Abstract. \(L\)-edge X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectra (XAS) in several rare-earth elements have been studied in high magnetic fields up to 40 T using a pulsed magnet. XMCD spectrum of Eu in a typical valence fluctuating compound, EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\), shows a characteristic two peak structure, reflecting the valence fluctuation. However, in another valence fluctuating compound, YbInCu\(_4\), it is found that the XMCD spectrum of Yb shows only a single peak. In contrast to XMCD, two absorption bands in XAS are observed in both EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\) and YbInCu\(_4\). The intensity ratio between the two absorption bands changes significantly with increasing magnetic field in these materials, suggesting the field-induced valence change. The high magnetic field XMCD and XAS measurements have also been conducted in an antiferromagnetic heavy fermion compound CeRh\(_2\)Si\(_2\). The Ce valence is found to be nearly trivalent and insensitive to magnetic field. The XMCD at Ce \(L_2\)-edge increases rapidly around 26 T corresponding to the metamagnetic transition. The XMCD spectra in CeRh\(_2\)Si\(_2\) at high magnetic fields show only a single peak as was reported in a heavy fermion ferromagnetic compound CeRu\(_2\)Ge\(_2\) [1].

1. Introduction
Synchrotron X-ray magneto-spectroscopy is promising means to investigate the electronic states in high magnetic fields and has attracted much interest. However, it is not technically very easy to combine synchrotron X-rays and high magnetic fields. This is mainly because a high-field magnet and its power supply become huge when one needs a steady magnetic field over 20 T.
that is the maximum field of a commercial-type superconducting magnet. Pulsed magnetic field technique is an effective way to obtain high magnetic field. So far, several groups have been developing the techniques for synchrotron X-ray experiments in high magnetic fields using pulsed magnets [2-5]. For a pulsed magnet, energies consumed by the Joule heating is small because of the short duration time of the field. Hence, only a small amount of electric power is required and the damage to the magnet by the heat is considerably reduced. Magnetic fields as high as 50 T is generated rather easily by a pulsed magnet. Although the typical duration time of the magnetic field is only 1 - 100 ms, various kinds of experiments can be performed thanks to the strong intensity of the synchrotron X-rays.

In this work, we use miniature magnets to perform X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) in high magnetic fields up to 40 T [3, 7-11]. We investigate three samples, (1) EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$, (2) YbInCu$_4$ and (3)CeRh$_2$Si$_2$. Former two samples exhibit valence fluctuation of Eu and Yb, respectively. Third one is a heavy fermion compound. Both phenomena, namely, valence fluctuation (VF) and heavy fermion (HF), are intriguing because they induce anomalies in their physical properties such as magnetic, electric and thermodynamic properties. One of the key things to understand these phenomena is the hybridization between the conduction electrons and f-electrons ($c-f$ hybridization). Magnetic field controls the electronic states through the Zeeman effect and can induces a valence transition [12, 13] and collapse of heavy fermion state [14]. It is intriguing to investigate the high-field electronic and magnetic states in VF and HF compounds by microscopic means such as an X-ray spectroscopy. In the present paper, the valence states in high magnetic fields are directly measured by XAS and the magnetic polarization of 5$d$-electrons of the rare-earth elements are detected by the valence-selective XMCD.

2. Experimental details
The high magnetic field XAS and XMCD experiments at L-edge (2p $\rightarrow$ 5d) of Eu, Yb and Ce are carried out at high magnetic fields at BL39XU in SPring-8 [9, 11]. Polycrystals of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ and CeRh$_2$Si$_2$ and a single crystal of YbInCu$_4$ are used. The crystals were powdered and diluted in order to achieve an effective sample thickness of about 10 $\mu$m for the transmission measurement. A Si-PIN photodiode (Hamamatsu S3590-09) is used to detect the field dependence of the transmitted X-ray intensity. The high-frequency cutoff of the diode is about 40 MHz. The output of the diode is amplified by a preamplifier and then recorded by a digital oscilloscope together with the pulsed magnetic field. A diamond X-ray phase plate is introduced to generate circularly polarized X-rays. The XMCD signal ($\Delta\mu t = \mu^+ - \mu^-$) is determined as the difference in the absorption intensities for right- ($\mu^+$) and left- ($\mu^-$) circular polarization. The $\mu^+$ and $\mu^-$ were measured by successive two shots of a pulsed field at a fixed X-ray energy, as the photon helicity was reversed every shot. An experimental setup for the high-field XMCD spectroscopy was similar to that for the high-field XAS described in Ref. [3]

