Application of miniature pulsed magnets to synchrotron X-ray spectroscopy and neutron diffraction

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Abstract. Synchrotron X-ray and neutron experiments in high magnetic fields have been performed using miniature pulsed magnets. In EuNi₂(Si₀.₈₂Ge₀.₁₈)₂, the drastic change of the L₃-edge absorption spectrum is found at the valence state transition. While, no changes of the spectra are found at the insulator-metal transitions in Kondo insulators YbB₁₂ and Ce₃Bi₄Pt₃. As a test experiment the high field neutron diffraction experiment of MnF₂ has been carried out at JRR-3M reactor.

1. Introduction

Quantum beams such as synchrotron X-rays and neutrons are useful tools to investigate the structural, magnetic and electronic properties of condensed-matters. Besides the diffraction study, a synchrotron X-ray is known as an element selective probe of magnetic and electronic states for the energy tunability. On the other hand, the neutron is the most useful tool for the study of magnetic structure and magnetic excitation.

A magnetic field is one of the most important environmental parameters of condensed-matters because of the strong coupling with the spins and the orbital motions of electrons. In fact, various interesting phase transitions are induced by the application of high magnetic fields. Hence, the combination of quantum beam and high magnetic field would be one of the most promising means to study condensed-matters.

To open this new frontier, several efforts for realizing combination of a pulsed magnet and the quantum beam have been made [1-4]. Recently, we have developed a miniature pulsed magnet technique and applied the technique to various systems [2-3]. The advantages of this small system are in portability, easy installation and flexible magnet design. In this article, we report the application of the miniature magnets to X-ray absorption spectroscopy of rare-earth intermetallics and the development of the techniques for neutron diffraction.
2. Application to X-ray absorption experiments

A magnetic field as high as 51 T is generated by a solenoid magnet whose dimensions are 3 mm in inner diameter and 15 mm in length for the X-ray experiment. The magnets are wound by a AgCu wire of 0.7 mm in diameter. The typical pulse duration is 1 ms.

The experiments have been made in the beam line BL22XU at SPring-8. The X-ray absorption spectra (XAS) are measured by a transmission method. In a single shot pulsed field, a magnetic field dependence of the transmission at a fixed photon energy is measured as a function of time with the time resolution of 10 $\mu$s. The field dependence of the whole spectrum is obtained by repeating the procedure at 30 $\sim$ 40 different photon energies. The interval time between the procedures is about 15 minutes which is determined by waiting time for cooling the magnet. A helium gas flow cryogenic system is used for cooling and the magnet is set at the bottom of the sample rod.

2.1. XAS of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$

Valence transitions found in some rare-earth intermetallics have attracted much interest because the physical properties such as the magnetic susceptibility and electrical resistivity significantly change at the transition. EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ is a valence fluctuation compound that shows a magnetic field-induced valence transition. The transition temperature at zero-field is about 70 K and the first-order metamagnetic transition due to the valence transition is observed in the field range of 20 to 40 T at low temperatures [5]. Since the direct determination of the Eu valence is important to understand the field-induced transition, we have investigated the valence state by means of the XAS in high magnetic fields.

![Figure 1. (a) The XAS of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ at 5 K. Closed and open circles denote the experimental results at 0 and 40 T, respectively. The spectrum at 197 K and 0 T is also shown by a dashed gray curve for comparison. (b) Magnetic field dependence of the Eu mean valence deduced from the XAS.](image)

The XAS of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ at near the $L_3$ edge of the Eu ions are shown in figure 1(a). The distinct two peaks are observed in the spectrum at 40 T and 5 K as well as in the spectrum at 0 T and 197 K; these two peaks are corresponding to the $L_3$ transitions ($2p_{3/2} \rightarrow 5d$) of the Eu ions with different valence states. It is found that the intensity ratio of the two peaks changes significantly by temperature and magnetic field, showing the mean value of the Eu valence changes. The Eu valence $v$ is deduced by the standard method; the spectrum is analyzed by two sets of $L_3$ edge using analytic functions and the relative intensities of the two
components determined by the curve fit give the mean valence [5]. The results of the curve fit are shown by solid curves. We found that at 5 K the valences at 0 T and 40 T are 2.80 and 2.47, respectively, while the valence at 197 K and 0 T is 2.22.

In figure 1 (b) the Eu mean valence obtained from the XAS is plotted as a function of magnetic field. The valence decreases significantly with increasing magnetic field. Since the Eu\(^{2+}\) (f\(^7\)) has a large total angular momentum (7/2) while that of the Eu\(^{3+}\) (f\(^6\)) is 0, the decrease in the mean valence toward 2 is roughly corresponding to the metamagnetic transition of this material [5]. Further analysis and a theoretical study are required for understanding the interplay between the valence and magnetization, and the mechanism of the field-induced valence transition.

