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Bulk and surface valence in $YbPd_x$ compounds

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The bulk and surface valence $\overline{v}$ of Yb is investigated for $YbPd_x$ intermetallic compounds (with $x=1,1.33,3$) by photoemission using synchrotron radiation. YbPd is found to be of intermediate valence ($\overline{v}\simeq2.75$), while Yb_3Pd_4 and $YbPd_3$ are identified as bulk trivalent systems. The outermost atomic surface layer of both YbPd and Yb_3Pd_4 is found to be divalent, while only a fraction of Yb surface atoms turns divalent in $YbPd_3$. The results are compared with bremsstrahlung isochromat spectroscopy measurements and predictions based on Miedema's scheme.

I. INTRODUCTION

The $YbPd_x$ intermetallic phases (with $x=1,1.33,3$) are highly interesting compounds with respect to their electronic structure. YbPd and Yb_3Pd_4 were reported to be of intermediate valence,[1-3] while the compound with the highest Pd content, $YbPd_3$, is trivalent.[4] Very recently, the coexistence of intermediate valence and magnetic ordering was claimed for YbPd and Yb_3Pd_4. The trivalent compound $YbPd_3$ also shows an interesting valence-band structure, namely a filled Pd $4d$ band and probably a band gap above the Fermi level.[5,6] On the other hand, the application of Miedema's widely successful scheme on compound formation predicts trivalency for all three compounds with only minor differences in stability,[7] regardless of their crystal structures [YbPd:CsCl (Ref. 1) Yb_3Pb_4:Pu_3Pd_4 (Ref. 8) $YbPd_3$:$AuCu_3$ (Ref. 4)].

The aim of the present work was to clarify the electronic structure of these intermetallic phases by photoelectron spectroscopy using synchrotron radiation. In addition, the stabilities of the Yb $4f$ configurations at the surface were investigated, particularly the question whether more [as, e.g., in $YbAl_2$ (Ref. 9)] or less than one atomic layer [as, e.g., in $EuPt_5$ (Ref. 10)] is involved in a surface-induced valence change. We find a single divalent surface layer on YbPd and Yb_3Pd_4, whereas on $YbPd_3$ divalency is restricted to only part of the surface, namely atoms with particularly low coordination. In the bulk, only YbPd is identified as intermediate valent, while Yb_3Pd_4 and $YbPd_3$ are found to be trivalent.

II. EXPERIMENTAL

The measurements were performed at the TGM-3 beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung, BESSY, employing a display-type electron analyzer, equipped with an ellipsoidal mirror in an angle-integrating mode. Part of the measurements on $YbPd_3$ were done at the BESSY SX-700 beamline using a double-cylindrical mirror analyzer. The combined-system resolution (monochromator plus analyzer) was about 0.5 eV for the TGM-3 and 0.3 eV for the SX-700 monochromator, respectively. The monochromators were calibrated by observing the Yb $4f_{7/2}$ line in Yb metal, the binding energy of which relative to E_F is known to be 1.2 eV. The polycrystalline samples were prepared either by arc melting (in case of $YbPd_3$) or by inductive melting in a closed Ta crucible (in case of YbPd and Yb_3Pd_4). They were found to be single phase by Debye-Scherrer analysis, with the usual limit of sensitivity of this method.

The surfaces were cleaned *in situ* by scraping with a diamond file at intervals of 5 to 30 min in an ultrahigh vacuum of $\simeq10^{-10}$ mbar. The cleanliness of the surfaces was checked via the O $2p$ photoemission signal at about 6 eV binding energy, employing 25 eV photons in order to suppress $4f$ photoemission. Valence-band photoemission spectra up to binding energies of $\simeq15$ eV were taken at a photon energy of 120 eV, where the cross section for Pd-$4d$ photoemission is in the well-known Cooper minimum,[11] and Yb $4f$ emission dominates. The contributions from the Pd $4d$ band could be observed separately by taking spectra at $h\nu=50$ eV.

