# Revisiting the Yb electronic structure with low-energy photoemission spectroscopy

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Low-energy photoemission spectroscopy in the photon energy range between 5.5 and 21 eV is used to investigate the valence electronic structure of Yb polycrystalline films. With the lowering of the photon energy below 11 eV, additional spectral features, nearly absent at higher photon energy, become predominant, in particular a peak located right at the Fermi level. With the help of an *ab initio* theoretical calculation, we interpret the peak as due to the joint influence of filled and empty densities of states, identifying a *p*-band contribution close to the Fermi level, whose intensity is strongly enhanced at certain photon energies corresponding to modulation of the empty *d* band.

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#### I. INTRODUCTION

The electronic structure of rare-earth elements and their compounds has been intensively studied, over the years, because of its peculiar partially filled 4f band. The localized 4f core level electrons are closer to the positive ions than the 5d and 6s bands and therefore do not participate to the chemical bonding and carry strong magnetic moments. Of particular interest is the investigation of the valence states in rare earths and their compounds, which is linked to the degree of the hybridization of f electrons with delocalized s-d bands.<sup>1</sup> Recently, for example, the valency of Yb metal has been confirmed as 2+ by means of hard x-ray excited photoelectron emission spectroscopy (PES) supported by theoretical calculations.<sup>2</sup> This study suggests that in the bulk, as at the surface, the 4f states in Yb metal are fully occupied and that the observed spectral weight at the Fermi level has to be attributed to 6s electrons. The occupation of the Yb valence band has been the subject of several investigations over the years, intended in particular to separate the contribution of 5d states.<sup>3</sup> Early theoretical band calculations of hcp Yb located a very steep 5d empty band just at the Fermi level<sup>4</sup> and high-resolution PES experiments, with an excitation energy of 40 eV, explained a weak peak observed at the Fermi level with such a structure.<sup>5</sup> A prominent peak at the Fermi level has been on the other hand generally observed in PES experiments from single-crystal close-packed lanthanide surfaces and attributed to a localized d-like surface state.<sup>6</sup> This was also the case of PES spectra from fcc Yb(111) thin film: In the photon energy range  $h\nu = 25-45$  eV a prominent peak was observed at the Fermi level, sharply localized in the normal emission direction.<sup>7</sup> On the other hand, theoretical calculations from the same authors were unable to confirm that the observed structure was a surface state.

It has to be noted that early experimental PES spectra at very low excitation energy (hv < 10 eV) have reported a spectral modulation in the region close to the Fermi level that was attributed to the emission from a 5*d* band.<sup>8,9</sup> The reference for this work was a theoretical calculation in which the Yb valence band was described as a hybridization between the 6sp band and the broad 5d band that crosses the Fermi level.<sup>10</sup> The poor energy resolution did not allow however a detailed investigation of such spectral features. In recent years this lowenergy photoemission spectroscopy (LEPES) encountered a renewed interest, under the stimulus of the extremely high energy resolution obtainable with laser excited LEPES,<sup>11</sup> and given the expectation of a large increase of the bulk sensitivity at these low energies.<sup>12</sup> Actually, we pointed out that the bulk sensitivity in the LEPES regime may be lower than the expectation and it may strongly depend on the material, with the further warning that theoretical efforts have to be undertaken for a clear interpretation of the photon energy dependence of the LEPES spectra.<sup>13</sup> Furthermore, we recently monitored the 4f spectral intensity in polycrystalline Yb films in the LEPES regime, observing a moderate increase of the electron attenuation length and, thus, a moderate increase of the information depth when we reach the lowest energies.<sup>14</sup> Since the 4fphotoemission cross section strongly decreases by decreasing the photon energy, additional features can be observed in the photoemission spectra and are here investigated at different temperatures, emission angles, and photon energies. In this way, with the help of ab initio theoretical calculations of the Yb bulk electronic structure in the framework of density functional theory (DFT), we infer the orbital character of the Yb valence band, identifying, at odds with earlier reports, a p-band contribution close to the Fermi level, whose intensity is strongly enhanced at certain photon energies corresponding to modulation of the empty d band. The latter conclusion is drawn by interpreting LEPES as a probe of the joint density of states (DOS).<sup>15</sup>

