# $L_{III}$ x-ray absorption in Yb compounds: Temperature dependence of the valence

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We report x-ray-absorption measurements near the Yb $L_{III}$ absorption edge of $YbAl_3$, $YbCu_2Si_2$, $YbAgCu_4$, and related compounds. Our results suggest that the bulk Yb valence changes with temperature in a manner consistent with predictions of the single impurity Anderson model. We discuss the relationship between these results and recent valence-band photoemission results in the same compounds where the existence of temperature dependence has been disputed.

## INTRODUCTION

Whether the theoretically expected temperature dependence of the Kondo resonance (KR) is observed in the photoemission spectra (PES) of mixed-valent (MV) and heavy-fermion (HF) compounds is currently subject to debate. For Yb compounds the spectral weight in the resonance should vary proportionally to $1-n_f$ where $n_f$ is the number of holes in the Yb $4f$ shell, so that the Yb valence ($z = 2 + n_f$ for Yb) should change as the temperature is raised through the Kondo temperature $T_K$, approaching the value $z=3$ at high temperature.[1] Recent reports claim that for ultraviolet photoemission (UPS) no $T$ dependence of the $4f$ PES occurs in the compounds $YbCu_2Si_2$,[2] $YbAgCu_4$,[3] and $YbAl_3$.[4] [These are mixed-valent, heavy-fermion compounds whose Kondo temperatures 40, 100, and 400 K, respectively (see below), allow determination of the temperature dependence well below and well above $T_K$.] However other reports claim observation of the predicted temperature dependence in $YbAgCu_4$ (Ref. 5) and $YbAl_3$.[6]

A widespread method for determining the bulk valence of Ce and Yb compounds is $L_{III}$ x-ray absorption (XAS).[7,8] In this paper we report $L_{III}$ spectra for $YbCu_2Si_2$,[9,10] $YbAgCu_4$,[11,12] and $YbAl_3$.[13] Using standard procedures to interpret the $L_{III}$ data we find that the bulk valence varies with temperature in a manner consistent with the single-impurity Anderson model. We propose that discrepancies between the $L_{III}$ and PES results might occur either due to the possibility that UPS does not allow simple determination of the bulk valence (because of the difficulty of subtracting background and of the extreme surface sensitivity of UPS), or to final-state effects in XAS and/or PES.

## EXPERIMENTAL DETAILS

The starting materials were flux-grown crystals of $YbCu_2Si_2$, $YbAl_3$, $LuAl_3$, and $YbPb_3$, and polycrystalline samples of $LuCu_2Si_2$, $YbAgCu_4$, $LuAgCu_4$, and $YbAuCu_4$ grown in sealed tantalum tubes. These were powdered and diluted with BN powder to minimize self-absorption,

and pressed into a 1-mm-thick slotted aluminum sample holder windowed with kapton tape. The x-ray-absorption measurements were performed in the transmission mode on beamline 7-3 at the Stanford Synchrotron Radiation Laboratory (SSRL). A Si(220) double-crystal monochromator was used, detuned 50% at the end of the scan (344 eV for Yb, 9644 eV for Lu) to minimize harmonic contamination in the incident radiation. For the room-temperature measurements the samples were studied in air; for the low-temperature spectra the samples were loaded in a continuous flow LHe cryostat (Oxford Instruments CF1208). X-ray intensities $I_i$ and $I_t$ of the incident and transmitted beams were measured with $N_2$-filled ionization chambers of standard design. The photon energy was calibrated using an internal copper foil standard. We extended the scans from 200 eV below to 400 eV above the Yb and Lu $L_{III}$ edges; the absorption coefficient was fit to a linear background function below the edge and, after subtracting this background, the spectra were normalized to unity in the extended x-ray-absorption fine-structure (EXAFS) region.

## RESULTS AND ANALYSIS

The absorption coefficient $\mu = \ln(I_i/I_t)$ for all three compounds at 10 and 300 K is shown in Fig. 1. The spectra for related trivalent Lu compounds are also shown; the energy scale for these compounds has been shifted by approximately 300 eV, the difference between the Lu and Yb $L_{III}$ thresholds. We make the standard assumption[7,8] that absorption from trivalent Yb compounds would be identical to these Lu spectra. For each of the three Yb compounds, there is enhanced absorption near 8940 eV, representing absorption from the divalent component of the mixed-valent ground state, and reduced absorption near 8947 eV, representing decreased absorption from the trivalent component. These effects increase systematically as the temperature is lowered, giving the primary evidence that the bulk valence changes with temperature in the range 10–300 K.

