Definitive Evidence for Fully Occupied $4f$ Electrons in YbS and Yb Metal

A wide variety of physical properties in solids arise from the delicate balance between the localized and itinerant states of electrons. It is absolutely necessary to know the degree of electron localization to understand novel phenomena. Therefore, the mean valence of ions, which provides a direct measure of the degree of electron localization, must be determined with a high level of accuracy. High-energy spectroscopies, such as photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), have been used as fundamental probes for the directly observation of the electronic structure, including mean valence determination. Nonetheless, the reported valence values have often been inconsistent with respect to basic physical properties. For example, YbS and Yb metal have been considered as prototypical divalent Yb systems, in which the $4f$ shell is completely filled (f^{14} configuration), at ambient pressure. However, a low trivalent (f^{13} configuration) signal intensity has been observed in Yb L_{III}-edge XAS and Yb $L_{\alpha 1}$ resonant inelastic X-ray scattering (RIXS) [1]. Hence, it is important to clarify whether YbS and Yb metal have intrinsically mixed-valence ground states. In particular, YbS has been identified as the ionic insulator $Yb^{2+}S^{2-}$. Only at high pressures above 10 GPa, a mixed-valence state is realized, coupled with the insulator-to-metal transition [2]. Thus, it seems contradictory that XAS and RIXS indicate mixed-valence states in YbS coexisting with the insulating ground state. Compared with XAS and RIXS, rare-earth $3d$ core-level PES is a preferable probe for determining the mean valence because, with the PES, signature features of divalent and trivalent states are well separated. However, Yb $3d$ core levels, located at binding energies of 1500~1600 eV, could not be excited by a conventional soft X-ray source. Recent advances in hard X-ray photoelectron spectroscopy (HAXPES) make it possible to observe not only the valence band but also the Yb $3d$ core levels under bulk-sensitive conditions, based on the increased probing depth [3].

In this paper, we report the HAXPES of Yb $3d$ core levels and valence band for YbS and Yb metal [4]. The measured HAXPES spectra are compared with the energy loss functions in the bulk and surface, measured by optical spectroscopy. This comparison enables us to distinguish between the energy loss satellite of the Yb^{2+} peak and the Yb^{3+} multiplet. The obtained results clearly indicate the purely divalent Yb state of bulk YbS and Yb metal.

HAXPES experiments were carried out at a photon energy of 7.94 keV in the undulator beamline **BL29XUL**. The total energy resolution was set to 200 meV. The clean surfaces of YbS and $YbCu_2Si_2$ (as a reference of typical mixed valence compound) were obtained by cleaving *in situ*. Yb metal was prepared as films by *in situ* evaporation under ultrahigh-vacuum conditions.

Figure 1 shows the Yb $3d$ core-level spectra of YbS, Yb metal, and $YbCu_2Si_2$ recorded at two emission angles. Since θ is defined as shown in the inset in Fig. 1, $\theta = 0°$ and $80°$ are bulk- and surface-sensitive configurations, respectively. These spectra are separated into $3d_{5/2}$ and $3d_{3/2}$ components by spin-orbit splitting. In addition, for $YbCu_2Si_2$, both spin-orbit components show the final state configuration $3d^9 4f^{14}$ (Yb^{2+}) line and $3d^9 4f^{13}$ (Yb^{3+}) multiplets, which result from valence fluctuations. From the ratio of their integrated intensities, the Yb valence of $YbCu_2Si_2$ can be estimated as +2.8, which agrees well with its bulk value. As is clear from the
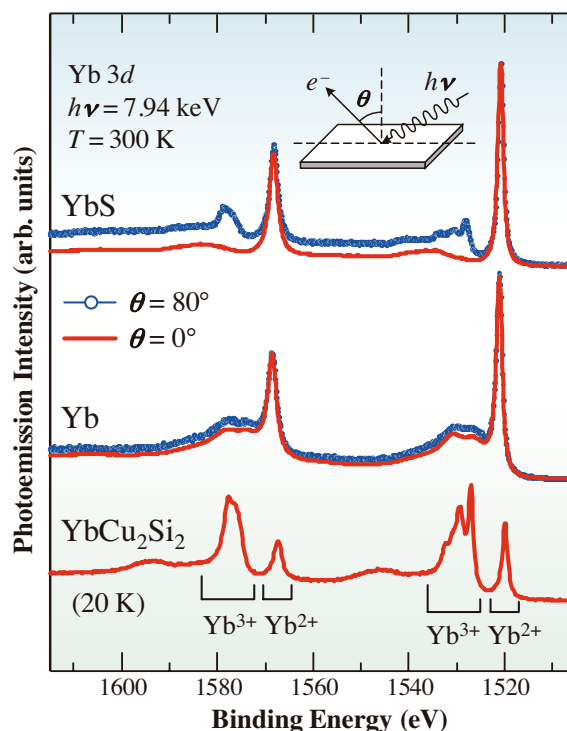

