I. INTRODUCTION

In $4f$-electron systems Eu, Sm, Tm, and Yb compounds often show the valence fluctuation phenomena because of the small energy difference between the two charge states [1]. Physical properties of the valence fluctuation systems are well described by the competition between magnetic order caused by the Rudermann-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect with the Doniach phase diagram [2,3]. The magnetic order is caused by localized nature, while the Kondo effect is the screening of the local moment through the Kondo singlet formation. The Kondo interaction has been described theoretically by the simple impurity Anderson or periodic Anderson models, where thermodynamic properties can be characterized by the Kondo temperature ($T_K$) and the $c$-$f$ hybridization strength. It is noted that hydrostatic pressure can control the Kondo temperature of the system ideally without local distortion, which is possibly caused by chemical substitution. In the Yb compound, the Yb valence often fluctuates between magnetic $4f^{13}$ (Yb$^{3+}$) and nonmagnetic $4f^{14}$ (Yb$^{2+}$) states. In the Yb system, $T_K$ decreases with pressure and the Yb$^{3+}$ state is favored at higher pressures because of the smaller ionic radius of Yb$^{3+}$ ions compared to the ionic radius of Yb$^{2+}$ ions.

In the phase diagram of the Yb-Cu binary alloy system, the compositions of YbCu, YbCu$_2$, YbCu$_{1.5}$, YbCu$_{2.5}$, YbCu$_{4.4}$, YbCu$_{4.5}$, and YbCu$_{6.5}$ appear [4–7]. X-ray absorption spectroscopy at the Yb $L_3$ edge showed the valence fluctuating Yb valence state; the Yb valence of YbCu, YbCu$_2$, YbCu$_{3.5}$, YbCu$_{4.5}$, and YbCu$_{6.5}$ were 2.37, 2.39, 2.89, 2.96, and 2.40, respectively [8]. A compound with YbCu$_5$ stoichiometry had been thought not to exist [5]. However, it was synthesized with a high-pressure technique later [9]. YbCu and YbCu$_2$ have orthorhombic crystal structures of FeB-type and CeCu-type, respectively [4]. The crystal structures of the Cu-rich phases were very complicated. The crystal structure of YbCu$_{3.5}$ has not been clarified yet [4]. YbCu$_{4.4}$ and YbCu$_{4.25}$ were based on AuBe$_5$/MgCu$_2$-type substructures with approximately 4570 and 2780 atoms per unit cell, respectively [7]. YbCu$_{4.5}$ is related to the CaCu$_3$ structure including the 18% Ca site occupied by pairs of Cu atoms [5]. Among them, YbCu$_{4.5}$ may be the most interesting compound because of the specific heat coefficient of $\gamma \sim 635$ mJ/mol K$^2$, which is so far the heaviest fermion state among the Yb-based systems with a nonmagnetic ground state [5,10,11]. The heavy-fermion state was enhanced under pressure to 740 mJ/mol K$^2$ at 0.82 GPa [8,12]. In YbCu$_{4.5}$, no magnetic order was observed up to 23.5 GPa and down to 50 mK [13].

In this paper we report the pressure-induced change in the electronic state and crystal structure of YbCu$_{4.5}$. We employ partial fluorescence yield x-ray absorption spectroscopy (PFY-XAS) to study the valence of the Yb ions [14,15]. In YbCu$_{4.5}$, the electronic structure under pressure has not been explored so far. We find a first-order reentrant valence transition to the lower valence state induced by pressure, where the structural transition also occurs. Magnetic susceptibility measurements and x-ray diffraction (XRD) are performed. We also measure the temperature dependence of the Yb valence. The results of the magnetic susceptibility and the temperature-induced change in the Yb valence are compared to the single Anderson impurity model. The theoretical fits are not satisfactory. This suggests that the Yb valences are site dependent due to the complex crystal structure.
the effective magnetic moment from the slope of the linear part of $1/\chi$ ($100 < T < 300$ K) to be 2.51 emu/mol K, $-22.3 \text{ K}$, and 4.48 $\mu_B$, respectively. The effective magnetic moment is consistent with the values of 4.36 $\pm$ 0.04 $\mu_B$ measured by Sperdeler et al. [8]. The effective magnetic moment of Yb$^{3+}$ is 4.53 $\mu_B$ and the Yb valence of YbCu$_4$I$_5$ is nearly Yb$^{3+}$. However, negative Weiss temperatures suggest that Yb of YbCu$_4$I$_5$ is slightly valence fluctuating.

