

# The valence state of Yb ion in YbInAu<sub>2</sub> compound at high pressure determined by x-ray diffraction and x-ray absorption near edge structure measurements

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X-ray diffraction patterns and  $L_{III}$ -edge x-ray absorption near edge structure (XANES) spectra of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> compounds have been measured at high pressure and room temperature using a diamond anvil cell and a synchrotron radiation at SPring-8. YbInAu<sub>2</sub> is more compressible at pressures lower than 4 GPa than above it; the evaluated bulk modulus by Birch-type equation of state is 54.7 GPa which is one-half of that of the LuInAu<sub>2</sub> (112.5 GPa). The mean valence  $\bar{v}$  of Yb ion in YbInAu<sub>2</sub> determined by the XANES measurement is an increasing function of pressure: 2.71(2) at normal pressure and 2.94(2) at 10 GPa. The rate of increase in  $\bar{v}$  with pressure is two times larger at pressures below 4 GPa than that above 4 GPa. However, the  $\bar{v}$  is described by a linear increasing function of the lattice compression:  $\bar{v} = \bar{v}_0 + 2.9|\Delta V/V_0|$  where  $\bar{v}_0$  is 2.71. The extrapolation to the trivalent state gives the critical pressure of 13 GPa. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335388]

## I. INTRODUCTION

The magnetic properties of most rare earth compounds are described by the well-localized  $4f$  electronic state of rare earth ion. However, the compounds containing Ce, Sm, Eu, and Yb are known to have the intermediate valency (IV) due to their unstable  $4f$  electronic states. They show the peculiar physical properties originating from the strong correlation between conduction and  $4f$  electrons. The electronic states of IV compounds are sensitive to external stimuli such as temperature, pressure, magnetic field, chemical doping, and so on. In particular, the application of pressure is an effective means for searching the mechanism of valence instability in such strongly correlated electron systems since it is able to tune the electronic states effectively without introducing any disorder in the lattice. In fact, Yb compounds are expected to have pressure-induced transition from IV to trivalent magnetic states when we notice the difference in the ionic radius of divalent and trivalent Yb ions:  $r(\text{Yb}^{2+}) > r(\text{Yb}^{3+})$ . Therefore, it is most desired to examine the close relation between the lattice volume and the valence state at high pressure to resolve the issues in the IV Yb compounds. It should also be noted that there have not been so many Yb compounds prepared as other rare earth compounds. Furthermore, the preparation of single phase Yb compounds is very difficult due to

the rather low melting and boiling points of Yb metal ( $T_m = 819$  °C,  $T_b = 1194$  °C). It is, therefore, indispensable to investigate the mechanism of valence fluctuation, Kondo effect, and heavy fermion phenomena in more Yb compounds.

Marazza *et al.* prepared  $R\text{InAu}_2$  ( $R$ : rare earth) compounds in 1975.<sup>1</sup> Except for the compound with La, the crystal structure of  $R\text{InAu}_2$  series was found to be the cubic Heusler type at room temperature from the x-ray diffraction study. The  $R\text{InAu}_2$  compounds show the following characteristic structural and magnetic properties depending on the size of rare earth ion in the compounds; only light rare earth compounds undergo the structural phase transition below room temperature, while the compounds containing heavy rare earth ion show the magnetic transition.<sup>2,3</sup> We have previously revealed that the structural transitions in  $R\text{InAu}_2$  ( $R = \text{La}, \text{Ce}, \text{Pr}, \text{and Nd}$ ) are suppressed by pressure,<sup>4</sup> which indicates that the structural instabilities of  $R\text{InAu}_2$  depend mainly on the lattice spacing.

YbInAu<sub>2</sub> also has the Heusler-type structure at room temperature. However, its lattice parameters deviate from the lanthanide contraction in the  $R\text{InAu}_2$  series, indicating the intermediate valence state of Yb ion in the compound. There is only one crystallographic site for Yb ion in YbInAu<sub>2</sub> compound. These facts suggest that YbInAu<sub>2</sub> is a good candidate for the investigation of the IV state in the homogeneously mixed valent Yb compounds. The experiment of Yb  $L_{III}$ -edge x-ray absorption near edge structure (XANES) reported a valence of 2.68 for YbInAu<sub>2</sub>.<sup>5</sup> A broad maximum appears at  $T_{\text{max}} = 100$  K in the magnetic susceptibility, and no magnetic order is observed down to 1.8 K.<sup>6</sup> Previous high-pressure studies have indicated that the Yb ion in YbInAu<sub>2</sub> tends to

