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3*d* core-level photoemission spectra of intermetallic Yb compounds

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The Yb 3*d* core-level photoemission spectra of trivalent YbAs, mixed-valence $\mathrm{YbAl_3}$, and divalent $\mathrm{YbPb_3}$ were measured with a Si $K\alpha$ x-ray source. Significant intensities of divalent peaks were observed even for trivalent YbAs and mixed-valence $\mathrm{YbAl_3}$. This is probably due to the divalent surface layers, which makes difficult the estimation of the 4*f* hybridization strength from the 3*d* core-level spectra. The 4*d* core-level and the 4*f* spectra are consistent with this interpretation.

I. INTRODUCTION

Recently, rare-earth metals and their compounds have presented a strong challenge to solid-state physicists because of valence-fluctuation phenomena[1] and heavy-fermion properties,[2] which are believed to originate from the highly correlated *f* electrons. Electron-spectroscopic measurements such as photoelectron spectroscopy (PES) and bremsstrahlung isochromat spectroscopy (BIS) have been of central importance for understanding the electronic structures of these materials.[3] From the $4f^n \rightarrow 4f^{n-1}$ (electron-removal) spectral weight measured by PES and $4f^n \rightarrow 4f^{n+1}$ (electron-addition) spectral weight studied by BIS, we can obtain valuable information such as the electron correlation energy and hybridization strength between the 4*f* level and conduction-band states.

Ce and its compounds are probably the best systems studied so far. Because one of the configurations is the empty valence shell $4f^0$, experimental spectra and theoretical treatments are relatively simple, and many detailed comparisons between theory and experiment were performed.[3-5] The general physics that came out of these studies is that valence-electronic structures can be described by the Anderson impurity model Hamiltonian, and the strength of the hybridization between the 4*f* level and conduction-band states is the controlling factor that determines various physical properties.

Yb is the last element of the 4*f* rare-earth series and has the electron-hole symmetry in the 4*f*-level structure with Ce. Therefore we can use the same model calculation of Ce compounds and simply interchange the role of the 4*f* electron with that of the 4*f* hole to understand the electronic structures of Yb compounds. There have been already several PES and/or BIS works on interesting Yb compounds,[6-8] and they show that the hybridization parameters in mixed-valence Yb compounds are not significantly smaller than those in Ce compounds.

Core-level x-ray photoelectron spectroscopy (XPS) is also valuable in studying electronic structures of these compounds. Core-level spectra can be understood by the following Anderson impurity Hamiltonian including the Coulomb interaction between the core hole and the 4*f* electron:

$$H=\sum_{k,\sigma}\varepsilon_k n_{k\sigma}+[\varepsilon_f-U_{fc}(1-n_c)]\sum_{m,\sigma}n_{m\sigma}+\varepsilon_c n_c + \sum_{k,m,\sigma}(V_{km}\varphi^{+}_{m\sigma}\varphi_{k\sigma}+\mathrm{H.c.})+U_{ff}\sum_{\substack{m,m'\\ \sigma,\sigma'}}n_{m\sigma}n_{m'\sigma'} .$$

ε_k describes the energy of the conduction states, ε_f is the energy of the 4*f* level, and ε_c describes the energy of a core level. The 4*f* level has N_f-fold degeneracy, whose quantum numbers are denoted by m,σ. If the spin-orbit splitting is neglected, $N_f=14$. The hopping between the 4*f* level and the conduction state is described by V_{km} and the Coulomb interaction between 4*f* electrons is given by U_{ff}, where multiplet effects are entirely neglected. U_{fc} is the Coulomb interaction between a core hole and an *f* electron. Thus, while the $|f^n\rangle$ and the $|f^{n+1}\rangle$ states are nearly degenerate in the initial state, they have an energy separation of U_{fc} in the final state, because the energy of the $|f^n\rangle$ level is pulled down by the amount nU_{fc} (n is the number of *f* electrons) by the core-hole created in photoionization (see Fig. 1). This gives rise to the satellite structure in the deep core-level XPS spectra, whose intensity depends on the strength of V_{km}. Therefore, by analyzing deep core-level XPS spectra, we can get information on the valence electronic structure indirectly, which can be checked for self-consistency with parameters obtained by the 4*f* level PES and BIS. This analysis is much simpler than the 4*f* spectra itself, and 3*d* core levels are usually needed for this purpose because 4*d* core-level XPS shows complicated multiplet structures due to the unfilled 4*f* shell (they have the same principal quantum number $n=4$).

