Synchrotron X-ray spectroscopy study on the valence state and magnetization in \(\alpha\)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\) (\(x = 0.115\)) at low temperatures and high magnetic fields

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Abstract. Valence fluctuation phenomena in rare-earth intermetallic compounds have attracted attention because the quantum criticality of the valence transition has been proposed theoretically. Recently, it was found that \(\beta\)-YbAlB\(_4\) shows quantum criticality without tuning and has a strong mixed-valence state. In this study, we measured the magnetization curve and X-ray magnetoabsorption in \(\alpha\)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\) (\(x = 0.115\)), which is a locally isostructural polymorph of \(\beta\)-YbAlB\(_4\). The magnetization and X-ray experiments were performed in fields up to 55 and 40 T, respectively. A small increase in the Yb valence was observed at fields where the magnetization curve exhibited a change in slope.

1. Introduction
The quantum critical point (QCP) in heavy fermion systems arises from competition between the Kondo effect and RKKY interaction [1]. Around QCP, exotic phenomena, such as unconventional superconductivity, are observed and most can be explained by spin fluctuation theory [2]. However, in the last decade, phenomena that cannot be explained by the spin fluctuation theory, such as non-Fermi liquid behavior, have been discovered [3]. Although several theoretical mechanisms, including the Kondo breakdown [4] and valence transition QCP [5], have been proposed, the origin of quantum criticality is still under debate.

\(\beta\)-YbAlB\(_4\) (\(T_c = 80\) mK) is the first Yb-based heavy fermion system superconductor [6]. At a low temperature, it shows non-Fermi liquid behavior, indicating quantum criticality without tuning of any control parameters [7]. Theoretical work suggests that \(\beta\)-YbAlB\(_4\) is located very close to QCP of the valence transition [8]. However, \(\alpha\)-YbAlB\(_4\) has a similar structure to \(\beta\)-YbAlB\(_4\) and shows Fermi liquid behavior [9]. Photoemission spectroscopy measurements show that both \(\beta\)-YbAlB\(_4\) and \(\alpha\)-YbAlB\(_4\) are strong valence fluctuation compounds. Valence states in \(\beta\)-YbAlB\(_4\) and \(\alpha\)-YbAlB\(_4\) are Yb\(^{2.73+}\) and Yb\(^{2.75+}\), respectively, at 20 K [10]. The strong valence fluctuation is closely related to quantum criticality of the valence transition [5, 8]. Valence state of Yb can be changed by changing temperature, pressure, chemical composition, and magnetic field. Moreover, Fe substitution of the Al site of YbAlB\(_4\) can change the ground state [11]. The ground state of \(\alpha\)-YbAl\(_{1-x}\)Fe\(_x\)B\(_4\) (\(x = 0.115\)) is antiferromagnetic and it shows valence fluctuation [12].
In this paper, we report the field dependence of the Yb valence and that of magnetization in α-YbAl$_{1-x}$Fe$_x$B$_4$ (x = 0.115) at low temperatures and high magnetic fields.

2. Experiment
A single crystal of α-YbAl$_{1-x}$Fe$_x$B$_4$(x = 0.115) was grown by the Al flux growth technique [11]. The magnetization is measured with a pulse magnet. The sample is ground into powder to suppress heating by eddy current induced by applied pulsed high magnetic field. The sample temperature is lowered to 1.4 K using a liquid He cryostat.