III. RESULTS AND DISCUSSION

The valence-band photoemission (PE) spectra taken at $h\nu=120$ eV are shown in Fig. 1 for the three intermetallic compounds studied. At this photon energy they are clearly dominated by emission from Yb $4f$ states. At binding energies between 5 and 13 eV, PE lines from the Yb $4f^{12}$ final state multiplet are observed, while the $4f^{13}$ doublet is identified close to the Fermi level; these two multiplets are attributed to trivalent and divalent Yb, respectively (see below). At the used photon energy, PE from the Pd 4d band is very weak due to the Cooper minimum at $h\nu\simeq120$ eV.[11]

An inspection of Fig. 1 clearly shows that the Yb^{3+}-to-Yb^{2+} intensity ratio increases with increasing Pd content in the sequence YbPd-Yb_3Pd_4-$YbPd_3$. In order to obtain the exact binding energies of the Yb $4f$ multiplet ground state and to allow a separation of possible surface and bulk contributions via the well-known surface core-level shifts (SCS), least-squares fits of the spectra were performed. To this end theoretical spectral shapes were set up by a superposition of Yb^{3+} ($4f^{12}$ final state) and Yb^{2+} ($4f^{13}$ final state) multiplets plus a relatively weak back-

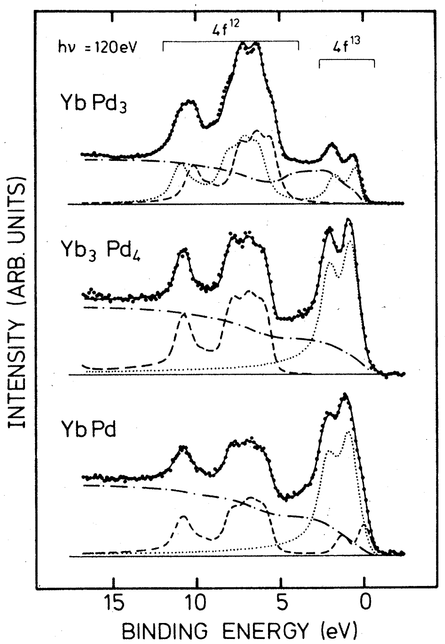

FIG. 1. Valence-band PE spectra of YbPd, Yb_3Pd_4, and $YbPd_3$ taken at $h\nu=120$ eV. The solid lines represent the results of least-squares fits (see text). In addition, the $4f$-derived subspectra from bulk (surface) Yb atoms are indicated by dashed (dotted) curves; the backgrounds from inelastically scattered electrons plus weak emission from the conduction band are given by the dash-dotted lines.

ground, describing contributions from inelastically scattered electrons and PE from the conduction band. The $4f^{12}$ multiplet was taken from the calculations of Gerken,[12] with slightly changed relative intensities. In the Yb^{2+} $4f^{12}$ doublet, the $I_{5/2}$-to-$I_{7/2}$ intensity ratio was set equal to 0.65—0.70,[13] instead of the theoretical value of 0.75. Best fits were obtained by nearly symmetric Doniach-Šunjić shapes for the bulk and surface lines, with the theoretical spectral envelope convoluted with a Gaussian spectrometer function. The effective binding energies of the Hund's-rule ground-state multiplet components, resulting from the least-squares fits, are given in Table I for divalent and trivalent Yb atoms in the bulk and at the surface. The least-squares fits provide also values for the relative intensities I_b and I_s of bulk and surface subspectra, respectively, both for the Yb^{3+}-derived $4f^{12}$ and the Yb^{2+}-derived $4f^{13}$ multiplets. These are summarized in Table II and will be discussed further below.

TABLE I. $4f$ binding energies of the Hund's-rule ground-state multiplet components for trivalent and divalent surface-Yb as well as bulk-Yb atoms, compared with the theoretical stability values, $\Delta E_{\mathrm{II,III}}$ (Ref. 7). The energies are quoted in eV, with the estimated errors given in parentheses in units of the last digits.