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have the magnetic electronic configuration ( $4f^{13}$ ) even under low hydrostatic pressure smaller than 2 GPa or quasihydrostatic high pressure; an application of pressure enhances the magnetic moment of the compound, shifts the  $T_{\max}$  to lower temperature in the magnetic susceptibility,<sup>7</sup> and depresses the Kondo maximum temperature in the resistivity.<sup>8,9</sup>

It is, therefore, of particular interest to make a systematic examination of these unusual pressure responses of the Yb ion in YbInAu<sub>2</sub> in terms of the valency of Yb ion at high pressure. As mentioned above, there should be the close relation between the IV states and the unit-cell volume in the compound. In the present study, we have determined the valency of Yb ion in YbInAu<sub>2</sub> as precise as possible by the Yb  $L_{\text{III}}$ -edge XANES spectroscopy at high pressure and observed the lattice compression curves of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> compounds by the x-ray diffraction (XRD) measurement using intense synchrotron radiation (SR) x-ray sources, in order to discuss the relation between the valence state of Yb ion and the physical properties of YbInAu<sub>2</sub>.

## II. EXPERIMENT

### A. Sample preparation

Polycrystalline samples of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> compounds were prepared by melting the constituent elements in a tetra-arc furnace under a Ti-gettered high-purity argon atmosphere. The weight loss of volatile Yb was found in the melting, so that the excess amount of Yb element (3 wt %) from the stoichiometry was added to the starting composition. After melting, the compounds were annealed in a quartz ampule under vacuum at 500 °C in an electrical furnace for 7 days, followed by slow cooling to room temperature. The shots of Yb and Lu elements were from Rhône-Poulenc Basic Chemicals Co. and the purity was 99.9% for both. The granular In metal with 99.999% purity was used from Asahi Metal Co. Au foil was from Tanaka Kikinzoku Co. and its purity was 99.99%. The ingot thus prepared was cut into pieces by a spark erosion cutter and then powdered for the XRD and XANES measurements.

### B. X-ray diffraction

The powder XRD measurement at normal pressure was made using a RINT-2000, Rigaku, with Cu  $K\alpha$  radiation to confirm the single phase of the prepared ingots. The high-pressure XRD measurement was conducted using synchrotron radiation at the BL04B2 beamline in SPring-8. The pressure was generated up to 17 GPa with a diamond anvil cell (DAC) and the pressure increment in the measurements was about 0.5 GPa up to 10 GPa. A 4:1 methanol-ethanol mixture was used as the pressure transmitting fluid. The pressure at the sample position in DAC was determined by the ruby fluorescence method with an accuracy of 0.2 GPa. The wavelength was 0.3275 Å. The diffraction patterns of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> were recorded with an imaging plate. A typical error in the lattice parameter is 0.0005 Å.

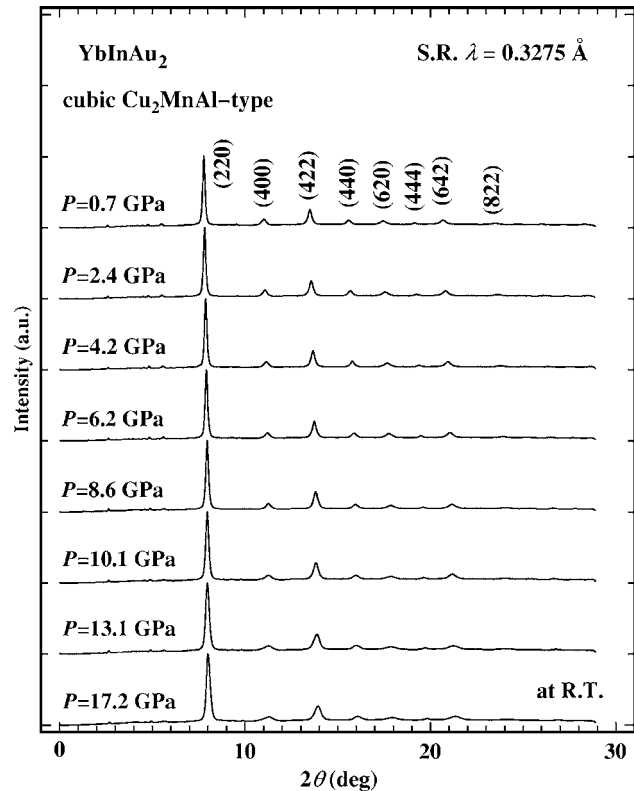


FIG. 1. XRD patterns of YbInAu<sub>2</sub> under various pressures at room temperature.