Pulsed magnetic fields as high as 40 T is generated using a portable capacitor bank and a miniature magnet [3, 8]. The magnet is a solenoid magnet with a 3 mm bore, a length of 30 mm, and an outer diameter of 30 mm. The pulse duration is about 2 ms. The magnet with the sample is set inside an ILL (Institut Laue-Langevin)-type Orange Cryostat (AS Scientific Products Ltd.) and is cooled with exchange helium gas.

3. Results and Discussion
3.1. Valence fluctuating compounds: EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ and YbInCu$_4$
We first show the results of XAS in high magnetic fields for EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ and YbInCu$_4$. The absorption spectra are expected to change significantly with magnetic field due to the valence state transitions [12, 13] along with the metamagnetic transitions. The valence
transition fields are 36 and 33 T in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ [13] and YbInCu$_4$ [12, 15], respectively. Since the XMCD is evaluated by $\Delta \mu_t = \mu^+ - \mu^-$, it is very important to check the field dependence of the absorption spectra to investigate XMCD. The X-ray absorption is obtained by $\mu_t = (\mu^+ t + \mu^- t)/2$. $L_3$-edge XAS at different magnetic fields of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ and YbInCu$_4$ are shown in Fig. 1 and 2, respectively.

![Figure 1. X-ray absorption spectra in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ at different magnetic fields. Various symbols denote the experimental data and the solid lines are the results of the curve fitting. Eu valences obtained from the absorption spectra are plotted as a function of magnetic field in the inset.](image1)

![Figure 2. X-ray absorption spectra in YbInCu$_4$ at different magnetic fields. Various symbols denote the experimental data and the solid lines are the results of the curve fitting. Yb valences obtained from the absorption spectra are plotted as a function of magnetic field in the inset.](image2)

In EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$, the spectrum at 0 T is dominated by the absorption peak at around 6.980 keV due to the Eu$^{3+}$ state; the absorption band around 6.972 keV due to the Eu$^{2+}$ state is weak and observed as a shoulder structure. We found that the spectrum shape changes significantly by applying a magnetic field. The relative intensity of the divalent state (Eu$^{2+}$) absorption peak to that of the trivalent state (Eu$^{3+}$) increases, suggesting a change of Eu valence toward 2.0. The Eu valence is deduced by the relative intensity of the absorption peaks by using a standard curve fitting analysis [11]. The magnetic field dependence of Eu valence is in good agreement with the results in our previous high field XAS work in which a diamond phase plate was not used [11]. (see Fig. 1)

The magnetic field variation of XAS in YbInCu$_4$ seems to be qualitatively similar to that of EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$. The two absorption bands attributed to different valence states depend on magnetic field opposite way each other. In this case, however, the divalent state (Yb$^{2+}$) band (around 8.937 keV) diminishes and the trivalent state (Yb$^{3+}$) band (8.945 - 8.950 keV) enlarges. The finite double peak structure around 8.945 - 8.950 keV is likely to be owing to the crystal field effect [16]. Following the previous work [3], we assume that the fine splitting of the peak exists in Yb$^{2+}$ band when we conduct curve fitting, even though it is not observable in the spectrum. Relative absorption intensity deduced from the fitting between the Yb$^{2+}$ and Yb$^{3+}$ bands gives the Yb valence. The inset of Fig. 2 shows the magnetic field dependence of the Yb valence and it agrees with the previous work [3].