## **II. METHODS**

## A. Experiments

The experiments were performed at the BaDElPh beamline of the ELETTRA synchrotron radiation facility of Basovizza,

Trieste (Italy).<sup>16</sup> PES spectra were detected by a hemispherical electron analyzer of variable acceptance angle and energy resolution. Unless otherwise indicated, room temperature normal emission spectra were taken with an overall energy resolution of 110 meV and with an angular acceptance of  $\pm 7^{\circ}$ . The binding energy scale was determined by the Fermi level position of the clean polycrystalline W substrate. Yb was evaporated by resistive heating of high-purity pieces (99.9% purity) contained in a tungsten basket on a sputtered clean W polycrystal. The pressure during evaporation increased from its base value of low  $10^{-8}$  Pa to about  $10^{-6}$  Pa and the evaporated films did not show any low-energy electron diffraction (LEED) patterns. Freshly evaporated Yb films were oxygen free, within the limits of the experimental sensitivity, as established by the absence of the O 1s core level peak in Al  $K\alpha$  excited PES spectra and the absence of the O 2pband at about 6 eV of binding energy in PES spectra excited by  $h\nu = 21$  eV. We show in the next sections results from Yb films of thickness such that no spectral features from the tungsten substrate were discernible with Al  $K\alpha$  excited PES in a 45° emission angle geometry. Taking into account this observation, under the common hypothesis that a core level peak from the substrate is attenuated exponentially from the overlayer,<sup>17</sup> we could attempt a rough estimation of the minimum thickness of the Yb film. Since the 4f core level electrons from W are emitted with a kinetic energy of about 1450 eV, their inelastic mean-free path in Yb is about 28 Å.<sup>18</sup> By making the further approximation that in our experimental condition this parameter is close to the effective electron attenuation length, the peak from the substrate would be reduced to 5% of its initial (i.e., without overlayer) value for an overlayer thickness of about 84 Å in a normal emission geometry or to 59 Å in our 45° emission geometry. This last value is thus what we can quote as an approximate minimum thickness of our Yb film.

#### **B.** Numerical simulation

We performed *ab initio* theoretical calculations of the Yb bulk electronic structure in the framework of DFT. The Yb bulk has been modeled by an fcc lattice. The cell parameter for the calculation is a = 5.485 Å. We used the exchange-correlation potential within a generalized gradient approximation as proposed in Ref. 19. The full potential approach is used together with the linearized augmented plane wave (FLAPW) basis set. The kinetic energy cutoff for the plane wave expansion has been fixed to 16 Ry and the spherical expansion into the muffin tin, containing the atoms, goes up to l = 8. The *k*-point mesh is  $22 \times 22 \times 22$ , corresponding to 1012 inequivalent *k* points for the integration in the irreducible Brillouin zone.

## **III. RESULTS**

Figure 1 compares room temperature normal emission spectra taken at different photon energies from an as-deposited film. The spectra acquired at hv = 21 eV from the clean sample (black solid line) shows two sets of spin-orbit split features, each consisting of a bulk (*B*) and a surface (*S*) component, in agreement with early reports from polycrystalline films.<sup>20</sup> By



FIG. 1. Photoemission spectra acquired at room temperature in a normal emission geometry taken at selected photon energies.

fitting this spectrum with Voigt profiles for each component, plus integral background, we estimate a surface core level shift of  $0.59 \pm 0.01$  eV, a result in line with that obtained in polycrystalline samples<sup>21</sup> and quite larger than that reported for single-crystal Yb(111) thin films.<sup>7</sup> The spin-orbit splitting of  $1.27 \pm 0.01$  eV compares well with literature results.<sup>2</sup> The width of the surface core level shifted component is quite larger than the bulk one, accounting for surface atoms with different coordination numbers.<sup>22</sup> Upon changing photon energy, spectral features are largely modified compared to the spectrum taken at  $h\nu = 21$  eV as can be seen in Fig. 1, where photoemission spectra acquired in a normal emission geometry and for selected photon energy of  $h\nu = 15$  eV,  $h\nu = 10$  eV,  $h\nu = 8$  eV, and  $h\nu = 7$  eV are also reported. In particular, by lowering the photon energy a prominent peak develops close to the Fermi level followed by a larger bump at higher binding energy, labeled in the spectrum taken with hv = 7 eV as A and C, respectively.