In fact, most of the Anderson-impurity-Hamiltonian parameter values for Ce compounds were obtained by the analyses of the Ce 3*d* core-level spectra. The 3*d* core-level spectra of mixed-valence Yb compounds are interesting in the same sense. However, experimental data are very scarce up to now because of one experimental difficulty. The binding energies of 3*d* levels known from x-ray emission spectra of Yb atom[9] are 1576.3 eV (for $3d_{3/2}$) and 1527.8 eV (for $3d_{5/2}$), which are larger than the photon energy of typically used x-ray sources, Al $K\alpha$ ($h\nu=1486.6$ eV) and Mg $K\alpha$ ($h\nu=1253.6$ eV). So, an x-ray source with higher photon energy is needed, but

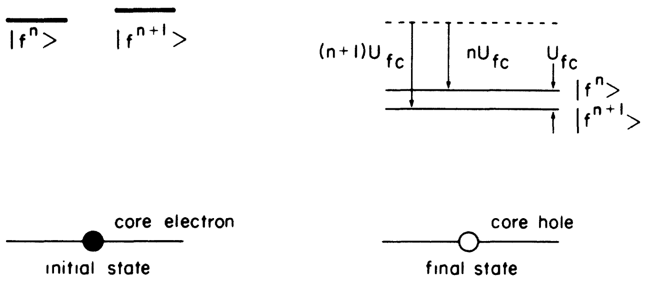

FIG. 1. Schematic drawing of energy levels before and after 3*d* core-level photoemission.

usually high-energy x-ray sources have linewidths that are too large. Si *Kα* x-ray ($h\nu = 1739.4$ eV) seems to be the best practical source as a compromise, and here we use Si *Kα* source to study 3*d* core-level spectra of three representative Yb compounds: trivalent YbAs, mixed-valence $YbAl_3$, and divalent $YbPb_3$. Still, the experimental resolution with the Si *Kα* [linewidth $= 1.0$ eV full width at half maximum (FWHM)] source is not as good as Mg *Kα* (linewidth$=0.7$ eV) or Al *Kα* (linewidth$=0.8$ eV) sources.[10] And there is one more complication: the kinetic energy of electrons ejected from Yb 3*d* core levels is about 200 eV with the Si *Kα* x ray. In this energy range, the mean free path of ejected electrons is very short, and there is a strong contribution from the surface layers, which must be kept in mind when interpreting the data.

II. EXPERIMENTAL

The samples were polycrystalline ingots of YbAs, $YbAl_3$, and $YbPb_3$, which were grown in the vacuum furnace with a SiC heater, where appropriate amounts of elements were sealed in the quartz tube with an alumina boat. These samples were annealed after growth, and their crystal structures and stoichiometry were checked by x-ray analysis. The samples were then cut into rectangular forms, and bonded to the sample holder with silver-based epoxy adhesive to get good electrical contact. Just before taking spectra, the samples were scraped by a knife in the preparation chamber at the pressure better than 3×10^{-10} Torr to get a fresh surface, and transferred to the analysis chamber without breaking the vacuum.

The measurements were made in an ultrahigh-vacuum photoelectron spectrometer manufactured by VSW Scientific Instruments Ltd. in England, which is equipped with the concentric hemispherical analyzer (CHA) with a multichannel detector system. As photon sources, Al *Kα* and Si *Kα* x rays were used. Si target was made either by evaporating Si onto the copper anode or by bonding the thin SiC crystal onto the anode. Al target was made by evaporation as usual. The operating power of the x-ray source was 300 W (12 kV, 25 mA) for Al *Kα* and 150 W (10 kV, 15 mA) for Si *Kα* source. During the experiments the pressure was maintained better than 2.5×10^{-10} Torr. Sample cleanliness was checked by monitoring 0 1*s* and C 1*s* signals. For YbAs and $YbAl_3$, the data reported here are from clean surfaces with a negligible amount of oxygen contamination, but for $YbPb_3$ we did not succeed in getting completely clean spectra even after many repeated scrapings. We suspect either that $YbPb_3$ is extremely sensitive to contamination or that there is Yb_2O_3 phase left in the sample.