Fig. 1. Yb $3d$ core-level spectra for YbS and Yb metal recorded at emission angles $\theta = 0°$ and $80°$, in comparison with that of $YbCu_2Si_2$ ($\theta = 0°$). The definition of θ is also shown in the inset.

spectral shape, the Yb^{3+} multiplet feature also appears in the 80° spectrum for YbS. This is due to the growth of Yb_2O_3 [i.e., $(Yb^{3+})_2(O^{-2})_3$] by surface oxidation, which can be regarded as the origin of the previously reported trivalent signal. In contrast, the spectra at 0° for YbS and at both angles for Yb metal show the Yb^{2+} peak and its broad satellite feature as discussed in the following.

Figure 2 shows a comparison of the satellite features in Yb $3d_{5/2}$ core-level spectra of YbS and Yb metal with their bulk and surface loss functions, where the loss functions are plotted relative to the Yb^{2+} $3d_{5/2}$ peak energy. For YbS, the satellite feature in the 0° spectrum shows good correspondence with the peaks in the bulk loss function. Hence, the satellite is attributed to the energy loss caused by electronic interband transitions. On the other hand, the main feature in the 80° spectrum shows no such correspondence with the energy loss functions, indicating that such a feature is mainly due to the Yb^{3+} multiplet. For Yb metal, both loss functions are mainly composed of two features, which are due to the plasmon excitations at 8-10 eV and the interband transitions at 5-7 eV. The satellite features at both angles can be well reproduced by combining bulk and surface loss functions. In addition, the spectral shapes of the satellites at both 0° and 80° are very different from that of the Yb^{3+} multiplet. As a result, this method unambiguously elucidates the purely divalent Yb state of bulk YbS and Yb metal.
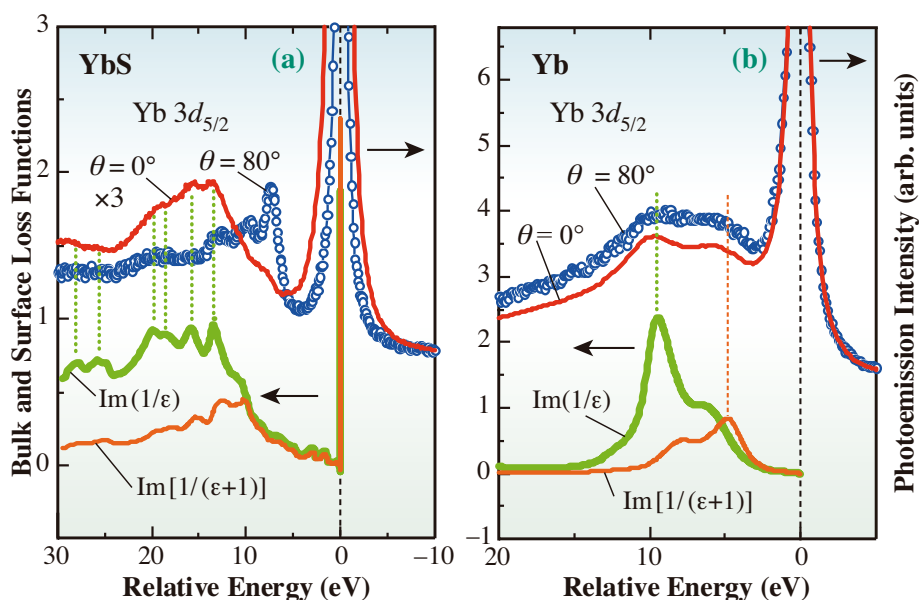

Fig. 2. Satellite structures in Yb $3d_{5/2}$ core-level spectra for YbS (a) and Yb metal (b), in comparison with energy loss functions in bulk Im(1/ε) and surface Im[1/(ε+1)], where ε is complex dielectric function obtained by Kramers-Kronig analysis of optical reflectivity. Dotted lines indicate main peak positions in the loss functions.

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