

## Pressure-tuning of the $c$ - $f$ hybridization in Yb metal detected by infrared spectroscopy up to 18 GPa

Hidekazu OKAMURA\*, Kazuyoshi SENOO, Masaharu MATSUNAMI<sup>1</sup> and Takao NANBA

*Graduate School of Science and Technology, Kobe University, Kobe 657-8501.*

<sup>1</sup>*RIKEN/SPring-8, Sayo 679-5198.*

(Received August 1, 2006)

It has been known that the elemental Yb, a divalent metal at ambient pressure, becomes a mixed-valent metal under external pressure, with its valence reaching  $\sim 2.6$  at 30 GPa. In this work, infrared spectroscopy has been used to probe the evolution of microscopic electronic states associated with the valence crossover in Yb at external pressures up to 18 GPa. The measured infrared reflectivity spectrum [ $R(\omega)$ ] of Yb has shown large variations with pressure. In particular,  $R(\omega)$  develops a deep minimum in the mid-infrared, which shifts to lower energy with increasing pressure. The dip is attributed to optical absorption due to a conduction ( $c$ )- $f$  electron hybridization state, similarly to those previously observed for heavy fermion compounds. The red shift of the dip indicates that the  $c$ - $f$  hybridization decreases with pressure, which is consistent with the increase of valence.

KEYWORDS: Yb metal, valence crossover, infrared synchrotron radiation, high pressure, diamond anvil cell

Physical properties of strongly correlated “heavy fermion” compounds, most typically Ce- or Yb-based compounds containing partly filled  $4f$  shell, have attracted much attention.<sup>1)</sup> In heavy fermion compounds, the hybridization between the conduction ( $c$ ) electrons and the otherwise localized  $f$  electrons leads to many interesting phenomena, such as a crossover between itinerant and localized characters of the  $f$  electrons, and the formation of heavy fermion.

Elemental Yb is a divalent metal at ambient pressure, hence the  $f$  electron configuration is  $4f^{14}$  with no local magnetic moment. However, it has been shown using X-ray absorption spectroscopy (XAS) that the valence of Yb increases under external pressure, reaching  $\sim 2.6$  at 30 GPa.<sup>2,3)</sup> Namely, Yb is a mixed-valent metal in this pressure range. Since the number of localized  $4f$  holes increases with this valence crossover, it can be viewed from the  $4f$  hole point of view as a crossover from an itinerant to a localized regime. Equivalently, it can be also viewed that the  $c$ - $f$  hybridization becomes weaker as the applied pressure increases. Hence Yb can be regarded as an  $f$  electron system where an itinerant-localized crossover can be caused, and where the  $c$ - $f$  hybridization can be tuned, by the external pressure. In addition, Yb has another interesting property: its resistivity ( $\rho$ ) *increases* under pressure up to  $\sim 4$  GPa.<sup>4)</sup> It has been suggested by band structure calculation that the increase of  $\rho$  with pressure is due to a pseudogap formation at the Fermi level ( $E_F$ ).<sup>5)</sup>

In this work, we have probed the interesting electronic structures of Yb metal under pressure using infrared (IR) reflectivity [ $R(\omega)$ ] measurement. IR spectroscopy has been quite successful in probing the electronic structures associated with the  $c$ - $f$  hybridized state in mixed-valent heavy fermion compounds.<sup>6-9)</sup> We have used a diamond anvil cell (DAC) to produce high pressure. It

is technically challenging to do reflectivity experiment within the limited sample space in a DAC using long wavelength IR radiation. To overcome this, we have used an IR synchrotron radiation source and an IR microscope at the beam line BL43IR of SPring-8. With this combination, a nearly diffraction-limited beam diameter ( $\sim 15 \mu\text{m}$  in the mid-IR region) could be obtained on the sample. The measurements were made in the range 0.03-1.1 eV ( $240$ - $9000 \text{ cm}^{-1}$ ) at room temperature. The Yb sample used was a film deposited directly on the diamond anvil by evaporating 99.99 % purity Yb in a high vacuum. A gold film deposited next to the Yb film on the diamond anvil was used as the reference of  $R(\omega)$ . The films were approximately  $50 \times 100 \mu\text{m}^2$  wide, and  $0.5 \mu\text{m}$  thick. Diamond anvils with a culet size of 0.6 mm were used. The pressure was monitored using ruby fluorescence, and fluorinert was used as the pressure medium. The gasket was a tension-annealed SUS 301 plate with a thickness of 0.26 mm. The pressure variation at different portions in the sample space was roughly 1 GPa when the average pressure was 18 GPa. This variation did not cause a serious problem in our analyses since the valence crossover in Yb with pressure is known to be very gradual.<sup>2,3)</sup>

Figures 1(a) and 1(b) summarize the  $R(\omega)$  spectra taken at different pressures between 0 and 18 GPa. Before analyzing these spectra, one should note that the measurements were done on Yb films *directly deposited on diamond*, so that the  $R(\omega)$  spectra in Fig. 1 are relative to diamond, in contrast to the usual case of  $R(\omega)$  relative to vacuum or air. Due to the large refractive index of diamond,  $\sim 2.4$ , the  $R(\omega)$  spectra in Fig. 1 are lower than those relative to vacuum.<sup>10)</sup> Hence one should carefully analyze the spectra in Fig. 1, since the optical properties of metals are usually represented by those relative to vacuum.<sup>10)</sup> Nevertheless, it is quite clear from Fig. 1 that the  $R(\omega)$  spectra show significant changes with varying pressure. This means that the electronic