In order to shed light on their origin we investigate in Fig. 2 their angular dependence. In particular, Fig. 2(a) displays spectra taken at room temperature with photon energy hv = 7.5 eV and analyzer acceptance angle of about  $\pm 4^{\circ}$  for different polar emission angles  $\theta$  ( $\theta = 0$  corresponds to normal emission direction). Barely visible in the spectra are the 4f bulk components, as indicated by the vertical dotted line, whose binding energy position is unchanged by varying the emission direction. On the other hand, the bump observed at a binding energy of about 0.7 eV in the normal emission spectrum shows a pronounced angular dependence,



FIG. 2. (a) LEPES spectra taken at hv = 7.5 eV at different emission angles as indicated. (b) Binding energy position versus polar emission angle of the bump labeled in (a) by short arrows.

as evidenced by the short arrows indicating the bump position. This is quantified by determining the binding energy position of the bump maxima plotted versus the emission angle  $\theta$  in Fig. 2(b) as solid symbols. The dashed line superimposed on the experimental points is the result of a fit with a function of the form  $y = a + bx^2$ . The minimum of the curve, i.e., the maximum binding energy, corresponds to normal emission direction ( $\theta = 0$ ).<sup>23</sup> From Fig. 2(a) one can also see that the peak at the Fermi level does not appear to have an angular dispersion within the experimental resolution of the spectra and, furthermore, does not show an evident intensity variation, taking into account that its shape is modified at some emission angles by the angular dispersion of the bump *C*.

The temperature dependence of peak A is displayed in Fig. 3(a), where two spectra from the same sample taken at hv = 9 eV in normal emission are shown at T = 255 K (open circles connected by thin solid line) and T = 10 K (thick solid line). Due to the large difference in the acquisition temperature between the two spectra, the contribution of thermal broadening is much different, being larger in the spectrum taken at 255 K. It is evident that the spectrum taken at lower temperature shows a much narrower peak, with the maximum shifted toward the Fermi level. This effect might be attributed to a temperature dependence of the spectral features, and/or simply to the fact that the decrease of thermal broadening has the same effect of improving the energy resolution. Therefore in Fig. 3(b) two spectra are compared taken with hv = 7.5 eV at the same temperature, T = 10 K,



FIG. 3. (a) LEPES spectra taken in normal emission for hv = 9 eV with the sample at 255 K (open circles connected by thin solid line) and 10 K (thick solid line); (b) the peak at the Fermi level measured for hv = 7.5 eV at T = 10 K is reported as acquired with two different energy resolutions of  $\Delta E = 25$  meV (open squares and line) and  $\Delta E = 8$  meV (solid circles and line).

with two different analyzer pass energy (PE) of 5 eV and 1 eV, corresponding to an overall energy resolution ( $\Delta E$ ) of about 25 meV and 8 meV, respectively. Indeed, the spectrum taken with the best energy resolution peaks even more toward the Fermi level, with a narrower width than the spectrum taken at worst energy resolution.

Theoretical calculations have been performed to help the interpretation of the experimental results and in Fig. 4 the calculated DOS is plotted versus binding energy for every orbital components of interest, as labeled in the different panels. The vertical dashed line crossing all four panels corresponds to the position of the Fermi level, the zero of the binding energy scale. Spin-orbit coupling was not included in the calculation; thus in the f orbital panel only a single peak is observed. Its binding energy position is moreover much smaller than what is experimentally observed in Fig. 1. As emphasized in Ref. 24 a better description of the 4f core level would have been obtained by allowing on-site Coulomb potential applied to these states which was not performed here since the interest was more focused on the valence band behavior. Note that the left ordinate scale is the same for the s, p, and d orbital components, while it is about 35 times larger for the f orbital. Indeed, the f DOS dominates over the other orbital components and is sharply localized at a defined binding energy.



FIG. 4. *Ab initio* theoretical calculation of the orbital components of the Yb electronic structure.