III. EXPERIMENTAL DATA AND ANALYSIS

A. Yb 3*d* spectra

The Yb $3d_{5/2}$ spectra of YbAs, $YbAl_3$, and $YbPb_3$ taken with the Si *Kα* source are shown in Fig. 2. We have corrected for the effect of the Si $K\alpha_{3,4}$ x-ray satellite lines, which are 10.96 and 13.0 eV higher energy than the main Si *Kα* line with intensity ratios of 5.5% and 2.7%, respectively. This correction leaves the Ag 3*d* test spectra satellite free. Because of their low kinetic energy, Yb 3*d* peaks ride on an increasing secondary-electron background. To take this into account, we first subtracted linear background whose slope is determined as that of the low-binding-energy side tail in the raw spectra. After that we applied the iterative background subtraction pro-

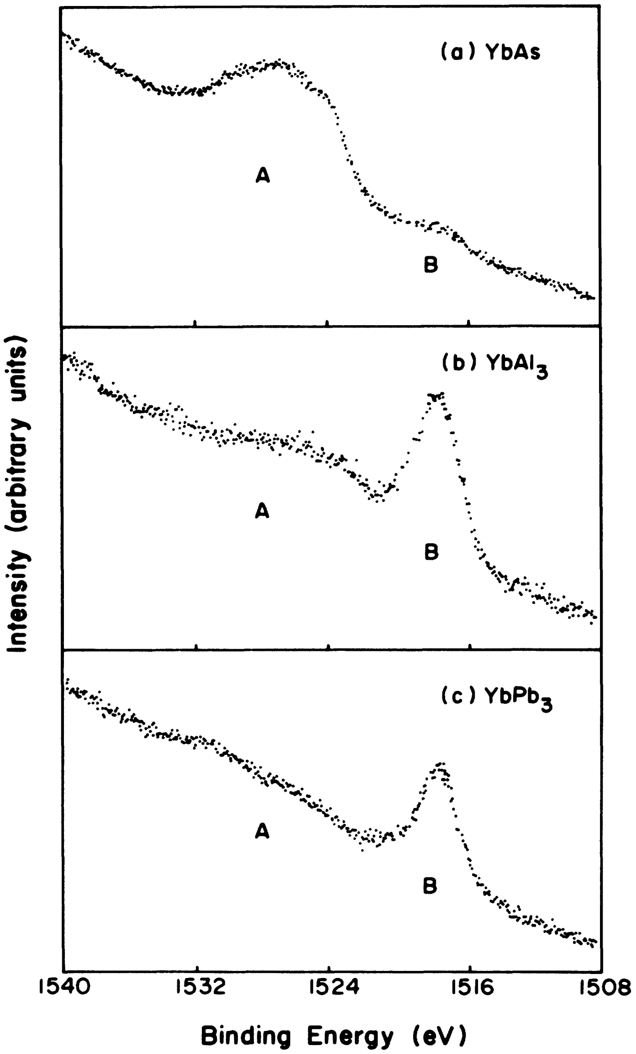

FIG. 2. Photoemission spectra of Yb 3*d* core level in (a) YbAs, (b) $YbAl_3$, and (c) $YbPb_3$ taken with Si *Kα* source. X-ray satellite contributions are subtracted from the raw data.

cedure,[11] which assumes that the scattering probability is independent of the amount of the energy loss. The resulting Yb $3d_{5/2}$ spectra are shown in Fig. 3.

In all three spectra, we can see two peaks *A* and *B*, although their intensity ratios are quite different depending on the compound. Peak A corresponds to the trivalent $(4f^{13})$ configuration, and peak B to the divalent $(4f^{14})$ configuration. $YbPb_3$ is known to be divalent from the magnetic susceptibility measurement,[12] and photoemission spectra using synchrotron radiation.[13] YbAs is trivalent,[14] and $YbAl_3$ is mixed valent with the bulk valence of 2.78 ± 0.03.[8] Therefore, the appearance of peak B in YbAs and peak A in $YbPb_3$ should be explained, as well as the intensity ratio between divalent and trivalent peaks in $YbAl_3$.