According to the Bethe-Ansatz solution of the Coqblin-Schrieffer model, the physical properties of a Kondo system are well scaled by a single energy parameter ($T_0$). The characteristic temperature is related to the magnetic susceptibility $\chi(0)$ at 0 K by $\chi(0)/T_0 = [N_A (v - 1) g_L \mu_B^2]/(24 \pi k_B)$, where $v$ is the ground state degeneracy, $g_L$ is the Landé factor, and $\mu_B$ is the Bohr magnetron [20,21]. We derived the characteristic temperature ($T_0$) from $\chi(0)$ to be $T_0 = 47$ K and $T_K = 25$ K assuming the relation $T_0 = (2J + 1)/2\pi$ and $T_K = 0.6475T_L$ for $J = 7/2$ [22]. This value is comparable to $T_K = 15$ K, which was derived from the maximum of the resistivity data and the minimum of the thermoelectric power of the temperature dependence [8,12].

The characteristic temperatures could be estimated by using the Rajan’s numerical result based on the Coqblin-Schrieffer model [21]. We fit the Rajan’s curve to the experimental result of the magnetic susceptibility, making $T_0$, $A_1$ a fit parameter as shown in Fig. 1(b). $T_0$ is estimated to be 28 K for $v = 6$ and 24 K for $v = 4$. The theory, however, does not reproduce the temperature dependence of the magnetic susceptibility well. Rajan also showed a relation of $T_0$ with $\gamma = \chi(0)/T_0$ from $\gamma = (N_A (v - 1) \pi k_B/(6J_L))[21]$. $T_0$ is estimated to be 48 K with this formula assuming $\gamma = 635 \text{ mK}^2/\text{mol}$.

We also apply a theoretical universal curve based on the single impurity Anderson model (SIAM) by Bickers et al. [23]. $T_0$ is estimated to be 42 K, which is in the same order as the values derived above. The theoretical fits to the experimental data are not fully satisfactory, indicating that the temperature independence of the magnetic susceptibility cannot be fully understood within the SIAM.

$T^2$ dependence of the resistivity was observed only at temperatures below 400 mK at 23.5 GPa [24]. The Kondo temperature decreases with pressure in Yb compounds and thus the coherent temperature may be much higher than 400 mK at ambient pressure. Normally the coherent temperature to form the Kondo lattice, where the $T^2$ dependence of the resistivity is observed, is one order less than the Kondo temperature [9,25]. The characteristic temperature $T_0$ is proportional to the Kondo temperature $T_K$ as described above. Therefore, the above estimated values of $T_0$ seems to be reasonable when we consider the coherent temperature.