To quantify the valence change, we first remind the reader that the final states of $L_{III}$ absorption must have $d$

symmetry about the absorption site. In trivalent rare earths, the $L_{III}$ spectra are dominated by a strong absorption peak ("white line") at threshold, for which there is evidence[14] that the $2p$ core hole localizes the transition $5d$ electron. In addition, there is a continuum of absorption extending several hundred eV above threshold into the EXAFS region, representing extended final states. We thus fit the absorption in the trivalent Lu compounds [e.g., Fig. 2(a)] as a sum

$$\mu_3(E)=\mu_{loc}(E)+\mu_{ext}(E) , \qquad (1)$$

where we approximate the white line $\mu_{loc}(E)$ as a Gaussian with a Lorentzian tail, and the extended emission $\mu_{ext}(E)$ is set equal to the difference between the total experimental spectrum and $\mu_{loc}(E)$. We then assume that the $L_{III}$ spectra for each mixed-valent Yb compound can be analyzed as a sum:

$$\mu(E)=n_f\mu_3(E)+(1-n_f)\mu_2(E) , \qquad (2)$$

where $\mu_3(E)$ (taken from the fits to the corresponding Lu compound) now represents absorption from the trivalent $4f^{13}$ component, and $\mu_2(E)$ the absorption from the divalent $4f^{14}$ component of the initial state. We assume
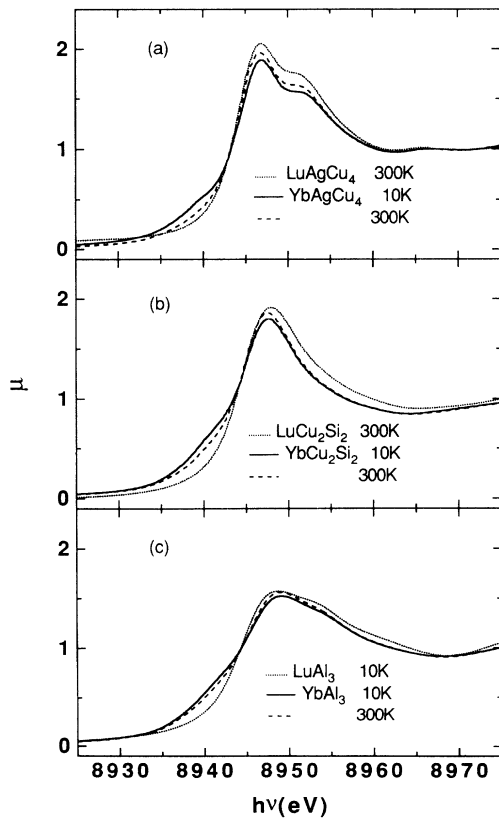


FIG. 1. X-ray-absorption coefficient $\mu$ near the Yb $L_{III}$ edge as a function of energy for $T=10$ and 300 K for the mixed-valent compounds (a) YbAgCu$_4$, (b) YbCu$_2$Si$_2$, and (c) YbAl$_3$. Data for the corresponding trivalent Lu compounds are shown for comparison. (The Lu $L_{III}$ edge occurs near 9248 eV; the energy scale for the Lu compounds has thus been shifted down by 301 eV.)
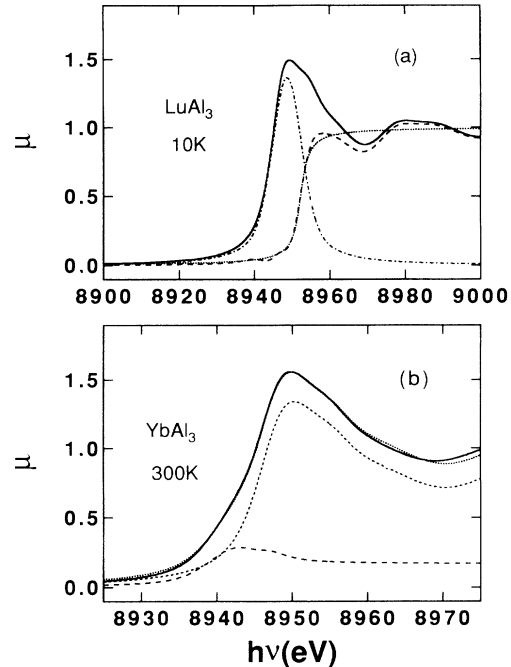