Most of the divalent peak B intensity in YbAs [Fig. 3(a)] must be the contribution from the divalent surface layer rather than the ground-state divalent component or $|\underline{3d}4f^{13}\rangle \rightarrow |\underline{3d}4f^{14}\rangle$ shakedown intensity (the bar denotes the hole). There are two main reasons for this interpretation. First, the $4f$ spectra taken with the Al $K\alpha$ x-ray source also show divalent $4f$ signals (see below), as does the $4f$ spectra taken with synchrotron radiation in the photon energy range $40 \leq h\nu \leq 140$ eV.[14] Furthermore, the intensity variation of this divalent signal with photon energy is consistent with the expected electron escape depth change (see below). Since the Yb $3d_{5/2}$ peak also has low kinetic energy, we expect similar contributions from the divalent surface layers. Second, this divalent signal is found to be extremely sensitive to the amount of contamination, easily destroyed by a small amount of oxygen dose. This property is characteristic of surface contributions. In this connection, we note that a similar peak which is sensitive to oxygen has been observed earlier in the $3d$ spectra of YbP,[15] but this was interpreted as due to the ground-state divalent component based on the fact that varying the electron detection angle did not change its intensity. However, this argument is valid only for the smooth, flat surface, and we imagine the scraped polycrystalline YbP sample surface may well not be flat. Therefore, we believe that even in the case of YbP, the divalent signal is probably from the surface layer, as supported by its observed sensitivity to only 3 L oxygen exposure.

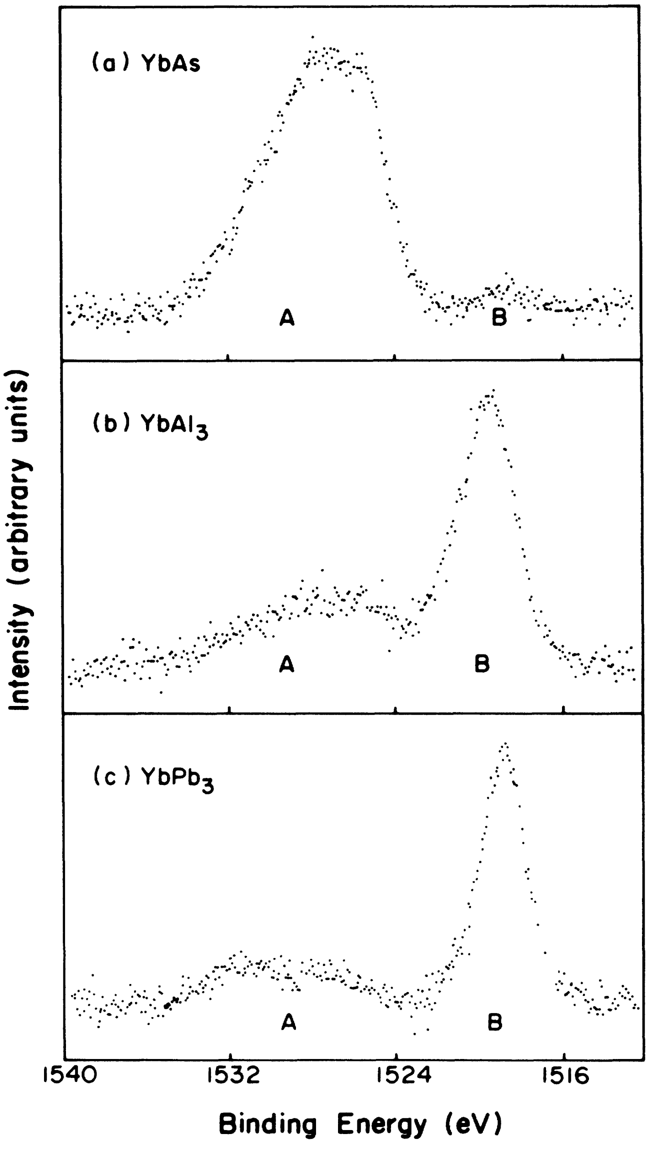

FIG. 3. Yb $3d$ spectra in Fig. 2 after background subtraction.