### C. X-ray absorption

The XANES measurement at high pressure was carried out at the BL10XU beamline in SPring-8 to investigate the valence state of rare earth ion in YbInAu<sub>2</sub> and LuInAu<sub>2</sub>. The foil sample of YbInAu<sub>2</sub> with thickness of 30 μm was prepared by compressing the powder and confined in the metal gasket (SUS304) hole of DAC that was also used for the XRD measurement. The pressure medium was also a 4:1 methanol-ethanol mixture. Data acquisition was performed both in increasing and decreasing pressure processes to confirm the reproducibility of the measurements. Single crystalline Si mirrors were used to eliminate the higher harmonics of the incident x-ray beam and to focus the incident x-ray beam on the sample in DAC. The transmission mode was employed for the XANES measurement with the ionization chambers filled with gases: N<sub>2</sub> 100% for the incident beam and N<sub>2</sub> 75% + Ar 25% for the transmitted one, respectively. A typical error in the valence determination is less than 0.02. The details of the high-pressure XANES experiment are given elsewhere.<sup>10</sup>

## III. RESULTS AND DISCUSSION

### A. High pressure XRD

XRD patterns of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> under various pressures at room temperature are shown in Figs. 1 and 2, respectively. Both compounds have the Heusler-type structure at normal pressure and room temperature. It is found that the structural transformation is not observed under pressure up to 17 GPa for YbInAu<sub>2</sub> and 11 GPa for LuInAu<sub>2</sub>,

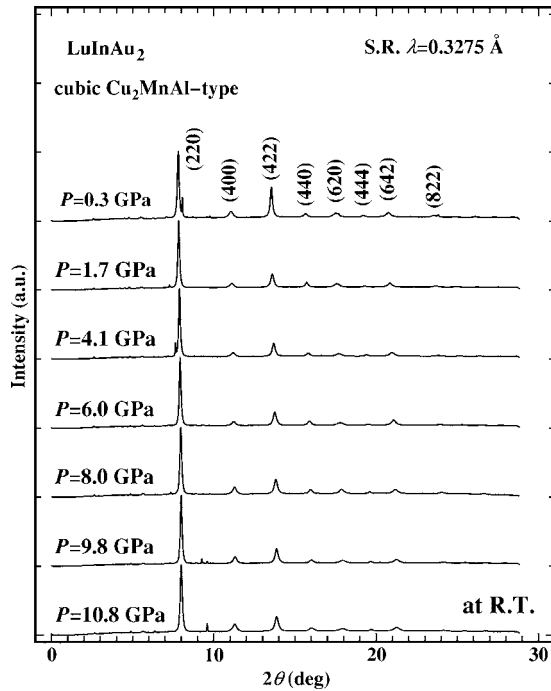


FIG. 2. XRD patterns of LuInAu<sub>2</sub> under various pressures at room temperature.

respectively. However, the compression curves of both compounds are apparently different from each other as seen in Fig. 3. YbInAu<sub>2</sub> is more compressible than LuInAu<sub>2</sub>. The lattice volume of YbInAu<sub>2</sub> is drastically decreased especially in the pressure range from 0 to 4 GPa in comparison with LuInAu<sub>2</sub>, while above 4 GPa the slope of the compression curve of the former compound approaches that of the latter. This finding suggests a rapid approach to the trivalent state of Yb ion in the low pressure below 4 GPa and a gradual increase in the valence of the Yb ion in the compound above 4 GPa.

To evaluate the bulk modulus of these compounds, we have applied the Birch type of equation of state (EOS) to the pressure-volume data from the high-pressure XRD measurement. The Birch type of EOS is expressed as follows:<sup>11</sup>

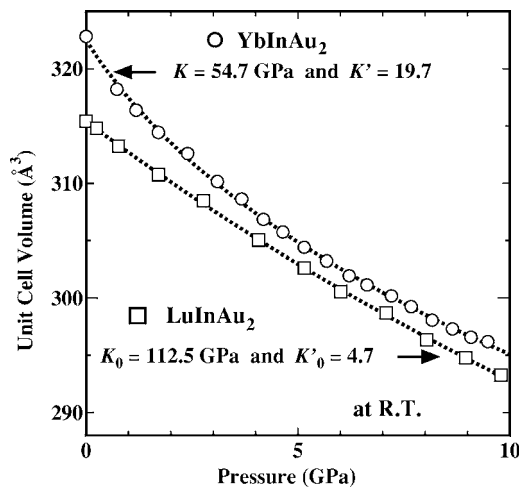


FIG. 3. Compression curves of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> at room temperature. Fittings are made by the Birch type of EOS.

