Development and application of high field and high pressure ESR system

T Sakurai¹, A Taketani², T Tomita³, S Okubo³, H Ohta³, H Tanaka⁴ and Y Uwatoko⁵

¹ Center for Supports to Research and Education Activities, Kobe University, 1-1 Rokkodai, Kobe 657-8501, Japan
² The Graduate School of Science and Technology, Kobe University, 1-1 Rokkodai, Kobe 657-8501, Japan
³ Molecular Photoscience Research Center, Kobe University, 1-1 Rokkodai 657-8501, Japan
⁴ Research Center for Low Temperature Physics, Tokyo Institute of Technology, Tokyo, 152-8551, Japan
⁵ Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan

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

Abstract. We have developed a high field and high pressure ESR system including a unique pressure calibration method. We have succeeded in the ESR measurements up to 16 T under the pressure region up to 1.1 GPa. We will present about the ESR system and its application to a spin gap system KCuCl₃. The energy gap between the singlet ground state and the triplet excited states are suppressed with applying pressure and the critical pressure of KCuCl₃ is estimated to be 0.90 GPa at 4.2 K.

1. Introduction
Pressure effect in quantum spin systems is one of the most attractive topics in the solid state physics. High field ESR is a powerful means to study the ground state and the low-lying excitations of the quantum spin systems and it has revealed various phenomena intrinsic to the quantum spin systems [1]. We have developed a high field and high pressure ESR system so far in order to clarify changes of the ground state and the excited states of the systems under pressure from the microscopic point of view [2, 3]. A spin gap system KCuCl₃, which consists of antiferromagnetically coupled $S = 1/2$ dimers, is expected to present a novel pressure-induced phenomenon [4]. In a previous paper, we reported for KCuCl₃ that the decrease of the gap energy between the singlet ground state and the triplet excited states with applying pressure was observed directly by this ESR system up to 0.3 GPa [5]. We have developed the system furthermore and succeeded in extending the pressure region up to 1.1 GPa [6]. In this paper, an outline of this high field and high pressure ESR system will be presented. The pressure dependence measurements of KCuCl₃ up to 0.73 GPa, in which newly developed pressure calibration method is used, will be also presented.

2. High field and high pressure ESR system
The high field and high pressure ESR apparatus basically consists of a pulse high field ESR system [1] and a pressure cell for the high field ESR measurements as shown in figure 1. The
pressure cell is a typical piston-cylinder type pressure cell. The most characteristic feature of this pressure cell is that all the inner parts are made of zirconia or sapphire which can transmit the millimeter and submillimeter waves. The outer cylinder is made of NiCrAl alloy. The pressure cell is inserted into a pulse magnet and a transmitted ESR spectrum of a sample under pressure can be obtained. In order to extend the pressure region, we designed a new pressure cell whose inner and outer diameter are 3 mm and 8 mm, respectively (right side in figure 1). For the new pressure cell, we confirmed that the pressure was generated up to about 1.1 GPa by SQUID measurements of the superconducting transition temperature of tin. The bore of the pulse magnet was also modified so that the new pressure cell can be inserted. The magnetic field region up to 16 T, the frequency region from 70 GHz to 700 GHz and the temperature region from 1.8 K to 4.2 K are available now in this system. The system also includes a unique pressure calibration method which uses a change of the crystal field of Ni\[H_2O\]_6 octahedron in NiSnCl_2-6H_2O under pressure. Figure 2 shows typical ESR spectra of NiSnCl_2-6H_2O under pressure. As the magnetic ion is Ni\(^{2+}\) (\(S = 1\)), which is in the trigonal field, the ESR signal splits into two with an interval of \(2D/g\mu_B\), where \(D\) is the single ion anisotropy. As shown in figure 2, the \(D\)-value changes from \(D_0\) at ambient pressure to \(D_p\) at a pressure \(P\) through the change of the crystal field as the pressure is applied. We have obtained the linear relation of \(D_p\) versus \(P\) up to 0.75 GPa [6]. Thus, we can determine a pressure by using this relation within the error of ±0.01 GPa when a NiSnCl_2-6H_2O single crystal is set in the pressure cell as well as a sample.

3. Application to spin gap system KCuCl_3

KCuCl_3 is an isostructural compound with TlCuCl_3, which is well known for the Bose-Einstein condensation of magnons in the presence of the magnetic field [7]. Recently, Matsumoto et al. suggested by their theoretical studies that a novel excitation mode which is called amplitude mode can be induced by pressure in these spin gap systems [4]. When the energy gap closes and the long range antiferromagnetic order occurs at \(P_c\), the amplitude mode emerges by the longitudinal fluctuations of the induced moments. Although inelastic neutron scattering measurements under pressure have been tried for TlCuCl_3, it does not succeed in observing the amplitude mode [8]. Therefore, we have performed the high field and high pressure ESR measurements on the isostructural compound KCuCl_3.