In the $3d_{5/2}$ spectrum of $YbAl_3$ shown in Fig. 3(b), the intensity ratio between trivalent and divalent peaks derived from their areas is 0.42:1, in striking disproportion to the bulk valence of 2.78. Again this discrepancy must be due to the divalent surface layers. From the hybridization strength $\Delta = 0.05$ eV between the $4f$ level and conduction-band states deduced from $4f$ XPS and BIS spectra and zero-temperature magnetic susceptibility,[8] we expect the ratio between trivalent and divalent peaks including shakedown effect to be 1.95:1.[16] Inclusion of divalent surface layers using the extrapolated value of the electron mean free path from synchrotron radiation data[17] brings this ratio to 0.50:1, closer to our experimental value of 0.42:1.

The trivalent peak *A* in $YbPb_3$ [Fig. 3(c)] is probably due to the small amount of Yb_2O_3 contamination in the sample rather than $|\underline{3d}4f^{14}\rangle \rightarrow |\underline{3d}4f^{13}\rangle$ shakeup mechanism reported in some Eu $3d$ core-level spectra.[18] The reasons for this interpretation are that (i) the shape and the energy position of peak *A* in $YbPb_3$ are different from those in YbAs and $YbAl_3$, and (ii) the $4f$ level spectra where shakeup mechanism is not possible also show a similar amount of $4f^{13} \rightarrow 4f^{12}$ signals.

From the energy separation of the divalent $\underline{3d}_{5/2}4f^{14}$ peak and the trivalent $\underline{3d}_{5/2}4f^{13}$ peak in $YbAl_3$ or YbAs, we can deduce the Coulomb energy U_{fc} between the $3d$ core hole and the $4f$ electron. Since the binding energy of the divalent peak is 1519.7 eV, and that of the centroid of the trivalent peak is 1529.5 eV, $U_{fc} = (1529.5 - 1519.7)$ eV$=9.8$ eV. This is close to the theoretical estimate of 9.5 eV obtained from the relativistic Hartree-Fock calculation using the renormalized-atom scheme,[19] and the value of 9.6 eV deduced from the YbP data.[15]

B. Yb 4*d* and Yb 4*f* spectra

Figure 4 shows Yb 4*d* spectra of YbAs, $YbAl_3$, and $YbPb_3$ taken with the Al $K\alpha$ source. (We have subtracted only x-ray satellites from the raw data.) The major peak *B* in $YbPb_3$ spectrum [Fig. 4(c)] is simply Yb $4d_{5/2}$ and $4d_{3/2}$ spin-orbit doublet, because the filled 4*f* shell gives no multiplet structure. On the other hand, the YbAs spectrum in Fig. 4(a) shows very complex structures due to the $4d^9 4f^{13}$ multiplets. In this case the As 3*s* peak also appears in this region, as indicated in the figure. Peak *A* in the $YbPb_3$ spectrum is probably due to the slight contamination giving rise to the $4f^{13}$ structure, and we see some hint of the divalent contribution from the surface in YbAs spectrum. Yb 4*d* spectra of $YbAl_3$ shown in Fig. 4(b) can be thought of as the superposition of the divalent [Fig. 4(c)] and the trivalent [Fig. 4(a)] structures.

In Fig. 5, we show Yb 4*f* spectra of YbAs, $YbAl_3$, and $YbPb_3$ taken with Al $K\alpha$ source,where x-ray satellite contribution is subtracted. As expected, the spectrum of YbAs is dominated by $4f^{13} \rightarrow 4f^{12}$ peaks labeled as *A* in the figure, and the peak *B* near the Fermi level contains $4f^{14} \rightarrow 4f^{13}$ peaks from divalent surface layers. (The As 4*p* states may show up in this region of peak *B*, but the observed intensity is about 4 times stronger than expected from the As 4*p* cross-section calculation.[20]) The ratio of the divalent 4*f* peak to the trivalent 4*f* peak, after taking into account the cross section of As states, is 0.062:1, which is smaller than the $3d_{5/2}$ core-level case of 0.083:1. This is as expected due to the fact that the electron mean free path increases with kinetic energy and more of the bulk is sampled in the valence-band spectrum. It is also consistent with the 4*f* spectrum taken with soft-x-ray synchrotron radiation.[13] The $YbPb_3$ spectrum shown in Fig. 5(c) is dominated by the divalent 4*f* peaks near the Fermi level, although there is a small contribution of peak *A* at ~9-eV binding energy, probably due to a