**B. X-ray diffraction**

Physical properties of YbCu$_4$I$_5$ are similar to the physical properties of cubic YbCu$_5$, but the crystal structure is very complicated. The crystal structure of YbCu$_4$I$_5$ was solved using x-ray diffraction and high-resolution transmission electron microscopy by Černý et al. [26]: a monoclinically distorted $7 \times 7 \times 6.5$ superstructure of the cubic AuBe$_5$ structure type with 7448 atoms per unit cell. This is one of the most complex systems found among intermetallic compounds. Such a
FIG. 2. Comparison of the XRD patterns of (a) YbCu$_{4.5}$ (present results as a function of pressure) and (b) YbCu$_{4.5}$ measured by Černý et al., cubic YbCu$_5$, and hexagonal YbCu$_6$ at room temperature [9,26,27]. The data in (a) and (b) were measured at 18 keV ($\lambda = 0.68467$ Å) and by the Cu $K\alpha$ line ($\lambda = 1.5406$ Å), respectively. Arrow in (a) is marked on a peak which disappears above 1.0 GPa. The horizontal axis is converted to the lattice distance ($d$) from the diffraction angle using the Bragg relation for comparison. The hexagonal phase of YbCu$_6$ is nominal composition. The intensity in (a) is normalized by the peak intensity. In (b) the calculated peaks for an AuBe$_5$-type crystal structure and Cu metal are also shown.

This suggests a structural transition at the pressure between 0 and 1.0 GPa, which corresponds to the pressure where the valance transition occurred as described below. In YbCu$_{4.5}$ in Fig. 2(a) the peaks around $d = 3.5$ Å ($2\theta = 10.1^\circ$), 2.49 Å ($2\theta = 14.4^\circ$), and 2.11 Å ($2\theta = 16.9^\circ$) correspond to (200), (220), and (311) reflections of the original AuBe-type subcell, respectively. This indicates that YbCu$_{4.5}$ is derived from the cubic AuBe$_5$-type crystal domains [26]. Figure 2(b) includes the XRD pattern of the present YbCu$_{4.5}$ sample measured using a laboratory source, which matched well with the reproduced XRD pattern measured by Černý et al. [26], indicating a reliability of the sample quality. In the high-pressure experiments we used the same samples. It is difficult to make Rietveld refinements only with the XRD data. Instead, the XRD patterns at $P = 0$ and 1 GPa were analyzed by the Le Bail method using the JANA2006 software [28]. The analysis was performed with the four-dimensional superspace based on the structure model suggested by Černý, where the AuBe$_5$-type monoclinic subcell is modulated along the $c$ direction to form a $7 \times 7 \times 13$ supercell [26]. Figures 3 and 4 show the XRD patterns measured at the pressure of 0 and 1 GPa with the peak indices obtained by the Le Bail analysis. The lattice constants of the monoclinic subcell at $P = 0$ GPa were given to be $a = 7.0042(11)$ Å, $b = 7.0198(12)$ Å, $c = 7.0640(11)$ Å, $\beta = 91.381(6)^\circ$, while those for $P = 1$ GPa were obtained to be $a = 6.9867(13)$ Å, $b = 7.0041(18)$ Å, $c = 7.0509(15)$ Å, $\beta = 91.363(6)^\circ$. It is found that the peak indexed by (113-1) shows a sudden drop in
its intensity between 0 and 1 GPa. This change occurs suddenly at this pressure range, pointing to the existence of a structural phase transition.

The change in the d spacings for the peaks corresponding to the (200), (220), and (311) reflections of the original AuBe$_5$-type subcell are shown in Fig. 5. The lattice shrinks smoothly up to 8.9 GPa, while the trend changes above 10.6 GPa. The disappearance of the (113-1) peak for the supercell above 1.0 GPa seems not to change the lattice parameters significantly. At present, the details of this structure change is unclear. Since there is no clear anomaly in the pressure dependence of the d spacings for the peaks corresponding to the (200), (220), and (311) reflections of the original AuBe$_5$-type subcell. Hence, the lattice volume is not likely to change drastically at the phase transition pressure $P_c$. Instead, it is more likely that the local coordination environment of Cu atoms around Yb may change at $P_c$, which should be addressed in the future. Note that comparison with the XRD patterns of cubic YbCu$_5$ and hexagonal YbCu$_3$ indicates no structural transition to the hexagonal crystal structure above 1.0 GPa.