## **IV. DISCUSSION**

The photon energy dependence of the Yb spectra reported in Fig. 1 shows several interesting features, namely: (i) a strong decrease of the 4f emission intensity upon decreasing photon energy and a concomitant increase of the emission close to the Fermi level (peak labeled A in Fig. 1); (ii) the presence of a bump C at binding energy 0.5–0.8 eV, whose intensity and shape are very sensitive to the used photon energy and emission angle (see Fig. 2); (iii) a strong decrease in intensity of the 4fsurface components relative to the bulk one, due to increased volume sensitivity at lower excitation energy.<sup>14,25</sup> This latter aspect has been investigated in some detail in Ref. 14 where, from the ratio between the intensity of the surface and the bulk components, it was possible to estimate the energy dependence of the effective electron attenuation length.

We want to discuss here in some detail the possible origin of the peak A. We recall that prominent peaks close to the Fermi level have been measured, at selected photon energy excitations, from several single-crystal surfaces of lanthanides and attributed to d-like states confined at the surface (*surface state*).<sup>6</sup> More specifically, also the peak at the Fermi level observed in photoemission spectra from Yb(111) films grown on Mo(110) in an energy range between hv = 25 eV and hv = 45 eV was interpreted as a surface state.<sup>7</sup> However, the same authors pointed out that quenching of the state by oxygen exposure was not satisfactory and theoretical calculations did not reveal the explicit presence of a surface state for the Yb(111), making the hypothesis less straightforward than for the other lanthanides. In any case,

it has to be noted that the peak measured in Ref. 7 showed a prominent angular dependence, disappearing for emission angles larger than about  $5^{\circ}$  from the surface normal. This is obviously not the case for the structure we measured here, since, as shown in Fig. 2(a), the peak at the Fermi level presents a rather smooth angular variation. Furthermore, we recall that the experiments reported here have been performed on polycrystalline surfaces; thus the narrow prominent peak we observe is the result of an average over all the possible microcrystallite orientations, not so easily related to the presence of a surface state at selected crystal orientations. Having ruled out the hypothesis of a surface state to explain the observed peak, also some more exotic explanations, where electron correlations come into play, do not seem to have strong basis. For example, theoretical calculations have shown that even elemental Yb, under pressure, features valence transition and charge fluctuation, resulting in a hole doping of the 4fshell and increasing hybridization of the 4f with the valence band.<sup>26</sup> As a consequence, quasiparticle-like contribution at the Fermi level is predicted. In the present case it is however hard to put forward an explanation of this sort, since the only parameter we changed, giving rise to the appearance of the peak at the Fermi level, is the photon energy. The obvious relation to the increased bulk sensitivity<sup>14</sup> is ruled out by the fact that bulk-sensitive hard x-ray excited PES (HAXPES), with a total energy resolution of about 200 meV, does not measure such a peak.<sup>2</sup>