TABLE I. The bulk modulus  $K$ , its first pressure derivative  $K'$ , and the volume at normal pressure  $V_0$  of YbInAu<sub>2</sub> and LuInAu<sub>2</sub>.

Compound	$K$ (GPa)	$K'$	$V_0$ (Å <sup>3</sup> )	$P$ range (GPa)
YbInAu <sub>2</sub>	54.7	19.7	322.51	0–9.5
LuInAu <sub>2</sub>	112.5	4.7	315.45	0–9.8

$$P = \frac{3}{2}K \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4}(4 - K') \right. \\ \left. \times \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}, \quad (1)$$

where  $P$ ,  $V$ , and  $V_0$  are the external pressure, lattice volume at  $P$ , and volume at normal pressure, respectively. The  $K$  and  $K'$  denote bulk modulus and pressure derivative of  $K$ , respectively. The derived  $K$ ,  $K'$ , and  $V_0$  are listed in Table I for YbInAu<sub>2</sub> and LuInAu<sub>2</sub>. The compression curve for YbInAu<sub>2</sub> is characterized by the smaller bulk modulus  $K$  (54.7 GPa) being less than half of that of LuInAu<sub>2</sub> and extremely high value of  $K'$  (19.7) when we fit the curve in the whole pressure range (dotted curve in Fig. 3).

## B. High pressure XANES

The observed Yb  $L_{III}$ -XANES spectra of YbInAu<sub>2</sub> at various pressures and room temperature are shown in Fig. 4. Even at ambient pressure, YbInAu<sub>2</sub> shows a double-peaked XANES spectrum. This proves that the Yb ion in YbInAu<sub>2</sub> is in the intermediate valence state at ambient pressure and room temperature. With increasing pressure, the low-energy peak originating from Yb<sup>2+</sup> ion is depressed, while the high-energy one originating from Yb<sup>3+</sup> ion is enhanced. This tendency indicates that the valence of Yb ion in YbInAu<sub>2</sub> is

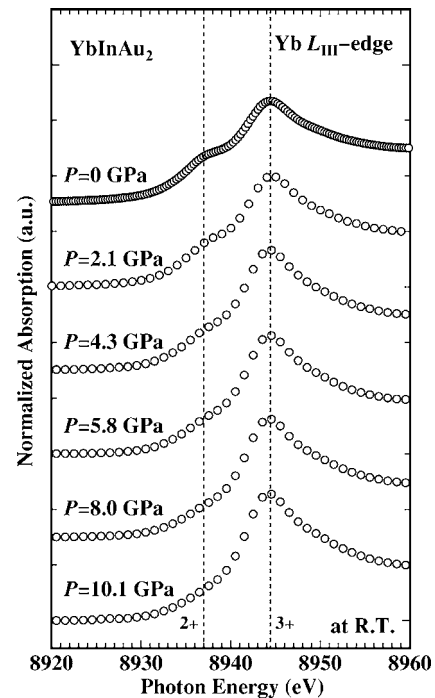


FIG. 4. Yb  $L_{III}$ -XANES spectra of YbInAu<sub>2</sub> at various pressures and room temperature.

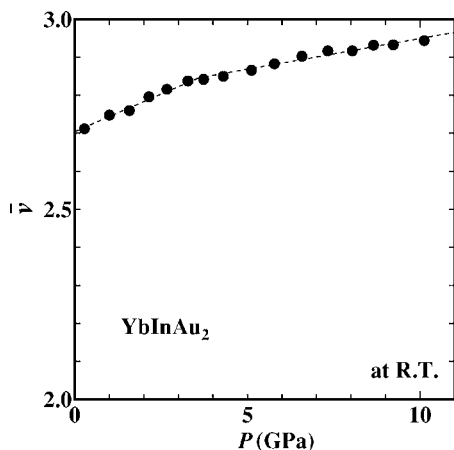


FIG. 5. Pressure dependence of mean valence of Yb ion in YbInAu<sub>2</sub> at room temperature.

increased toward 3 with pressure. However, even at the maximum pressure applied in this experiment, the XANES spectrum of YbInAu<sub>2</sub> remains a double-peak structure. Therefore, it is not definitely concluded that the valence of Yb ion in YbInAu<sub>2</sub> is fully trivalent at 10 GPa.