C. X-ray absorption spectroscopy

Pressure dependence of the PFY-XAS spectra is shown in Fig. 6(a). In Fig. 6(b) we show an example of the fit at 21.2 GPa assuming a quadrupole component at 8934 eV, one component for Yb$^{2+}$, and two components for Yb$^{3+}$. The Yb valence of YbCu$_{4.5}$ is approximately 2.96 at ambient pressure, which is nearly the same as that of cubic YbCu$_5$ [29]. A striking pressure-induced change in the Yb valence is observed at the low pressure range less than 2.7 GPa as shown in Fig. 6(c), indicating a first-order valence transition. Recently we found a pressure-induced reentrance to the Yb$^{2+}$ state in cubic YbAg$_x$Cu$_{5-x}$ without any structural transition [30]. On the other hand, in YbCu$_{4.5}$, this pressure range of the first-order valence transition corresponds to the occurrence of the structural phase transition pressure mentioned above. The Yb valence seems to continue decreasing slightly up to 6.3 GPa after the first-order valence transition and starts to increase gradually above 9.2 GPa, suggesting that two phases may coexist in the pressure range between 2.67 and 6.3 GPa. Such a pressure-induced reentrant valence transition with the structural transition has been observed in EuO [31,32].

In YbCu$_{4.5}$, anomalous behavior has been observed in the temperature dependence of the resistivity under pressure [8,13,24]. The resistivity took a maximum ($\rho_{\text{max}}$) with decreasing temperature, which has been considered to correlate to the Kondo temperature ($T_K$). Pressure dependence of $\rho_{\text{max}}$ showed a minimum at $\sim$10 GPa [8,13,24]. The increase of $T_{\text{max}}$ above 10 GPa does not connect to $T_K$ at high pressures because the Yb valence increases above 10 GPa as shown in Fig. 6(c), indicating the decrease of $T_K$ with pressure. This behavior can be attributed to the CEF effect, where $T_K$ is smaller than $T_{\text{CEF}}$ and a Kondo scattering with the state populated thermally to the higher CEF level occurred [24]. It is interesting that the resistivity data normalized to the maximum of the resistivity separated to be two groups: one below 3.1 GPa and one above 10 GPa [24]. This could be explained from the pressure-induced change in the Yb valence and the characteristic behavior of the resistivity at $<3.1$ GPa, which may originate from the valence transition.

Figure 7(a) shows the temperature dependence of the PFY-XAS spectra. A slight increase of the Yb$^{2+}$ intensity and decrease of the Yb$^{3+}$ intensity is observed. The mean Yb valence estimated is shown in Fig. 7(b) as a function of temperature. In Fig. 7(b) a $\chi T$ curve is also plotted. The $\chi T$ curve shows a similar trend as the change in the Yb valence. Such correlation between temperature dependence of the $\chi T$ and the Yb valence has also been observed in the YblnCu$_4$-based compounds [33].
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In the single impurity Anderson model, the temperature dependence of the valence $v(T)$ follows the equation $v(T) = 2 + n_f(\infty) - [\Delta n_f(T)/\Delta n_f(0)]\Delta n_f(0)$, where $n_f(\infty)$ and $\Delta n_f(T)$ are intermediate temperature limit of the valence and the total decrease in valence, respectively [14,23]. $\Delta n_f(T)/\Delta n_f(0)$ was calculated as a function of $T/T_0$. We use $T_0 = 42$ K, which was obtained from the fit to the susceptibility. $n_f(\infty)$ is estimated using the following
relations. Calculations using the large degeneracy expansion method suggested that the characteristic temperature related to the Kondo effect $T_0$ can be expressed as $T_0 = D \gamma_0 e^{-1/\gamma_0} / (\Delta \gamma)^{1/2}$, where $D$, $\Delta$, and $\gamma$ are the width of the conduction band, the energy of the spin-orbit coupling, and $g = 1 - n_f(\infty)$, respectively. We can deduce the $D$ according to the relations: $D = n_f(\infty W = 2.190n_f/\gamma(0)$, where $N(e_f)$, $n_f$, $W$, and $\gamma(0)$ are DOS at Fermi level, number of valence electrons, Gaussian DOS width, and electronic specific coefficient in units of $\text{mJ/mol K}^2$ for the case without hybridization, respectively. [29] We estimate $D$ value for the experimental value of $\gamma(0)$ and then obtain $n_f(\infty)$. However, here $\gamma(0)$ is not available in YbCu$_{4.5}$ and we assume $D = 0.5$ eV [$n_f(\infty) = 0.947$ and $\gamma(0) = 66 \text{ mJ/mol K}^2$] as a reasonable value [34]. In Fig. 4(b) a theoretical fit based on the single impurity Anderson model is also plotted assuming the characteristic temperature of 42 K derived in the fit to the magnetic susceptibility in Fig. 1(b). The fit curve describes temperature-induced overall behavior of the Yb valence roughly, but it does not reproduce the experimental result well.