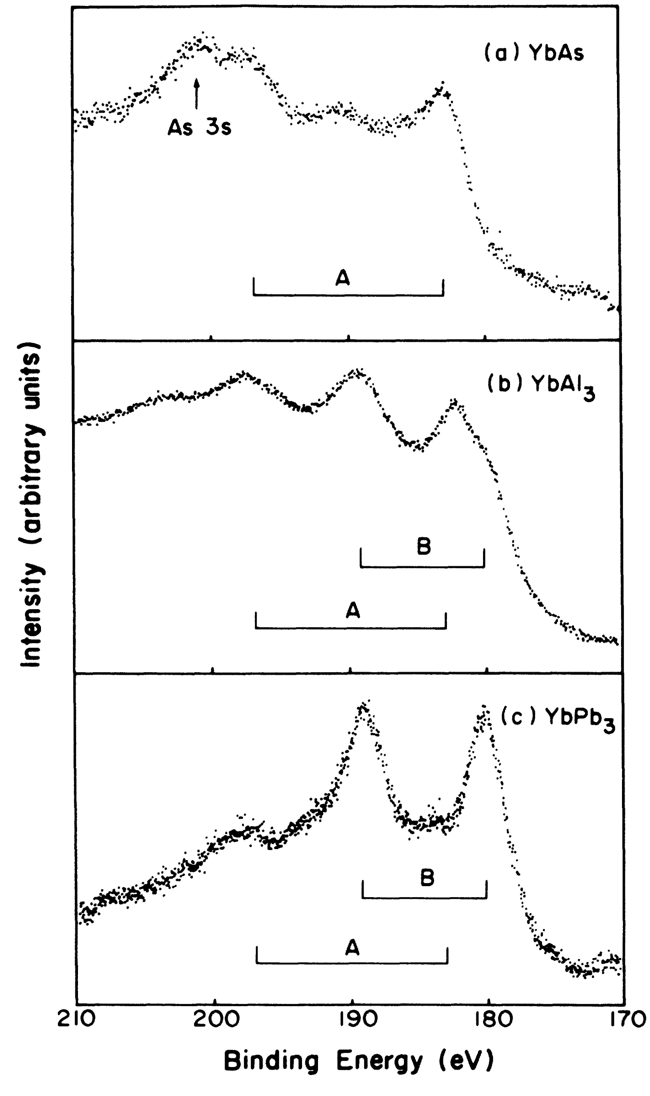

FIG. 4. Photoemission spectra of Yb 4*d* core level in (a) YbAs, (b) $YbAl_3$, and (c) $YbPb_3$ taken with Al $K\alpha$ source. X-ray satellite contributions are subtracted from the raw data.