Compound	E_s^{3+}	E_b^{3+}	E_s^{2+}	E_b^{2+}	$\Delta E_{\mathrm{II,III}}^{\mathrm{theor}}$
YbPd		6.02(2)	0.92(4)	0.10(5)	−0.4
Yb_3Pd_4		5.98(2)	0.89(2)		−0.5
$YbPd_3$	6.17(8)	5.40(8)	0.53(2)	−0.93[a]	−0.6

[a] BIS result (Ref. 5).

TABLE II. Relative intensities of the bulk (index b) and surface (index s) components of the Yb^{3+}- and Yb^{2+}-derived $4f$-multiplet subspectra, as obtained from the least-squares fits of the 120-eV PE spectra.

Compound	I_b^{3+}	I_s^{3+}	I_b^{2+}	I_s^{2+}
YbPd	0.75	0	0.25	0.98
Yb_3Pd_4	1.00	0	0	1.06
$YbPd_3$	1.00	0.98	0	0.22

It may be questioned whether the final-state multiplets observed reflect the respective Yb^{3+} and Yb^{2+} initial-state configurations in a quantitative way. This has been discussed, e.g., in Ref. 14 for the case of $YbAl_3$, and it was claimed there that the $4f^{13}$ final-state features observed in the PE spectrum of this compound were originating from initial-state Yb^{3+}, with the photo-hole pulling the unoccupied $4f$ level below the Fermi level (shake down). In the present case, such a mechanism can be excluded, at least for YbPd and Yb_3Pd_4, on the basis of constant-initial-state (CIS) measurements in the region of the giant $4d \rightarrow 4f$ resonance. This involves $4d \rightarrow 4f$ exitations followed by a super-Coster-Kronig transition and consequently enhanced $4f$ emission. Enhanced $4f$ emission at the $4d \rightarrow 4f$ resonance has been reported for trivalent Yb in Yb_2O_3.[15,16] We have performed CIS measurements by scanning the photon energy, the binding energy E_B of the recorded electrons fixed to either 2 eV ($4f^{13}$) or 7 eV ($4f^{12}$). A resonance enhancement at $h\nu=181$ eV is observed only for $E_B=7$ eV but not for $E_B=2$ eV (see Fig. 2). Since such a $4d \rightarrow 4f$ resonance can only be expected for the Yb^{3+} initial state, but not for Yb^{2+} (due to the filled $4f$ shell), this observation clearly proves that the $4f^{13}$ PE intensity originates from Yb^{2+} initial-state atoms. Any contribution from Yb^{3+} initial states to the $4f^{13}$ doublet would clearly result in a $4d \rightarrow 4f$ resonance signal contrary to observation.

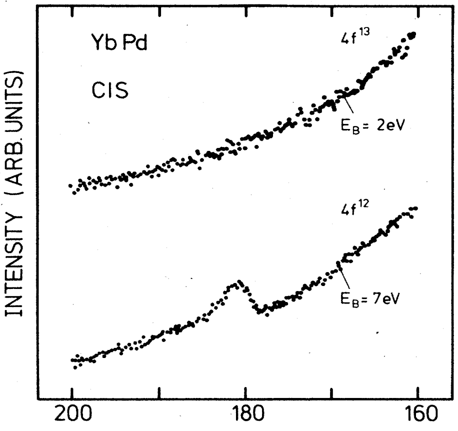

FIG. 2. Constant-initial-state (CIS) spectra of YbPd taken from states with 2 eV (top) and 7 eV (bottom) binding energy, respectively.