The magnetic field dependence of the valence state of Yb is measured by X-ray absorption spectroscopy in pulsed magnetic fields. There are several techniques other than X-ray absorption spectroscopy for investigating valence states, such as photoemission spectroscopy, X-ray emission spectroscopy, and Mössbauer spectroscopy. X-ray absorption spectroscopy has an advantage that it can be performed in magnetic fields as high as 40 T by using a pulse magnet [13]. Experiments have been done at the BL39XU beamline at SPring-8 [14], Japan. Pulsed fields are generated by a miniature magnet up to 40 T. The sample is ground into powder and mixed with epoxy resin so that it is diluted; the effective thickness, $\mu t$, is chosen to be close to 1, where $\mu$ and $t$ are the absorption coefficient and thickness of the sample, respectively. The crystal axes of the powder grains were oriented by a steady magnetic field of 14 T while the epoxy resin set. The grains are aligned with the c-axes parallel to the applied field. The degree of orientation is estimated to be 80 ± 10% from the magnetization measurements. The larger error bar is a consequence of the very low density of the sample because it is diluted with epoxy resin so that the effective thickness was around 10 $\mu$m. Further experimental details are described elsewhere [13].

3. Results and discussion
3-1 Magnetization in high magnetic fields

Figure 1 shows the magnetization ($M$) and field derivative of magnetization (d$M$/d$H$) up to 55 T at 4.2 K. The value of magnetization of this sample at 55 T is 1.07 $\mu_B$/Yb. For a free Yb$^{3+}$ ion ($J = 7/2$), the saturation value of the magnetization is 4 $\mu_B$/Yb. A typical valence fluctuation compound such as YbXCu$_4$ (X = In, Ag) has a saturation moment of around 4 $\mu_B$/Yb [15]. In contrast, α-YbAlB$_4$ should theoretically have $J_z = 5/2$ and a saturation moment of 2.85 $\mu_B$/Yb [16]. However, for $J_z = 7/2$ or 5/2, measured magnetization is far below the saturation value, even at a high field of 55 T. The small magnetization may be caused by strong valence fluctuation because localized magnetic moments of Yb ions are screened and non-magnetic behavior should appear when valence fluctuation is strong. The strong valence fluctuation is consistent with the fact that α-YbAlB$_4$ has a high Kondo temperature around 200–300 K [9]. A sharp change in the slope of the magnetization is observed around 28 T, which corresponds to a significant decrease in d$M$/d$H$. 
3-2 X-ray absorption in high magnetic fields

To investigate the field-induced valence change in magnetic fields where the magnetization anomaly is observed, we have performed X-ray absorption spectroscopy experiments in pulsed magnetic fields. Figure 2 shows the X-ray absorption spectrum (XAS) at the $L_3$ edge (2$p$ to 5$d$ transition) of Yb at 4.2 K.

![Graph](image)

**Figure 1.** Field dependence of the magnetization (upper) and its field derivative (lower) up to 55 T. Results are shown for only the up sweep of field.

**Figure 2.** (a) X-ray absorption spectra at 0 and 40 T of $\alpha$-YbAl$_{1-x}$Fe$_x$B$_4$ ($x = 0.115$). Red curve is the the result of the fitting for the zero-field spectrum that consists of a blue dashed curve ($\text{Yb}^{3+}$) and a green dashed curve ($\text{Yb}^{2+}$). Peaks of the $\text{Yb}^{3+}$ and $\text{Yb}^{2+}$ components appear at 8950 and 8944 eV, respectively. (b) Absorption difference spectra for $\alpha$-YbAl$_{1-x}$Fe$_x$B$_4$ ($x = 0.115$) at 0 and 40 T. Unfilled circles denote the experimental results. The solid curve is the result of the fitting analysis.
Figure 2 (a) shows spectra at 0 and 40 T. The red line is the result of the curve fitting for the spectrum at 0 T. The blue and green dashed lines show the Yb$^{3+}$ and Yb$^{2+}$ components, respectively, with peaks at 8950 and 8944 eV. These energies are in good agreement with results of a previous study [17]. The details of the fitting analysis are reported elsewhere [13]. When intensities of absorption peaks at 8944 and 8950 eV are defined by $I(2^+)$ and $I(3^+)$, respectively, the valence, $v^*$, is determined as $v^* = 2 + I(3^+)/(I(2^+) + I(3^+))$, and is found to be around 2.845. Because the observed absorption peak at 8944 eV is broad, the error bar for the fitting analysis to determine the absolute value of the valence is as large as 0.050 [17]. At first glance, the spectra at 40 and 0 T are almost overlapped. However, there is a small but definite difference that is clear when the spectrum at 0 T is subtracted from that at 40 T; the difference spectrum (dXAS) is shown in Fig. 2(b). The positive peak around 8950 eV and the negative peak around 8943 eV in dXAS spectrum show an increase of Yb$^{3+}$ component and decrease of Yb$^{2+}$ component, respectively, caused by applying a magnetic field. The continuous field variation of the valence is obtained from the magnetic field dependence of the X-ray absorption intensity at 8944 eV, where the Yb$^{2+}$ component is dominant. By assuming that the total absorption intensity remained constant under the applied magnetic field, the absorption intensity at 8944 eV and the simulation of the dependence of the spectrum shape on the valence state allows us to obtain the magnetic field dependence of the Yb valence state.