2.2. XAS of Yb\(_{12}\) and Ce\(_3\)Bi\(_4\)Pt\(_3\)

The electronic states of Kondo insulators are intriguing subjects because of the formation of the energy gap due to the strong c-f hybridization. Yb\(_{12}\) and Ce\(_3\)Bi\(_4\)Pt\(_3\) are typical Kondo insulators and the gaps of them are expected to be close at about 50 and 30 T, respectively [6,7]. We have carried out the \(L_3\) XAS experiments in high magnetic fields to investigate the change in the electronic states of these compounds at the insulator-metal transitions.

![Figure 2](image)

**Figure 2.** (a) Magnetic field dependence of the absorption intensity in Yb\(_{12}\). The XAS is shown in the inset. (b) Magnetic field dependence of the absorption intensity in Ce\(_3\)Bi\(_4\)Pt\(_3\). The XAS is shown in the inset.

The absorption spectrum in Yb\(_{12}\) at 5 K is shown in the inset of Figure 2(a). The peak at around 8.950 keV is due to the \(L_3\) transition of Yb\(^{3+}\), while the energy position denoted by the arrow is corresponding to the \(L_3\) transition energy of Yb\(^{2+}\). The total angular momentum of Yb\(^{3+}\) is 7/2 and that of Yb\(^{2+}\) is 0. When the energy gap is closed by the Zeeman effect it is expected that the transfer of a hole from the conduction band into the 4f orbital increases, because Yb\(^{3+}\) (f\(^{13}\)) states become more stabilized in high fields. This may cause a decrease of the absorption intensity at the energy for Yb\(^{2+}\) (f\(^{14}\)) denoted by the arrow. Figure 2 (a) show the magnetic field dependence of the absorption intensity at 8.943 keV for Yb\(^{2+}\). The intensity is found to be almost independent of magnetic field, suggesting that the change in the hole transfer between the conduction band and the 4f orbital is small at the closing of the gap.

In the inset of figure 2 (b) the spectrum in Ce\(_3\)Bi\(_4\)Pt\(_3\) at 3 K is shown. The peak at around 5.725 keV is due to the \(L_3\) transition of Ce\(^{3+}\), while the energy position denoted by the arrow is the \(L_3\) transition energy of Ce\(^{4+}\). The total angular momentum of Ce\(^{3+}\) is 5/2 and that of Ce\(^{4+}\) is 0. In analogy to the discussion for above-mentioned Yb case, we envisage that the absorption intensity of the \(L_3\) transition of Ce\(^{4+}\) decreases at the closing of the gap. However, we found
that the absorption intensity is almost independent of magnetic field as shown in figure 2 (b). It is likely that the change in the electron transfer is not significant at the closing of the gap.

3. Application to neutron diffraction
The neutron diffraction experiment is carried out at the triple axis spectrometer, AKANE of IMR, Tohoku University, which is installed at the JRR-3M reactor in JAEA. Magnetic field is generated by a miniature solenoid magnet (5 mm inner diameter and 10 mm length) [8]. The field dependence of neutron counts is measured by using a conventional time analyzer for TOF system. The measurement is made with the time resolution of 50 µs.

As the neutron source, the monochromatic beam from a reactor is used. To trace the shift of diffraction angle of peaks, a position sensitive detector system is installed. The maximum two theta angle is 25 degree with the miniature magnet. The magnet is attached at the cold plate of the conventional cryo-cooler and the temperature as low as 20 K is obtained.

The test measurement has been made up to 30 T and the field generation has been successfully made and more than 400 shots are generated without trouble. With the test sample of MnF₂, it is found that the accumulation time of a few seconds is necessary to obtain the practical signal level. This time period is corresponding to a few thousands of shots with 1 msec pulse duration. To reduce the number of shots, we have developed the system with additional choke coil. The extension of pulse duration to 20 msec is achieved. This modified miniature pulse magnet system is found to be useful for neutron diffraction experiments.

4. Summary
We have developed high magnetic field experimental techniques for synchrotron X-ray and neutron experiments using miniature pulsed magnets. The change in the Eu mean valence of EuNi₂(Si₀.₁₈Ge₀.₈₂)₂ at the field induced valence transition is directly observed by the high magnetic field X-ray absorption spectra. It is found that in YbB₁₂ and Ce₃Bi₄Pt₃ the valences of Yb and Ce show almost no changes in high magnetic fields at which the energy gaps are expected to be closing. The test experiment of neutron diffraction were carried out up to 30 T. It is found that the modified miniature magnet system with the long pulse duration is necessary.

Acknowledgments
This work is partly supported by Grant-in-Aid for Scientific Research B (17340111) and by Grant-in-Aid for Scientific Research on priority Areas gHigh Field Spin Science in 100Th(No.451) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT)D

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