The evaluation of the valence of Yb ion in YbInAu<sub>2</sub> from the obtained XANES spectra has been conducted as follows. Firstly, the background absorption is estimated by applying the Victoreen's formula to the total absorption below the absorption edge. Secondly, the spectrum intensity is normalized to that at the absorption edge. Then, the normalized spectrum is separated into two absorption lines. Each subspectrum is described by the sum of an arctangent function representing the  $L_{III}$ -edge absorption and a Lorentzian representing the white line. Then, the mean valence  $\bar{v}$  of Yb ion in YbInAu<sub>2</sub> is evaluated by the relative intensities of the two Lorentzians.

The obtained pressure dependence of the  $\bar{v}$  of Yb ion in YbInAu<sub>2</sub> at room temperature is given in Fig. 5. The value of  $\bar{v}$  is 2.71(2) at normal pressure, which is in good agreement with the earlier work.<sup>5</sup> The major finding is that the valence of Yb ion in YbInAu<sub>2</sub> is an increasing function of external pressure. The value of  $\bar{v}$  reaches 2.94(2) at 10 GPa. The tendency that magnetic  $4f^{13}$  state is stabilized under high pressure is supported by the previous magnetic study at high pressure.<sup>7</sup> It should also be stressed that the increasing rate in  $\bar{v}$  with pressure below 4 GPa is twice as large as that above 4 GPa. This finding is consistent with the result obtained in the present high-pressure XRD measurement.

Now, we discuss the relation between the valence states of Yb ion in terms of the lattice volume of the YbInAu<sub>2</sub> compound. Figure 6 illustrates the volume dependence of the mean valence of Yb ion in YbInAu<sub>2</sub> at room temperature. It is clear that the  $\bar{v}$  of Yb ion is increased linearly with compression of the lattice volume in YbInAu<sub>2</sub>;  $\bar{v} = \bar{v}_0 + 2.9|\Delta V/V_0|$  where  $\bar{v}_0$  is 2.71 at  $P=0$ . If this linear relation holds at further compression between the  $\bar{v}$  and the unit-cell volume, we could have the fully trivalent state of Yb ion in YbInAu<sub>2</sub> at 13 GPa where the lattice volume is reduced to about 90% of that at normal pressure.

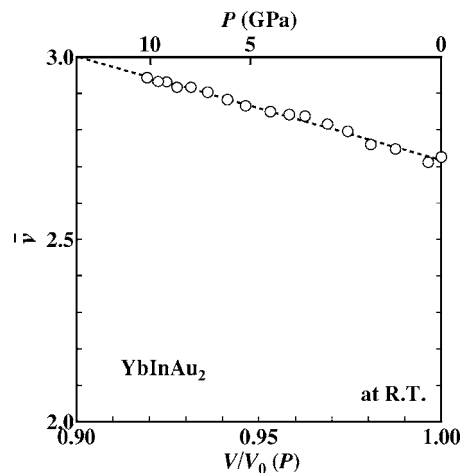


FIG. 6. Volume dependence of mean valence of Yb ion in YbInAu<sub>2</sub> at room temperature.

#### IV. CONCLUSION

We have measured the XRD patterns and XANES spectra of YbInAu<sub>2</sub> and LuInAu<sub>2</sub> at various pressures and room temperature using synchrotron radiation at SPring-8. We have elucidated that the valence state of Yb ion in YbInAu<sub>2</sub> is strongly correlated to the unit-cell volume so that the magnetic  $4f^{13}$  state is stabilized at high pressure. YbInAu<sub>2</sub> is more compressible at pressures lower than 4 GPa than above it; the evaluated bulk modulus by Birch type of EOS is 54.7 GPa which is one half of that of the LuInAu<sub>2</sub> (112.5 GPa). The mean valence  $\bar{v}$  is increased linearly with the lattice compression:  $\bar{v} = \bar{v}_0 + 2.9|\Delta V/V_0|$ . The critical pressure has been evaluated to be 13 GPa for the Yb ion to occupy completely the Yb<sup>3+</sup> state.

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