Figure 3 (a) and (b) show the XMCD spectra in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ at $L_3$ and $L_2$ edges, respectively. It is found that the two peaks are clearly observed in each spectrum. The main peak at around 6.972 keV in the $L_3$-edge (Fig. 3(a)) is attributed to the XMCD of Eu$^{2+}$ state;
the XMCD peak energy corresponds to the absorption peak energy of the Eu$^{2+}$ state as shown in Fig. 1. In the same sense, the small peak observed at 6.980 keV is XMCD due to the Eu$^{3+}$ state. An interesting point is that Eu$^{2+}$ and Eu$^{3+}$ have different magnetic ground states; Eu$^{2+}$ has $J=7/2$ and Eu$^{3+}$ has $J=0$, where $J$ is the total angular momentum. Since the non-magnetic ground state is expected in Eu$^{3+}$, the mechanism for the finite XMCD from the Eu$^{3+}$ state is a problem to be solved. Two possible mechanisms proposed so far are (1) the effects of the excited magnetic states, i.e., $J=1$ or higher levels of Eu$^{3+}$ state and (2) the spin polarization of conduction electrons by neighboring magnetic moments of Eu$^{2+}$ ($J=7/2$). The strong $c–f$ hybridization can induces these effects [9]. However, detailed theoretical study is required to understand the mechanism of the XMCD since the $L$-edge XMCD of rare-earth elements contains the complicated issues such as the wave function contraction due to the strong $df$-exchange interaction [17,18]. A possible theoretical approach is the one recently developed by Kotani [19-21] based on the extended single impurity Anderson model. By this model, two peak structure in XMCD spectra in a valence fluctuating compound, CeFe$_2$ [1], is well explained.

The $L_2$ -edge XMCD seems to be qualitatively similar to that found in the $L_3$-edge except for its sign. The Eu$^{2+}$ ($f^7$) XMCD is considered to be essentially the same with XMCD of Gd$^{3+}$ ($f^7$). The sign reversal observed for $L_2$ and $L_3$ edges was reported for Gd$^{3+}$ ($f^7$) and can be explained by a standard calculation of the transition probability [22]. The relative XMCD intensity between the $L_2$ and $L_3$ edges (so called the branching ratio) for Eu$^{2+}$ ($f^7$) can also be explained rather easily since the orbital momentum $L$ is zero [17,18]. However, the sign and the branching ratio for Eu$^{3+}$ ($f^6$) may not be trivial problems. From Fig. 3 (a) and (b), it is found that the branching ratio for Eu$^{3+}$ ($f^6$) is very similar to that for Eu$^{2+}$ ($f^7$); it is deduced to be about $-0.9 \pm 1$ from the integrated intensity of the XMCD peaks.

XMCD spectra at $L_2$ and $L_3$-edges in YbInCu$_4$ are shown in Fig. 4 (a) and (b), respectively. In contrast to the XMCD in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ , only a single peak due to the Yb$^{3+}$ ($f^{13}, J = 7/2$) is observed in the XMCD spectrum for each edge. Moreover, there exists another different point compared to the Eu case. The $L_2$-edge XMCD is much weaker than the $L_3$-edge XMCD; the intensity ratio between the $L_3$ and $L_2$-edges (branching ratio $L_3/L_2$) deduced by the integrated intensity is found to be $-3$ to $-4$. When we apply the above-mentioned Kotani’s theoretical model [19-21] to the Yb case, some features of the XMCD spectra can be successfully reproduced [20, 21], namely the single peak structure in XMCD and the weak XMCD in $L_2$ edge compared to $L_3$ -edge. A strong reduction of the strength of the hybridization in high magnetic fields can make the system come into the weak hybridization regime and the XMCD due to Yb$^{2+}$