A. YbPd

Two doublets contribute to the Yb^{2+} feature in the $4f$-derived PE spectrum of YbPd (see Fig. 1), which can be attributed to surface and bulk atoms, respectively, on the basis of the well-known surface core-level shift (SCS). From the relative intensities of the bulk subspectra given in Table II, we can derive the bulk mean valence as 2.75 $[I_b^{3+}/(I_b^{2+}+I_b^{3+})=0.75]$. This agrees rather well with values obtained by other methods.[1,3] The surface-to-bulk intensity ratio $[I_s^{2+}/(I_b^{2+}+I_b^{3+})]$ is very close to 1.0. This latter ratio can be used to obtain an estimate for the thickness Δs of the divalent surface layer employing the relation $(I_b+I_s)/I_b=\exp(\Delta s/\lambda\cos\theta)$;[9] here λ is the electron escape depth and θ stands for the electron emission angle. Assuming $\lambda\simeq 6$ Å (Ref. 17) and $\langle\cos\theta\rangle=0.7$, we obtain $\Delta s\simeq 3$ Å. Since the shortest Yb-Yb distance in YbPd is 3.4 Å, the size of Δs shows that only the outermost surface layer is divalent in intermediate valent YbPd. A very similar conclusion was previously reached for $\mathrm{YbPd_2Si_2}$,[17] whereas in the case of intermediate valent $\mathrm{YbAl_2}$ two layers were found to turn divalent on the surface.[9]

As is typical for intermediate valent compounds, the effective binding energy of the ground state of the Yb bulk-$4f$ multiplet, measured by PE, is very small (0.1—0.2 eV). Due to the valence instability, the real binding energy must be zero. The difference is due to contributions caused by the method used, i.e., the effect of the $4f^{n-1}$ impurity remaining after the $4f$ emission and the $4f$-hole screening. Both contributions are obviously very small compared to the case of the pure metal, where they were found to be about 0.5 eV.[18] Furthermore, it follows from the intermediate valence that the cohesive energy of YbPd relative to a free Yb atom is compensated exactly by the $4f\rightarrow 5d$ promotional energy (3.1 eV). At the surface, the $4f$ binding energy is higher due to the reduced coordination. From the measured SCS of 0.8 eV it can be concluded that the cohesive energy at the surface is about 25—30% lower than in the bulk, which agrees well with the observations for other systems.[19,20] The Coulomb correlation energy, i.e., the energy difference between the lowest-binding-energy components of the Yb^{2+} and Yb^{3+} multiplets, is found to be 5.90 ± 0.07 eV, which is very close to the value obtained for $\mathrm{YbPd_2Si_2}$.[17] This underlines the localized nature of the $4f$ electrons in the present Yb compounds.

B. $\mathrm{Yb_3Pd_4}$

The Yb^{2+}-derived $4f^{13}$ multiplet in the valence-band PE spectrum of $\mathrm{Yb_3Pd_4}$ can be described by one doublet only, which means that the bulk is trivalent with only the surface layer turning divalent. This observation is at variance with the conclusion of a recent publication, where it was claimed that $\mathrm{Yb_3Pd_4}$ is intermediate valent with a mean valence of 2.95.[2] The divalent component is almost completely quenched upon exposure to $\simeq 5L$ of oxygen; at most 2%, if any, remains uneffected, i.e., the mean valence of $\mathrm{Yb_3Pd_4}$ is definitely not lower than 2.98. For clean $\mathrm{Yb_3Pd_4}$, the Yb^{2+}-to-Yb^{3+} intensity ratio is $\simeq 1.06$ (see Table II), very close to the value found for YbPd. This again means that only one surface layer is converted to the divalent state in this compound.

As can be seen from an inspection of Table I, only a very slight shift of the Yb $4f^{12}$ and the Yb $4f^{13}$ final-state binding energies to lower values is observed when turning from YbPd to $\mathrm{Yb_3Pd_4}$. This shows that the divalent-$4f$ configuration in the bulk is still above, but very close to the Fermi level in $\mathrm{Yb_3Pd_4}$.

C. $\mathrm{YbPd_3}$

In the valence-band PE spectrum of $\mathrm{YbPd_3}$ only a minor divalent feature is observed. Despite the Cooper minimum in the Pd $5d$ PE cross section around $h\nu=120$ eV, some residual emission from Pd $5d$ states seems to occur, which we have fitted with the theoretical band structure calculated by König for the related compound $\mathrm{YPd_3}$.[6] The intensity ratio I^{2+}/I^{3+} is found to be 0.1, leading to the interpretation that only part of the surface turns divalent. Such a conclusion is further confirmed by the observation of a surface component in the trivalent $4f$ emission, separated from the bulk signal by a SCS of 0.77 eV. The sum of the surface-derived intensities of the divalent and the trivalent component again gives a surface-to-bulk ratio close to 1.0, in agreement with the results derived for YbPd and $\mathrm{Yb_3Pd_4}$.