The only plausible explanation is, thus, that we are detecting a band of ytterbium, rather extended in k space to be observed also on experiments on polycrystalline targets. Its large increase by decreasing photon energy might be related to a photoionization cross section effect. Even if the classical Yeh and Lindau tables of atomic photoionization cross section do not cover the low-energy regime investigated here,<sup>27</sup> still the extrapolation at energies lower than 20 eV of the data available for Yb 4f would suggest a decrease of their photoionization cross section, thus supporting our experimental observation. Indeed, the photoemission experiments in the LEPES regime on Yb conducted in the past, mainly devoted to localizing the energy position of the 4f orbitals upon excitation with extreme ultraviolet light,<sup>8</sup> also suggested that the 4f photoemission cross section decreases upon decreasing photon energy, as confirmed by our results. In addition, they reported a prominent peak close to the Fermi level measured at an excitation energy of  $h\nu = 5.3$  eV, whose intensity was decreasing upon increasing photon energy and disappearing at about  $h\nu =$ 9 eV.<sup>9</sup> The peak was attributed to a structure in the band located immediately below the Fermi level, its disappearance for photon energy above 9 eV reflecting the absence of available final states, thus estimating the upper of the d bands in Yb to be approximately 9 eV above the Fermi level. The present results reveal on the other hand that a structure at the Fermi level persists at higher photon energies than earlier suggested. Figure 1, for example, shows that a peak at the Fermi level is clearly present in the spectrum taken at hv = 10 eV. Actually, the intensity at the Fermi level is not completely flat even in the spectrum excited with the maximum photon energy used in the present work, namely 21 eV. Early high energy resolution PES spectra, taken at even higher photon energy, hv = 40.8 eV, from Yb films grown on a sapphire substrate, also revealed the presence of a weak peak culminating at the Fermi level; it was attributed to a structure of the band, more precisely to the onset of the 5d band.<sup>5</sup> As mentioned in the introduction, this conclusion was supported by theoretical calculations of hcp Yb, locating the Fermi level in a dip just at the onset of a very steep peak in the density of states, predominantly of d character.<sup>4</sup> Our experimental data might support this interpretation if we assume that with decreasing photon energies, concomitant with the decrease of the 4f photoionization cross section, there is a strong increase of, for example, the 5d or 6p photoionization cross section, which is partly occupied. Indeed, for example, the 5d level in atoms, which begins to be occupied from the element lanthanum, shows a photoionization cross section which strongly increases with decreasing photon energies being more than two orders of magnitude larger than the 6s atomic photoionization cross section at energy of 10 eV.<sup>27</sup> We might thus suppose that also in Yb, with decreasing photon energy, the photoionization cross section of the 5d band becomes higher and higher than the one of the 6s band. Since this 5d band is partially occupied and steeply increases while crossing the Fermi level, a peak may result in the spectral function, where the density of states is cut by the Fermi function itself. It would than be understood why by improving the energy resolution [see Fig. 3(b)], the maximum of the peak shifts toward the Fermi level. A qualitative support to this interpretation derives from the simulation of our experimental results making use of the theoretical calculations shown in Fig. 4. In Fig. 5 open circles represent the normal emission PES spectrum taken with a photon energy of hv = 7 eV at a temperature of T = 20 K, displayed in a narrow energy range around the Fermi level, while the solid line has been obtained by summing up the DOS for each orbital component (see Fig. 4) multiplied by a Fermi function at the appropriate temperature, and convoluted by a Gaussian function with a full width at half maximum equal to the overall experimental energy resolution of 25 meV. The curve better representing the experimental data, namely reproducing the peak at the Fermi level and having an almost flat intensity for binding energy larger than 0.2 eV, was obtained by allowing a d contribution



50 times larger than the other orbital components. However, a

FIG. 5. Photoemission spectra (symbols) taken at excitation energy of hv = 7 eV and temperature of 20 K compared with theoretical calculations (see text for more details).

shift of the energy scale of the calculation by 50 meV toward higher binding energy has to be introduced. While such a small correction may be considered insignificant on an absolute scale, it has a strong influence in defining the character of the band at the Fermi level, since both the p and the d orbitals have some intensity crossing the Fermi level, as a close look to Fig. 4 reveals. The argument is thus not conclusive for what concerns the definition of the orbital character of the A peak. Moreover, it has to be taken into account that the intensity of the peak A is quite temperature independent, as shown in Fig. 3(a), where the two spectra have been normalized above the Fermi level and at about 0.5 eV of binding energy. On the contrary, if the peak was due to a band crossing the Fermi level, a strong temperature dependence would have been observed, due to the temperature dependence of the Fermi function. This is demonstrated in the inset of Fig. 5, where the curve obtained at T = 20 K (black line) is compared with the theoretical calculation multiplied by a Fermi function at T = 300 K (gray line). The curve obtained at larger temperature presents a smaller and larger peak at higher binding energy than the one obtained at T = 20 K. This variation is not observed in our experimental results [see Fig. 3(a)]. Summarizing this discussion we can thus state that an energy dependence of the photoionization cross section may indeed play a role in enhancing the emission at the Fermi level at low photon energy, but this effect alone does not completely account for our experimental results.