FIG. 2. The method for extracting the $4f$ hole occupation number $n_f$ for the Yb compounds. (a) Data for LuAl$_3$ (solid line), the local trivalent absorption $\mu_{loc}(E)$ (dash-dotted line), and the extended state absorption $\mu_{ext}(E)$ (dashed line). The dotted line approximates $\mu_{ext}(E)$ as an arctangent. (b) Fit (dotted line) to the data (solid line) for YbAl$_3$ at $T=300$ K using Eq. (2). The short-dashed and long-dashed lines represent $n_f\mu_3(E)$ and $(1-n_f)\mu_2(E)$, respectively (see the text for the definition of these terms).

that the divalent white line is a replicate of the trivalent peak, i.e.,

$$\mu_2(E)=\mu_3(E-\Delta E) , \qquad (3)$$

where $\Delta E=7$ eV is the difference between the $f^{13}$ and $f^{14}$ absorption edges. These differ in energy, by an amount also calculated to be of order 7 eV, because the interaction between the core hole and the final-state electron is screened differently by the two configurations.[15] For $\mu_2$ we approximated $\mu_{ext}(E)$ by an arctangent curve as in Fig. 2(a), but shifted by 7 eV. For a given Yb compound we let the ratios of the heights of the white lines to the EXAFS step heights vary by as much as 10% from the ratios for the corresponding Lu compound, to improve the overall fits. We constrained these ratios as well as the various widths and positions, so that $n_f$ was the only parameter varying with temperature; a typical fit is shown in Fig. 2(b). The resulting occupation numbers $n_f$ are shown as a function of temperature in Fig. 3. [The compound YbAuCu$_4$ was found to be nearly trivalent ($n_f=0.985$) by this procedure.]

Krill has argued[8] that the shape of the divalent spectrum $\mu_2(E)$ is not necessarily a replicate of the trivalent spectrum $\mu_3(E)$; the width and height of the white line and the shape of the extended state absorption can all differ. For example, a secondary maximum 4–5 eV above the white line appears to be a common feature of
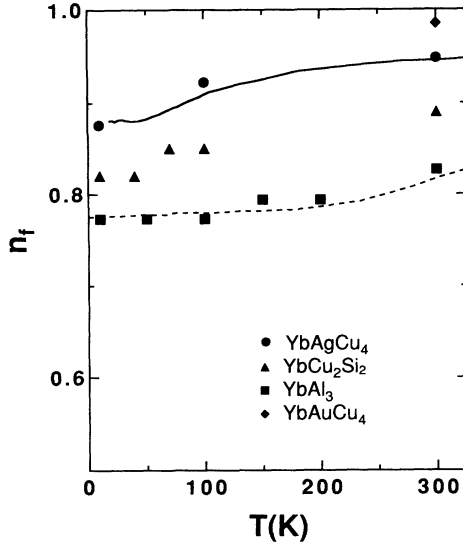
FIG. 3. The $4f$ hole occupation number $n_f$ vs temperature for all three compounds, extracted by fitting Eq. (2) to the $L_{III}$ absorption data, as in Fig. 2. The solid and dashed lines are the predictions of the Anderson impurity model for $YbAgCu_4$ and $YbAl_3$, respectively (see text).
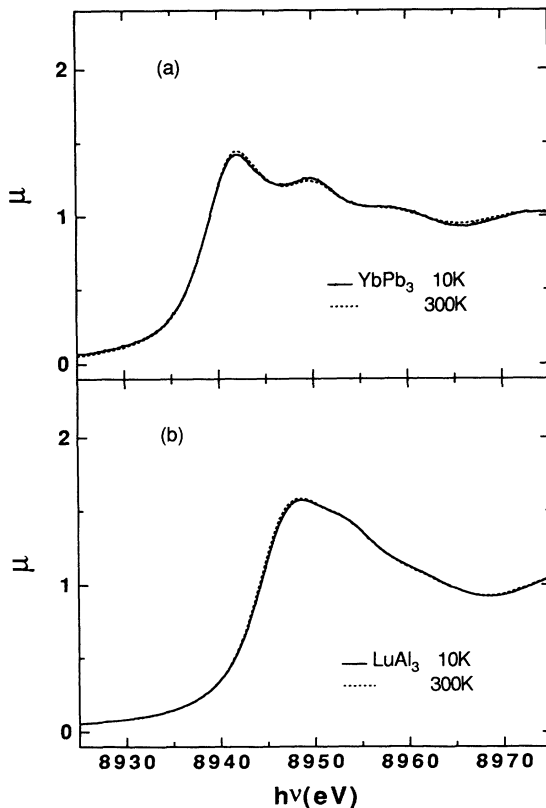


FIG. 4. The $L_{III}$ absorption coefficient at $T=10$ and 300 K for (a) the divalent compound $YbPb_3$, and (b) the trivalent compound $LuAl_3$, demonstrating that the temperature dependence observed for the mixed valent Yb compounds in Fig. 1 is not a background effect.

trivalent $RXCu_4$ compounds (see below) but should not be expected *a priori* to exist for divalent compounds. Given such uncertainties, we believe our method of data analysis correctly determines the magnitude of $n_f$ to only 5–10 %, but determines the relative variation with greater accuracy (to 1–2 %).