A basic understanding of this unusual behavior can be obtained by comparing with energy positions of the $4f^{14}$-bulk configurations in $\mathrm{YbPd_3}$ with those in YbPd. Recent bremsstrahlung isochromat spectroscopy (BIS) measurements on $\mathrm{YbPd_3}$ reveal the unoccupied $4f^{14}$-bulk state at 0.93 eV above the Fermi level.[5] For intermediate valent YbPd, BIS measurements have not yet been performed, but an energy position at about 0.1—0.2 eV above the Fermi level may be expected on the basis of the PE results. Thus, a chemical shift of 0.7—0.8 eV is observed when going from YbPd to $\mathrm{YbPd_3}$, due to an increase in cohesive energy. It is well known that the cohesive energy decreases at the surface by 25—30%, which will result in a shift of the surface components by only 0.5—0.6 eV. From the energy position of the divalent surface multiplet in YbPd, a $4f$ surface binding energy of about 0.3 eV is expected for $\mathrm{YbPd_3}$, which is slightly smaller than the measured value of 0.53 eV. This corresponds to a hypothetical SCS for the divalent component, which is higher than expected. On the other hand, the observed SCS for the trivalent configuration is smaller than expected: using Johansson's scheme[18,21] and the previous BIS result, the cohesive energy of $\mathrm{YbPd_3}$ can be estimated as 3.9 eV. On the basis of the 25—30% decrease in cohesive energy at the surface, this leads to an expected SCS for the trivalent component of 1.0—1.2 eV, whereas the experiment gives only 0.77 eV. The discrepancies can be explained by considering the different coordination numbers of surface atoms. Surfaces of polycrystalline compounds will normally contain atoms with various coordination numbers, leading to an averaged value for the SCS. It is known that Yb metal films show a SCS, which is dependent on the coordination number of the Yb atom;[13] the lowering in cohesive energy relative to the bulk is 20% and 33% for a coordination number of 9 and 7, respectively. We may apply this observation to $\mathrm{YbPd_3}$, since it also crystallizes in an fcc-like structure. In this way we find that highly coordinated surface atoms in $YbPd_3$ will show a SCS, which is not sufficiently large to stabilize divalent Yb, but surface atoms with even lower coordination may become divalent. Thus, we identify the divalent feature in the PE spectrum with coordination-7 surface atoms and the trivalent surface feature with coordination 9. A similar situation may exist in $EuPt_5$, where only a partial surface valence transition had been reported.[10]

IV. COMPARISON WITH MIEDEMA'S SCHEME

The effective binding energy of a divalent atom measured by photoemission reflects directly the energy difference between the divalent and the trivalent compound. By $4f$ photoemission, an initial-state divalent atom $[4f^n(sd)^2]$ is converted into a final-state trivalent atom $[4f^{n-1}(sd)^3]$. This is actually an "impurity" in an otherwise divalent matrix, supposedly the $4f$ hole is fully screened. On the basis of Miedema's scheme for calculating cohesive energies,[22] all the Yb-Pd compounds should be trivalent with energy positions of the divalent configuration between 0.4 eV (YbPd) and 0.6 eV ($YbPd_3$) above the Fermi edge.[7] In the case of YbPd and Yb_3Pd_4, this prediction is evidently wrong. Similar deviations were found for Eu-Pd compounds.[19]

The reasons for this discrepancy become clear when looking at the basis of Miedema's theoretical approach. A trivalent configuration is stabilized relative to the corresponding divalent configuration if the $4f \rightarrow 5d$ promotional energy is compensated by the gain in formation enthalpy of the compound. Using Miedema's scheme, the compound is built up by mixing the Wigner-Seitz cells of the pure constituents, and formation enthalpies are then calculated by extrapolating their physical properties as, e.g., electron density, molar volume, and contact potential. In the case of Ni, Pd, and Pt compounds, one has to start with a high density of d states at the Fermi level, neglecting the fact that these d bands may be occupied in the compound. As is well known for Pd, a filling of the d shell takes place even in the case of the free atom, and with chemical bonding, such an effect may be enhanced by charge transfer and mixing with ligand orbitals.