\*E-mail: okamura@kobe-u.ac.jp

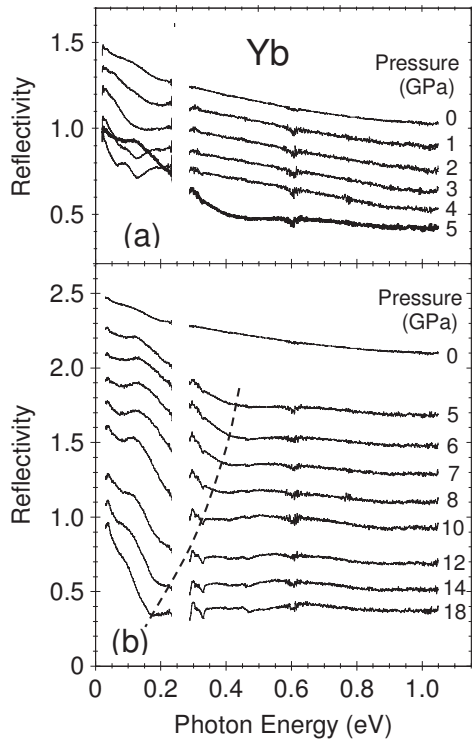


Fig. 1. Reflectivity spectra of Yb metal at room temperature at external pressures of (a) 0-5 GPa and (b) 0-18 GPa. For clarity, each spectrum is offset along the vertical axis by 0.1 in (a) and by 0.2 in (b). The broken curve in (b) is a guide to the eye, indicating the shift of the dip discussed in the text. The spectra in the 0.24-0.28 eV range are absent due to strong absorption by diamond, and the weak dip at 0.6 eV is an instrumental artifact.

structures of Yb near  $E_F$  strongly varies with pressure. In this paper we only make qualitative analyses based on the  $R(\omega)$  in Fig. 1, and more quantitative analyses including the correction for diamond's refractive index will be presented in a future publication.

Figure 1(a) shows the  $R(\omega)$  spectra at pressures up to 5 GPa. In this pressure range, the Yb valence determined by XAS does not change very much,<sup>3)</sup> but the resistivity of Yb increases with increasing pressure until an fcc-bcc structural phase transition occurs at approximately 4 GPa.<sup>4)</sup> After the transition, the resistivity drops to a value close to that at ambient pressure.<sup>4)</sup> The most significant spectral change in Fig. 1(a) is the progressive development of a deep minimum in  $R(\omega)$  at 0.1-0.2 eV range with increasing pressure, and the sudden disappearance of this minimum between 4 and 5 GPa. Since the changes in  $R(\omega)$  show good correspondence with those in the resistivity, we attribute the changes in  $R(\omega)$  to a development of pseudogap at  $E_F$  with increasing pressure, and to the disappearance of the pseudogap upon the structural phase transition at  $\sim 4$  GPa. The magnitude of the pressure-induced pseudogap in Yb has been predicted to be  $\sim 0.1$  eV by the band calculation.<sup>5)</sup> This magnitude agrees well with the energy scale of the dip in  $R(\omega)$ .

Figure 1(b) shows the evolution of  $R(\omega)$  above 5 GPa. The main spectral feature in this pressure range is the

appearance and shift of another dip in  $R(\omega)$ , indicated by the broken curve: This dip appears at  $\sim 0.45$  eV at 5 GPa, and it progressively shifts toward lower energy, to below 0.2 eV at 18 GPa. A similar dip has been observed in  $R(\omega)$  of many mixed-valent, heavy fermion compounds.<sup>6-9)</sup> Corresponding to this dip, the mixed-valent compounds have a marked absorption peak in their optical conductivity  $\sigma(\omega)$ .<sup>6-9)</sup> This absorption has been interpreted as resulting from optical excitations across the  $c$ - $f$  hybridization gap<sup>1)</sup> formed in the electronic dispersion near  $E_F$ .<sup>6-9)</sup> The peak energy of absorption in  $\sigma(\omega)$  roughly gives the magnitude of the  $c$ - $f$  hybridization gap, and also the hybridization energy. Since Yb is also an mixed-valent metal under high pressure,<sup>2,3)</sup> the dip of  $R(\omega)$  in Fig. 1(b) are also likely to result from a  $c$ - $f$  hybridized state, similarly to the case of heavy fermion compounds. This interpretation is consistent with the red shift of the dip with increasing pressure, since an increase of the Yb valence should be accompanied by a decrease of the  $c$ - $f$  hybridization energy.<sup>1)</sup> For more quantitative analyses, however, we need to take into account the diamond's refractive index as mentioned above, then need to evaluate the optical conductivity. This will be done in a future work.

In conclusion, measured infrared  $R(\omega)$  of Yb metal have revealed two remarkable spectral evolutions under pressure: the development of a dip at  $\sim 0.15$  eV at pressures up to 4 GPa, and that of another dip appearing at  $\sim 0.4$  eV at 5 GPa and shifting toward lower energy with increasing pressure. The former is attributed to a pseudogap formation at  $E_F$ , which is also responsible for the previously reported increase of resistivity. The latter is interpreted in terms of a  $c$ - $f$  hybridized electronic state. The shift of the latter dip is taken as evidence for a decrease of  $c$ - $f$  hybridization with pressure.

We would like to thank Dr. H. Yamawaki of AIST for providing the gasket material. The experiments at SPring-8 were done under the approval by JASRI (2005B0526 and 2006A1346). We acknowledge technical support by the staff at BL43IR.

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