In order to establish the orbital character of the A peak, we tried to quantify the photon energy dependence of its intensity variation. We analyzed the room temperature spectra by normalizing each spectrum to zero intensity above the Fermi level by subtracting a linear background and we then subtracted the spectral intensity of an appropriate, in term of energy resolution and temperature, Fermi function. As an example Fig. 6(a) shows as thick solid line the spectrum taken at hv = 8.5 eV and the Fermi function (thin solid line)



FIG. 6. (a) LEPES spectrum (thick solid line) at hv = 8.5 eV after subtraction of a linear background; thin solid line is a Fermi function with an edge consistent with the experimental energy resolution of the spectrum, multiplied by a linear slope. (b) The same as in (a) in a narrower binding energy region. (c) Difference of the spectrum and the Fermi function of (b); the patterned region is the integral of the curve, used to estimate the intensity of the peak at the Fermi level in the experimental spectrum.



FIG. 7. Circles with error bars represent the intensity of the peak at the Fermi level, evaluated, as explained in Fig. 6(c), at the different photon energies. The line superimposed on the experimental points is a guide to the eyes. The thin solid line is the calculated density of states corresponding to the empty *d* band, while the dotted line represents the total empty DOS, broadened by the experimental energy resolution of the photoemission experiment.

multiplied by a linear function accounting for the behavior at larger binding energy. The same curves are replotted in Fig. 6(b) in a narrow binding energy region to highlight the peak at the Fermi level. Finally Fig. 6(c) shows as solid circles the result of the difference between the experimental spectrum and the Fermi function. Superimposed on the data is a curve representing a Gaussian best fit whose area (patterned region) has been taken representative of the intensity of the peak at the Fermi level. The peak intensity has been then normalized to the photon flux at each photon energy, as measured by a photodiode immediately before and after data acquisition. The result of this analysis for the spectra taken at the different photon energy is shown as solid circles with error bars in Fig. 7. The thick line superimposed on the experimental points is a guide to the eyes. One clearly sees the pronounced modulation of the intensity of the peak at the Fermi level, which grows upon decreasing photon energy down to hv = 5.5 eV, the minimum photon energy used in this work.

The trend of the experimental points of Fig. 7 recalls the photon-energy-dependent intensity variation of the total photoemission yield at low photon energy, attributed in the past to the dielectric response of a metal surface, enhancing the emission intensity due the microscopic fields generated by the spatially varying photon field.<sup>28</sup> This intensity enhancement is reported to become important just below the plasma frequency, and bulk plasmon excitation in Yb is indeed measured at 9.4 eV.<sup>29</sup> Moreover, also electron emission by surface plasmon deexcitation has been put forward in the past for explaining the increase of electron yield at low photon energy.<sup>30</sup> Both effects may indeed play a role in the present case, enhancing the photoelectron yield at the Fermi level; however, they cannot be put forward for explaining the modification of the spectral shape upon lowering photon energy, namely the presence of the peak observed in our experimental data. On the contrary, this effect could reflect the modulations of the joint DOS, since the electrons are excited, by the used low-energy photons,

