinder pressure cell. All inner parts of the pressure cell are made of zirconia which has good transmittance of the electromagnetic wave in the frequency region from 70 to 700 GHz. The magnetic field region is up to 55 T and the temperature region is from 1.6 to 4.2 K. We present the results of quantum spin systems SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2} and CsCuCl\textsubscript{3} as the application of this multi-extreme condition ESR technique and they will demonstrate its usefulness for studying the quantum spin system.

1. Introduction

High-field and multi-frequency electron spin resonance (ESR) measurement is a indispensable technique for studying quantum spin systems. It gives us microscopic information about electron spins responsible for the magnetic properties of the system, which cannot be obtained only by conventional X-band (~ 10 GHz) ESR measurement. For instance, ESR mode with zero-field gap which exceeds 10 GHz can be observed easily by the multi-frequency ESR measurement, as is demonstrated in this paper. Recently, we have succeeded in introducing a parameter of pressure into the high-field and multi-frequency ESR apparatus [1, 2, 3]. Now, we can perform ESR measurement with quasi-continuous frequency region from 70 to 700 GHz under hydrostatic pressure up to 14 kbar, at low temperature down to 1.6 K and at high magnetic field up to 55 T. In this paper, we present our high-pressure ESR apparatus briefly first.

We also present the recent results of the high-pressure ESR measurements of quantum spin systems. One is the result of the well-known $S = 1/2$ 2D orthogonal spin dimer system SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2}. The system has the energy gap of 35 K between the singlet ground state and the excited triplet states [4, 5]. It was found directly from our measurements that the energy gap
Figure 1. Clamped-type pressure cell for our ESR apparatus. The outer and inner diameter of the cylinder are 8 mm and 3 mm, respectively. The pressure cell is connected optically to the 10φ light pipe through the 2° tapered light-cone.

was suppressed by the pressure. Another result is concerned with a $S = 1/2$ triangular lattice antiferromagnet CsCuCl$_3$. It shows peculiar antiferromagnetic resonance (AFMR) modes in the low field region due to its 120° magnetic structure below the Néel temperature $T_N = 10.7$ K [6, 7]. We observed the drastic change of the antiferromagnetic gap of this compound by the pressure. These examples also demonstrate the usefulness of the high-pressure, high-field and multi-frequency ESR measurements for studying the quantum spin systems.

2. Outline of apparatus
The apparatus consists of the pulsed high-magnetic field ESR apparatus and a clamped-type piston-cylinder pressure cell made of NiCrAl alloy, as shown in Fig. 1. The magnetic field is generated up to 55 T by the combination of the pulsed magnet and the capacitor bank with the energy of 300 kJ [8]. Gunn oscillators and backward traveling wave oscillators are used as the light sources. As all inner parts made of zirconia have good transmittance of the electromagnetic wave in the frequency region from 70 to 700 GHz, the transmission-type ESR measurements can be made. The pressure is available up to 14 kbar in the temperature region from 1.6 to 4.2 K. It is confirmed by the change of the superconducting transition temperature of Sn around 3 K. The detailed setup is also found in refs. [3, 9].