In Fig. 7(c) we also show the temperature dependence of the peak energy positions of Yb$^{3+}$ (major peak) and Yb$^{2+}$ components. It is well known that the change in the charge state induces the shift of the absorption edge. The peak energy positions of the quadrupole Yb$^{2+}$ and major Yb$^{3+}$ components in Fig. 4(c) follow the temperature-induced change in the mean Yb valence well and show the change in the trend below 70 K, although the minor Yb$^{3+}$ component is relatively insensitive to the temperature.

It is noted that YbCu$_{4.5}$ has three types of Yb sites crystallographically: in the AuBe$_5$-type regions, near the antiphase boundaries, and near shear planes with the relative abundances of 2 : 1 : 1 [26]. The three Yb sites possibly show a different temperature-induced behavior for the Yb valence state and thus, it may be difficult to describe the result with a single characteristic temperature. It is also noted that the CEF effect was not taken into account in the present analyses [23]. The Yb valence will be changed if CEF is comparable or higher than $T_K$. Actually, if CEF is strong, it reduces the eightfold degeneracy of $J = 7/2$ in Yb$^{3+}$ at low temperature [9].

**D. Conclusion**

The XES and XRD studies have been performed under pressure for YbCu$_{4.5}$. The XRD spectra showed a structural phase transition at 0–1.0 GPa. The XES data showed a first-order valence transition at 0.6–2.7 GPa. This is an unusual valence transition since the Yb valence abruptly decreases from Yb$^{2.95+}$ to Yb$^{2.76+}$, which is contrasting to the normal behavior where the valence increases toward Yb$^{3+}$ state with pressure [30]. Both XRD and XES results indicate the first-order valence and structural transitions occur at 0.6–1.0 GPa in YbCu$_{4.5}$. Pressure-induced change in the Yb valence correlates to the resistivity data well. Temperature dependence of the Yb valence was also studied, showing the decrease of the Yb valence at low temperatures. Overall behavior in the temperature dependencies of the magnetic susceptibility and Yb valence could be described with the conventional single impurity Anderson model, but is not satisfactory, and the Kondo temperature seems to be overestimated. This may be partly attributed to the complex crystal structure including the three crystallographic Yb sites.

**ACKNOWLEDGMENTS**

The experiments were performed at Taiwan beam lines BL12XU and BL12B2 at SPring-8 under Proposals Nos. 2012A4265, 2012B4256, 2015A4129, 2015A4258, 2015B4258, and 2015B4133 (corresponding proposals Nos. 2011-2-021, 2012-3-012, and 2015-2-033 of NSRRC). This work is partly supported by a Grant in Aid for Scientific research from the Japan Society for the Promotion of Science (Kiban C 22540343 and Kiban C 15K05194). We deeply thank Jin-Min Chen, Jenn-Min Lee, and Takuma Kawai for their kind help in the XRD study. J.F.L. acknowledges support from HPSTAR. We also thank Radovan Černý for the use of their XRD pattern of YbCu$_{4.5}$ and useful discussion.

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