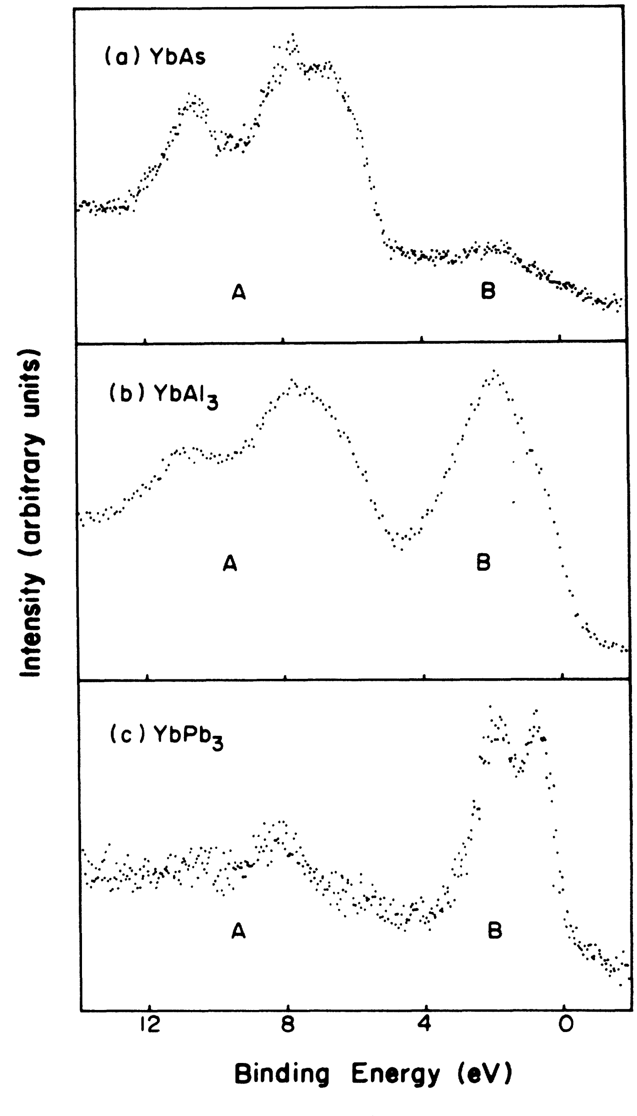

FIG. 5. Photoemission spectra of Yb 4*f* level in (a) YbAs, (b) $YbAl_3$, and (c) $YbPb_3$ taken with Al $K\alpha$ source. X-ray satellite contributions are subtracted from the raw data.

slight contamination of Yb_2O_3 as discussed above. (Pb valence states may also show up in this region, but the observed intensity is about 10 times stronger than expected from the Pb $6s^2$ cross section.[20]) The $YbAl_3$ spectrum in Fig. 5(b) contains both divalent and trivalent peaks, although the ratio is not the same as the bulk valence because of divalent surface layers.[8] According to the $YbAl_3$ $4f$ spectra taken with the tunable synchrotron radiation source,[13] the electron escape depth l varies with the electron kinetic energy E_{kin} as $l \propto E_{\text{kin}}^{0.38}$ in $YbAl_3$. This gives the expected intensity ratio between divalent and trivalent peaks in the $4f$ spectrum taken with Al $K\alpha$ source to be 0.66:1,[17] close to our observed value of 0.67:1.

IV. CONCLUSION

We have measured the Yb $3d$ core-level XPS spectra of trivalent YbAs, mixed-valence $YbAl_3$ and divalent $YbPb_3$ using Si $K\alpha$ x-ray source ($h\nu = 1739.4$ eV). The observed divalent peak intensities in YbAs and $YbAl_3$ are consistent with the interpretation that they are from divalent surface layer(s). It seems therefore difficult to estimate the hybridization strength between the $4f$ level and conduction-band states quantitatively from the $3d_{5/2}$ shakedown level intensity in these Yb compounds, unless we find a way to separate out surface contributions accurately. Similarly, there is no evidence for the shakeup peak in the $3d_{5/2}$ spectrum of $YbPb_3$, unlike the case of several Eu intermetallic compounds reported so far. These findings are consistent with other shallow core-level ($4d$ and $4f$) XPS spectra, as well as $4f$ spectra taken with soft-x-ray tunable synchrotron radiation source. The electron correlation energy U_{fc} between the $3d$ core level and the $4f$ state in Yb is deduced from our spectra, and the measured value of 9.8 eV is in good agreement with the theoretical estimate of 9.5 eV.

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[16] We used the formalism in Ref. 4 of calculating the Ce $3d$ core-level spectra by interchanging the role of $4f$ electron with that of $4f$ hole.

[17] In $YbAl_3$, the electron mean free path l divided by the surface layer thickness Δ_s is found to vary with the electron kinetic energy E_{kin} (measured in eV) according to the formula (see Ref. 13)

$$\log_{10}(l/\Delta_s) = 0.38 \times \log_{10} E_{\text{kin}} - 0.44 \ .$$

For the Yb $3d_{5/2}$ level measured with Si source, $E_{\text{kin}} \cong 210$ eV and we obtain $l/\Delta_s = 2.77$ from the above equation. Then the intensity ratio between the divalent (bulk+surface) peak and the trivalent (bulk) peak is given by (Ref. 13)

$$\begin{aligned} \frac{I(+2)}{I(+3)} &= \frac{I_B(+2)+I_S(+2)}{I_B(+3)} \\ &= \frac{I_B(+2)}{I_B(+3)} \left[1 + \frac{I_S(+2)}{I_B(+2)} \right] \\ &= \frac{I_B(+2)}{I_B(+3)} \left[1 + \frac{1}{3-v} [\exp(\Delta_s / l \cos\theta) - 1] \right] , \end{aligned}$$

where v is the bulk valence and θ is the angle between the surface normal and the analyzer entrance slit. Similar calculation applies to the Yb $4f$ case.

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