![Figure 3. XMCD spectra at several magnetic fields in EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ at 5 K. (a) $L_3$ edge, (b) $L_2$ edge.](image)
(f^{14}, J = 0) is not induced through the hybridization. The branching ratio deduced from the theory is, however, much smaller than the experimental value and the sign of \( L_2 \) edge is predicted to be positive [21]. Crystal field effect and the additional spin splitting of the 5d band are found to improve the theoretical results. The details of the theory are shown in Ref. [21]. Note here that, as for the possible Yb\(^{2+}\) XMCD, we may not be able to observe it only by a technical reason: The absorption intensity from Yb\(^{2+}\) state can be too weak in high magnetic fields (see Fig. 2) to measure the Yb\(^{2+}\) XMCD.

3.2. Heavy fermion compound: CeRh\(_2\)Si\(_2\)

CeRh\(_2\)Si\(_2\) is a typical heavy fermion antiferromagnetic compound and show a metamagnetic transition at around 26 T [23]. Figure 5 (a) shows the XAS and XMCD spectra at \( L_2 \) edge in CeRh\(_2\)Si\(_2\). In heavy fermion compounds the valence state possibly shows a slight fluctuation owing to the finite \( c - f \) hybridization. However, only the Ce\(^{3+}\) absorption peak is observed at around 6.166 keV in XAS. (No clear absorption is observed for Ce\(^{4+}\) that is expected around 6.172 keV [1].) Although valence state transition induces a metamagnetic transition like EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\) and YbInCu\(_4\), it is found that XAS is insensitive to magnetic field, and the Ce valence in CeRh\(_2\)Si\(_2\) is stable even at the metamagnetic transition. This suggests that the metamagnetic transition is due to the change in the structure of the magnetic moments. In Fig. 5 (a), it is found that the shape of the XMCD is similar to that reported for CeRu\(_2\)Ge\(_2\) that is a typical heavy fermion ferromagnetic material [1]. The XMCD increases rapidly at high fields over around 24 T. The magnetic field variation of the XMCD peak intensity (6.165 keV) in Fig. 5 (b) shows the rapid increase corresponding to the metamagnetic transition.

4. Summary

We have investigated the X-ray absorption spectra (XAS) and X-ray magnetic circular dichroism (XMCD) spectra in three rare-earth intermetallic compounds, EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\), YbInCu\(_4\) and CeRh\(_2\)Si\(_2\), at high a magnetic fields up to 40 T. In the former two valence fluctuating compounds, we observed significant magnetic field dependence of the valence state of the rare-earth elements. The XMCD spectra in EuNi\(_2\)(Si\(_{0.18}\)Ge\(_{0.82}\))\(_2\) show distinct two peak structure corresponding to the Eu\(^{2+}\) and Eu\(^{3+}\) states. Since the ground state of the Eu\(^{3+}\) state is non-magnetic (\( J=0 \)), a mechanism that possibly contains the \( c - f \) hybridization effects is required to understand this peculiar XMCD spectra. On the other hand, only a single peak due to Yb\(^{3+}\) state is observed in XMCD of YbInCu\(_4\). The branching ratio \( L_3/L_2 \) of XMCD in YbInCu\(_4\) is
found to be $-3$ to $-4$. The crystal field effect and an additional spin splitting of the Yb 5d band are possibly important to explain the branching ratio theoretically. The high field XAS and XMCD experiments in a heavy fermion compound CeRh$_2$Si$_2$ were also conducted. The Ce valence is close to 3+ and stable even in higher fields than the metamagnetic transitions field (26 T). The XMCD found at high fields over 26 T has a similar shape with that of XMCD in CeRu$_2$Ge$_2$, a typical heavy ferromagnetic compound.

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6. References

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Figure 5. (a) XAS and XMCD spectra in CeRh$_2$Si$_2$ in magnetic fields at $L_2$ edge. (b) Magnetic field dependence of XMCD intensity at 6.165 keV.