While it is well known that peaks in the EXAFS region become broader at high temperatures due to lattice vibrations, it is less clear the degree to which ordinary temperature dependence affects the near-edge region. To establish this, in Fig. 4 we exhibit spectra for the $L_{III}$ edge of the trivalent compound $LuAl_3$ and the divalent compound $YbPb_3$; there is no variation with temperature in the near-edge region. We conclude that the changes observed in the spectra of the Yb compounds in Fig. 1 do not arise from background effects.

## DISCUSSION

We consider first the $L_{III}$ spectrum of the compound $YbAgCu_4$ shown in Fig. 1(a). The "white line" at 8947 eV arises from the transition (from the trivalent component of the initial state)

$$2p^6 \cdots 4f^{13}(5d\,6s)^3 + h\nu \rightarrow 2p^5 \cdots 4f^{13}(5d\,6s)^3\varepsilon_d ,  \qquad (4)$$

where $\varepsilon_d$ represents the localized $5d$ final state. The maximum at 8952 eV is unusual in that secondary maxima are rarely observed so close to the white line in rare-earth compounds. The most likely interpretation of this secondary maximum (which we also observed 4–5 eV above the white line in the $L_{III}$ spectra of the trivalent compounds $YbAuCu_4$ (not shown) and $LuAgCu_4$ [Fig. 1(a)]) is that it arises from a peak in the density of rare-earth $(R)$ $5d$ conduction electron states 4–5 eV above the Fermi level $\varepsilon_F$. Such a peak in the density of states is seen in the inverse photoemission (BIS) spectra of $RXCu_4$ $(X=\text{Ag,Au,Pd}; R=\text{Yb,Lu})$.[16] A similar peak has been seen[17] in BIS spectra for $RPd_3$ compounds, where the interpretation is that hybridization with the top of the transition-metal $d$ band repels $R$ $5d$ weight from below to above $\varepsilon_F$; this interpretation is also plausible for $RXCu_4$. We note that there is a hint of a similar structure 5 eV above the white line in $LuAl_3$ [Fig. 1(c)].

We now turn to our primary result, which is the temperature dependence of $n_f$ (Fig. 3). To compare to theory we first note that the predictions of the Anderson impurity model are sensitive to both crystal-field and spin-orbit splittings. The latter is 1.3 eV for Yb. For $YbCu_2Si_2$, neutron-scattering[10] results suggest the presence of crystal-field excitations at 12, 30, and (possibly) 80 meV. The neutron quasielastic linewidth is 4–5 meV,[10] consistent with a Kondo temperature 50–60 K; and use of the Bethe-ansatz formula $T_K = \pi R/6\gamma$ relating the measured linear coefficient of specific heat[9] to $T_K$ for a Kondo doublet $(N_0 = 2)$ gives $T_K = 32$ K. For $YbAgCu_4$ the susceptibility[11] shows a maximum at 35 K; the quasielastic linewidth is 7–8 meV and no crystal-field excitations are seen in the neutron spectra.[12] These results suggest that $YbAgCu_4$ is a mixed-valence compound with ground-state degeneracy $N_0 = 8$, and a Kondo tem-