Figure 3 shows the field dependence of the absorption intensity at 8944 eV. Measurements were repeated six times and averaged values are plotted. The error bar for the relative change in the valence is as small as 0.003 because of the better statistics. The absorption error bar is determined by the standard deviation of the time-dependent data in zero magnetic fields.

Figure 3. Field dependence of the intensity of the XAS spectra at $E = 8944$ eV. The arrow indicates the field above which the intensity starts to decrease.

The field variation of the valence determined by the field variation of absorption at 8944 eV and that deduced from the spectra fitting at different magnetic fields are shown in Fig. 4. The field dependence of the valence determined by the absorption at 8944 eV was deduced by using the simulated field variation of the absorption at 8944 eV when the valence varies. The results obtained from two different experiments showed good agreement within the experimental error. Hence, the field variation of the valence was reliable. In Fig. 4, the valence starts to increase at about 28 T and this field corresponds to the field in which the magnetization anomaly was observed.

Interestingly, the field-induced valence increase was less than half that of typical valence fluctuation compounds, YbAgCu$_4$ [19] and YbInCu$_4$ [13]. A further difference was that $\alpha$-YbAl$_{1-x}$Fe$_x$Al$_4$ ($x = 0.115$) did not show any metamagnetism. Clear metamagnetism is observed in both YbAgCu$_4$ [19] and YbInCu$_4$ [13] because of their distinct field-induced valence transitions. In contrast, only a small field-induced valence change is observed in CeRu$_2$Si$_2$ [20], CeRh$_2$Si$_2$ [20], and YbRh$_2$Si$_2$ [21]. These two Ce-based compounds show metamagnetism, whereas YbRh$_2$Si$_2$ shows a slope change during the magnetization process. Because the change in the shape of the Fermi surface induced by a magnetic
field is thought to be important in CeRu$_2$Si$_2$ [20], CeRh$_2$Si$_2$ [20], and YbRh$_2$Si$_2$ [21], a small valence change can be induced by modifying the electronic state near the Fermi energy. The similarity between our results and the phenomena in YbRh$_2$Si$_2$ [20], suggests that the field-induced change in the magnetization and valence state in $\alpha$-YbAl$_{1-x}$Fe$_x$B$_4$ ($x = 0.115$) may be understood in terms of the magnetic field effect on the Fermi surface.

4. Summary
We have investigated the magnetic field dependence of the magnetization and that of X-ray absorption spectra in $\alpha$-YbAl$_{1-x}$Fe$_x$B$_4$ ($x = 0.115$). The field dependence of the Yb valence state was determined. The valence at 0 T is $2.845 \pm 0.050$ and it increases with magnetic fields above 28 T. The valence increase at 40 T is $0.007 \pm 0.003$. At around 28 T, a slope change during the magnetization was also observed, suggesting interplay between the valence and magnetization. We speculate that a change in the Fermi surface causes the slight change in the magnetization and simultaneously the change in the electronic state effectively modifies the occupancy of electrons in the 4f orbital.

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