in an energy region where variation of the empty DOS may be strong. To verify this hypothesis we plot in Fig. 7 as a thin solid line the theoretical empty d DOS, where the energy scale is, in absolute values, coincident with the photon energy, convoluted with a Gaussian function accounting for the energy resolution. Moreover, the thin dotted line in Fig. 7 is the total empty DOS, convoluted with the same Gaussian function. One can notice that the empty DOS is dominated by the contribution of the *d*-orbital component and, indeed, its intensity modulation may explain the intensity enhancement measured in the photoemission spectra. Furthermore, the theoretical curve corresponding to the *d*-band-only empty DOS presents a lower intensity in the region at about 10 eV photon energy, as the experimental data do, and at odds with the behavior of the total empty DOS. It has to be noted that a direct measure of the empty DOS made by bremsstrahlung isochromat spectroscopy (BIS) shows indeed the presence of a bump at about 7 eV,<sup>31</sup> thus not in disagreement with our experimental results. Making use of the classical electric dipole selection rule, under the hypothesis that we are probing a d-empty DOS, we thus conclude that the structure at the Fermi level has either a p or an f character. While some calculations do not exclude the presence of 4f components in the valence band,<sup>24</sup> it is most commonly believed that the 4f are well localized at binding energy larger than 1 eV, with negligible contribution at the Fermi level.<sup>2,32</sup> We have thus to conclude that the bulk electronic structure of Yb consists of a narrow p band located at the Fermi level strongly enhanced in PES spectra at selected photon energies due to the joint contribution of a photoionization cross section effect and a direct transition into an empty DOS of d character, on top of a general increase of the photoemission yield at low photon energy for the effects described above. On the other hand, a speculation that also involves hybridization with 4f it is not in conflict with this scenario. Following a recent work by Kummer *et al.*,<sup>33</sup> the prominent peak at the Fermi level observed in photoemission from Ce due to final-state hybridization between 4f and valence band is absent in Yb because its intensity is somehow distributed over the whole valence band width. In this context the peak we observe in our data could indeed be a signature of this hybridization peak, the p character of which causes the intensity enhancement at low photon energy by the mechanism discussed above. It would then be interesting to test this speculation on the two isostructural phases reported on Yb metal by Weschke et al..<sup>34</sup> Since the two phases may be characterized by a different 4f hybridization with valence states, a different weight may be expected in the peak we observe in the present experiment, similarly to what has been measured for the  $\gamma$ - $\alpha$  transition in Ce metal,<sup>35</sup> with the further generalization that a similar interpretation could be tested for the Fermi-level feature reported by Bodenbach et al.<sup>7</sup> In any case, the observation of a valence band state of pcharacter is compatible with the observation of Matsunami et al. that measured an increase of the Fermi level intensity in HAXPES.<sup>2</sup> They attributed an s character to the Fermi level, since the s photoionization cross section decreases much slower at high photon energies than the 4f photoionization cross section. On the other hand the same argument could be applied to the contribution of a p band, HAXPES being an *sp*-band sensitive probe.<sup>36</sup> The present results are thus not in conflict with what is deduced from the HAXPES experiments.

Up to now, we have neglected bump C appearing at binding energies of 0.5–0.8 eV at photon energies lower than about 10 eV. By looking, for example, at the spectrum taken with hv = 7 eV appearing in Fig. 1, one notes a surprising similarity of its shape with the general behavior of the spectral function when electron correlations are explicitly taken into consideration.<sup>37</sup> In this scenario the peak at the Fermi level would behave as the quasiparticle-like peak, while bump C at higher binding energies would represent the so-called incoherent part of the spectrum. However, as also discussed above, we have no support for an interpretation based on the fact that our spectra outline the presence of strong electron correlation. Moreover, the results of Fig. 2(a) suggest a different angular dependence of the two structures, weakening an interpretation in terms of coherent/incoherent bands. The pronounced parabolic dispersion of the bump [see Fig. 2(b)] might suggest that the origin of the bump resides in the band structure. Indeed, theoretical calculations for the fcc(111)surface suggest that the band structure of Yb metal has almost rotational symmetry around the  $\overline{\Gamma}$  point, with a quite similar parabolic dispersion in the  $\overline{\Gamma}\overline{M}$  and  $\overline{\Gamma}\overline{K}$  directions.<sup>7</sup> Thus, if the close-packed (111) surface mostly contributes to the surface of the Yb film,<sup>38</sup> a dispersing structure as the bump C might be expected in spite of the polycrystalline nature of the sample. Further experiments on single-crystal surfaces might clarify this description and eventually test the suggestive hypothesis that the bump is the result of the merging of quantum well state subbands,<sup>39</sup> dispersing in a free-electronlike parabolic behavior.<sup>40</sup>

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## V. CONCLUSIONS

Low-energy photoemission spectroscopy is used to investigate the electronic properties of Yb films grown on polycrystalline W substrate. By lowering the photon energy below about 11 eV a prominent peak at the Fermi level is observed. By analyzing its intensity variation versus photon energy and by comparing the experimental spectra with ab *initio* DOS calculations we attribute this structure to a p band crossing the Fermi level, enhanced at selected photon energies due to the influence of the empty DOS, probably amplified by a photoionization cross section effect and by the general increase of the photoelectron yield at low photon energy. In this respect LEPES may thus be considered as a probe of the joint DOS. A bump at about 0.5-0.8 eV binding energy is also observed at lower photon energy for which we do not have a conclusive explanation. This structure might be interpreted as reminiscent of an energy dispersing band or as due to the confinement of the electron wave function in the potential well created by the film surface (quantum well state); determination of its origin deserves further experiments on single-crystal surfaces supported by theoretical calculations.

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