perature of order 100 K. Similarly, for $YbAl_3$ our measurements of the susceptibility show that a maximum occurs at 125 K; and the quasielastic neutron linewidth[13] has been shown to be 40 meV. These results again suggest an $N_0 = 8$ ground-state manifold and $T_K \cong 400$ K. While, to the best of our knowledge, no calculations of $n_f(T)$ exist for these cases,[5] calculations[1,18] exist for mixed-valent $N_0 = 6$ and $N_0 = 8$ impurities in the absence of spin-orbit splitting and also for spin-orbit split mixed-valent Ce ($N_0 = 6$; $N_{SO} = 8$). Since in the latter case $n_f(T)$ follows approximately the same scaling law as in the former, and since the case of mixed-valent Yb ($N_0 = 8$; $N_{SO} = 6$) is similar, we have used the results of Ref. 1 to estimate the predictions of the Anderson impurity model for $YbAl_3$ and $YbAgCu_4$. Using $T_K = 400$ K, $n_f(0) = 0.775$ and $T_K = 100$ K, $n_f(0) = 0.875$, respectively, and the scaling law (Fig. 14 of Ref. 1), we generated the curves shown in Fig. 3. The agreement with experiment is satisfactory. For $YbCu_2Si_2$ the valence clearly changes with temperature, but $n_f(T)$ does not approach the high-temperature limit (0.98) fast enough, given the small $T_K = 40$ K. In addition, the ground state is more mixed valent than $YbAgCu_4$, even though $T_K$ is larger for the latter compound. These discrepancies may reflect the uncertainties of our fitting procedure (especially its 5–10 % uncertainty in absolute value of $n_f$); alternatively they may reflect an as-yet uncalculated crystal-field effect.

Insofar as these results imply that the bulk Yb valence varies with temperature, one might expect comparable changes in the PES spectral density with temperature, independent of any model. We now argue, however, that these results do not resolve the issue of whether such changes are, or should be, observed in photoemission.

We first emphasize that there is a real disagreement in the literature as to the correct form for the bulk 4f photoemission spectra. In large part this disagreement reflects the fact that the experiments have been performed on samples that are not well characterized by the standards of modern surface science. Samples are often polycrystals[3,5,6] that in some cases[6] are contaminated by significant amounts of a second phase; and whether polycrystal or single crystal, the near-surface structures and stoichiometries have not been determined. The samples oxidize rapidly, but the degree of oxidation is seldom quantified; however, it is known that oxidation can cause dramatic effects on the valence-band spectra, and can lead to false conclusions concerning temperature dependence.[4] The spectra are also history dependent; they vary for different cleaves[5] and depend on the sequence of thermal cycling.[4] In addition to this high level of irreproducibility, there is disagreement as to determination of the non-bulk-4f background in UPS. This background contains 5d and other non-4f emission, 4f surface states which are broad and which can change with temperature, and secondary emission. Different choices of background can lead to very different conclusions about the degree of temperature dependence of the spectra (e.g., Refs. 4, 5, and 6).

In addition to these experimental uncertainties, there are reasons why the UPS experiments might not determine the true blue valence. The first possibility concerns the extreme surface sensitivity of UPS. Various studies[19–21] of Sm and Yb films and compounds suggest that the surface tends to be divalent even when the bulk is trivalent or mixed valent; large surface reconstruction[20] due to the differing size of the $4f^{13}$ and $4f^{14}$ ion can occur. In the PES studies of $YbCu_2Si_2$,[2] $YbAgCu_4$,[3,5] and $YbAl_3$,[4,6] a clearly defined divalent surface signal is observed and can be subtracted off. We raise the possibility that the remaining "bulk" signal does not represent the true bulk but represents an intermediate layer extending several monolayers into the bulk where the lattice constant is somewhat expanded, the valence closer to $2^+$, and hence the Kondo temperature larger than in the bulk. The PES experiment would then fail to observe the thermal valence change in the range 10–300 K if the Kondo temperature in this intermediate region were much greater than 300 K.

A second possibility concerns final-state effects. Malterre[22] has shown for XRA that screening of the different final $f^n$ configurations can lead to a transfer of spectral weight so that the divalent/trivalent ratio deduced from the $L_{III}$ measurements would not be that of the ground state. In rare-earth core-level photoemission,[23] a typical final-state effect is a "shake down" satellite where an empty $f$ orbital captures an outer electron to improve the screening of the core hole. In Yb valence-band UPS it is plausible that screening might cause a transfer of weight from the trivalent peaks to the divalent peaks, making the system appear more mixed valent than in actuality.

## CONCLUSION

Our $L_{III}$ x-ray-absorption results for $YbAl_3$, $YbCu_2Si_2$, and $YbAgCu_4$ suggest that the valence changes continuously with temperature in a manner consistent with the predictions of the Anderson impurity model. This appears to contradict recent valence-band photoemission results in the same compounds, where little $T$ dependence is observed. Resolution of the discrepancy, in our opinion, requires a better understanding of surface effects and background effect in UPS. These difficulties are not unique to the Yb compounds discussed here; rather they plague the whole body of studies of heavy-fermion valence-band PES. In addition, a better understanding of final-state screening effects in both UPS and XAS is needed.

## ACKNOWLEDGMENTS

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