3. Application to quantum spin systems
In this section, the results of SrCu$_2$(BO$_3$)$_2$ and CsCuCl$_3$ are presented as application of the high-pressure ESR measurements to quantum spin systems. The orthogonal spin dimer system SrCu$_2$(BO$_3$)$_2$ has been investigated intensively since the discovery of the magnetic plateau phenomenon and it has still attracted much attention. Recently, an interesting magnetic phase was found at 24 kbar by NMR measurements [10]. In order to understand the detailed properties of this high pressure phase and the mechanism of its phase transition, we have tried the high pressure ESR measurements of this compound [9]. Figure 2 shows the typical frequency dependence ESR spectra of SrCu$_2$(BO$_3$)$_2$ obtained at 1.6 K under the pressure. For this measurement, the pressure was determined from the relationship between the load at room temperature and the pressure determined by the change of the superconducting transition temperature of Sn around 3 K. Absorption lines due to the transition between the singlet ground state ($S = 0$) and the lower branch of the triplet excited states ($S = 1$), which is schematically shown in the inset of Fig. 3, are clearly observed as indicated by arrows. The energy gap at zero-field can be determined precisely by the linear extrapolation in the frequency-field diagram.
The energy gap at 0 kbar is determined to be 723 GHz (34.7 K) which agrees well with the previous results by Nojiri et al. [5] and the pressure dependence of the energy gap is obtained as shown in Fig. 3. This is the only measurement that determines the gap energy of this compound under pressure directly, as far as we know. It was found that the energy gap is reduced when the pressure is applied. Strikingly, from the simple linear fitting to the obtained data, the ground state seems to be non magnetic even at 24 kbar where the magnetic phase was confirmed by NMR measurements. For the emergence of the magnetic phase under high pressure, it should undergo a phase transition such as structural phase transition, as is also indicated by Waki et al. [10]. We plan to perform ESR measurement under the higher pressure region.

Next we show the result of the triangular lattice antiferromagnet CsCuCl$_3$. The pressure effect on this compound is very interesting because the pressure may change the subtle balance between the quantum fluctuation and the weak magnetic anisotropy related to its unique magnetic phase transition [11]. Although we already made ESR measurement of this compound under pressure from this point of view, the pressure region was limited below 3 kbar [2]. Therefore, we have tried a measurement in the higher pressure region. We also focused on the more accurate determination of the pressure in this measurement. The pressure was calibrated very precisely by SQUID magnetometer measurement of Sn set in the pressure cell as well as the sample after each ESR measurement. Figure 4 shows the pressure dependence ESR spectra of CsCuCl$_3$ obtained at 130 GHz. As shown in Fig. 4, the AFMR due to the 120° structure was clearly observed. It shifts to the lower field side as the pressure is increased below 8.2 kbar and to the higher field side at 11.1 kbar. The inset of the Fig. 5 shows the typical frequency-field diagram and the obtained data set is reproduced very well by the theoretical AFMR mode with the parameter $\alpha$ which corresponds to the antiferromagnetic gap at the zero-field [6]. There exist two AFMR modes in this frequency and field region: The $\omega_+$ mode is a mode above the gap and the $\omega_-$ mode is a mode below the gap. Figure 5 shows the pressure dependence of the antiferromagnetic gap $\alpha$ obtained by fitting of the theoretical line to the data at each pressure as shown in the inset. The gap changes very sensitively and almost linearly to the pressure. Although the gap at 0 kbar obtained by this measurement coincides with that by the previous
Figure 4. Pressure dependence ESR spectra of CsCuCl$_3$ for B||c obtained at 4.2 K and 130 GHz.

Figure 5. Pressure dependence of the antiferromagnetic gap $\alpha$ at 4.2 K. The inset shows the frequency-field diagram obtained at 5.5 kbar.

work [2], that at 3 kbar by the previous work slightly deviates from the fitting line, presumably due to the lack of pressure accuracy. From Fig. 5, the behavior of the absorption line to the pressure shown in Fig. 4 is understood as follows. Below 8.2 kbar, the absorption line is due to the $\omega_+$ mode and it shifts to the lower field side as the pressure, or the gap $\alpha$, is increased. Once the antiferromagnetic gap exceeds the observed frequency (130 GHz) as is in the case at 11.1 kbar of Fig. 4, the observed mode changes to the $\omega_-$ mode from the $\omega_+$ mode and the absorption line shifts to the higher field side. The origin of the increase of the antiferromagnetic gap is expected to be attributed to the increase of the magnetic anisotropy by the pressure. A further investigation is in progress.

In summary, our high-pressure, high-field and multi-frequency ESR apparatus is presented as well as the results of the quantum spin systems SrCu$_2$(BO$_3$)$_2$ and CsCuCl$_3$ as its application. These results can never be done by any high-pressure X-band ESR apparatus, which were already developed [12], and they also show its usefulness clearly for studying the quantum spin system.

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