Figure 3 is the frequency dependence ESR spectra at 4.2 K for \(B || [211]\). The pressure standard NiSnCl_2-6H_2O was also set in the pressure cell and the pressure was calibrated to be 0.53 GPa by the method described above. As shown in figure 4, the absorption lines indicated
Figure 2. Typical ESR spectra of NiSnCl$_2$-6H$_2$O for $B \parallel [111]$ at 4.2 K obtained at 0 GPa (lower part) and at 0.75 GPa (upper part). The pressure was calibrated by the superconducting transition temperature of tin.

by arrows in figure 3 are due to the direct transition between the singlet ground state ($S = 0$) and the triplet excited states ($S = 1$). Although the ESR transition between different $S$ states is forbidden in general, it often can be observed when the interactions which mix these two $S$ states exist. The Dzyaloshinsky-Moriya (DM) interaction is considered as a candidate of such interaction. The [211] direction is the parallel direction to both the (10$\bar{2}$) plane and the (011) plane. We found that the signal intensity of direct ESR transition for $B \parallel [211]$ is strongest among all directions we measured and the relationship between the ESR intensity and the direction of the DM vector is a quite interesting subject. Figure 4 is the frequency-field diagram for $B \parallel [211]$ obtained at 4.2 K at various pressures. It shows apparently that the energy gap between the singlet ground state and the triplet excited states is suppressed with applying pressure. This is caused by the increase of the interdimer interactions and the decrease of the intradimer interaction [9]. These changes of the interactions correspond to the increase of the band width and the decrease of the average energy in the excited triplet magnon band, respectively. The obtained gap energies at various pressures are plotted in figure 5. The data which were obtained by the similar ESR measurements without the pressure standard are also plotted for comparison. As the pressures of these data were estimated from the loads at room temperature, they have ambiguity in their values and the data somewhat scatter. On the other hand, the data obtained in this study with the pressure standard have more accurate pressure values within the error $\pm 0.01$ GPa and less scatter. The solid line is the fitting curve with the equation

$$\Delta(\text{GHz}) = \sqrt{a + bP + cP^2},$$  

(1)

where $\Delta$ is the gap energy. The obtained data are well fitted by eq. (1) and the critical pressure $P_c$ is obtained to be 0.90 GPa. This is in agreement with the value of $P_c \sim 0.82$ GPa which is obtained by the magnetization measurements at various pressures [9]. The ratios of constants $a$, $b$ and $c$ are obtained to be $b/a = -1.49$ (GPa$^{-1}$) and $c/a = 0.42$ (GPa$^{-2}$). Equation (1) is
Figure 4. Frequency-field diagram for $B \parallel [211]$ obtained at 4.2 K under various pressures.

Figure 5. Pressure dependence of the gap energy of KCuCl$_3$ at 4.2 K.

obtained by the relation $\Delta = \sqrt{J(J-2)|\tilde{J}|}$ and an assumption that $J$ and $\tilde{J}$ are expressed by the first order term for pressure approximately, where $J$ is the intradimer interaction and $\tilde{J}$ is the linear combination of the interdimer interactions [9]. In ref. [9], the ratios $b/a$ and $c/a$ are estimated to be $-1.67$ (GPa$^{-1}$) and $0.48$ (GPa$^{-2}$), respectively, from the pressure dependence of $J$ and $\tilde{J}$ which are estimated by the susceptibility measurements at various pressures, and this result leads $P_c$ to a value of $0.77$ GPa. These values agree with our results sufficiently when the fact that $\tilde{J}$ is derived under several approximations is taken into account.

In summary, we have developed the high field and high pressure ESR system with the magnetic field region up to 16 T and the pressure region up to 1.1 GPa. The pressure calibration method using the change of the crystal field of NiSnCl$_2$·6H$_2$O with applying pressure is also established in the pressure region up to 0.75 GPa within the error of ±0.01 GPa. The system is applied to the spin gap system KCuCl$_3$ and the critical pressure is estimated to be 0.90 GPa at 4.2 K. In order to observe the amplitude mode, the measurements at higher pressures are required.

Acknowledgments
One of the authors (TS) acknowledges Dr. T. Takeuchi (Osaka Univ.) and Dr. S. Kimura (Osaka Univ.) for kindly help for the SQUID measurements. This work was supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Science and Technology of Japan (No. 17740228).

4. References
[1] Ohta H, et al. 2003 J. Phys. Soc. Jpn. 72 Suppl. B 26
[2] Ohta H, et al. 2002 J. Phys.: Cond. Matter. 14 10637
[3] Sakurai T, et al. 2003 J. Phys. Soc. Jpn. 72 Suppl. B 156
[4] Matsumoto M, et al., 2004 Phys. Rev. B 69 054423
[5] Ohta H, et al. 2005 Prog. Theor. Phys. 159 Suppl. 184
[6] Sakurai T, et al. to be submitted to Rev. Sci. Instr.
[7] Nikuni T, et al. 2000 Phys. Rev. Lett. 84 5868
[8] Ruegg Ch, et al. 2004 Phys. Rev. Lett. 93 287201
[9] Goto K, et al. 2006 J. Phys. Soc. Jpn. 75 064703