Figure 3 shows photoemission spectra of the three compounds studied here, taken at a photon energy of $h\nu = 50$ eV. At this energy, the photoionization cross section of the Yb $4f$ levels is low compared to the one of the Pd $4d$ bands, and the spectra reflect mainly the density of the Pd $4d$ states. We can see that the Pd bands are filled in all compounds studied. This is valid even in the case of $YbPd_3$, where BIS measurements did not provide any hint to the existence of Pd $4d$ states at the Fermi level.[5] Additionally, a strong band narrowing is observed with decreasing Pd content, which leads, in the case of YbPd, to a 40% reduction in the bandwidth as compared to pure-Pd metal. This value is consistent with the behavior of the Pt $5d$ bands in ThPt and UPt, which exhibit a similar narrowing due to the reduced overlap of neighboring d orbitals.[23] Such a band narrowing allows a more atomiclike description of the Pd bands, justifying a comparison of the solid-state results with theoretical LCAO calculations for the isoelectronic YPd molecule.[24] In this compound, the chemical bond is formed mainly by an overlap of Y $5s$ and Pd $5s$ states leading to a net charge transfer from Pd to Y atoms; the Y $5d$ electrons are not contributing to bonding. On the basis of Miedema's scheme, however, Y is assumed to be trivalent and according to the electronegativities, a strong charge transfer towards the Pd site is postulated. Applying the same arguments to YbPd, the assumptions of Miedema's scheme cause an overestimate of the formation enthalpy for the trivalent solid, which may actually be the reason of the observed deviations between theoretical predictions and experiment.

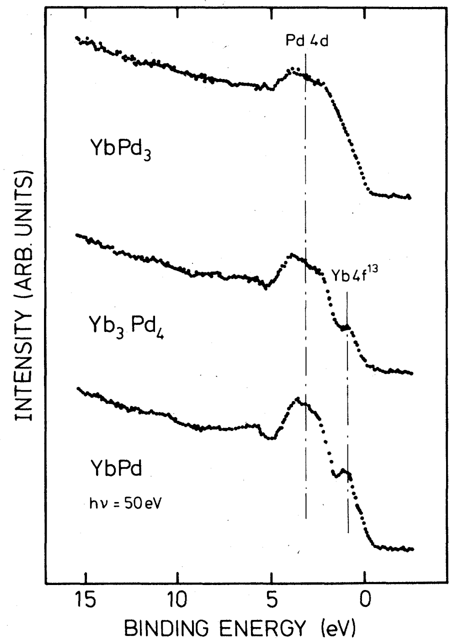

FIG. 3. Valence-band PE spectra of YbPd, Yb_3Pd_4, and $YbPd_3$, taken at a photon energy of 50 eV.

The situation is similar for Yb_3Pd_4, but different for $YbPd_3$. In the latter compound, each Yb ion is surrounded by a sphere of 12 Pd atoms. Band-structure calculations of König for the related compounds YPd_3 and $ScPd_3$ show an appreciable charge transfer from Y to Pd.[6] Furthermore, the geometrical arrangement of atoms in the $AuCu_3$ structure leads to a reduced overlap of neighboring valence orbitals and therefore to a narrowing of both the Pd $4d$ and Yb $5d$ bands; this causes even the formation of an energy gap near the Fermi level.[6] Although the direction of charge transfer is correctly predicted by Miedema's scheme, it cannot account for the enhanced stability of the trivalent configuration due to gap formation; in this way the formation enthalpy is underestimated. For $YbPd_3$, this slight imperfection of the theory causes only a minor deviation of the prediction by about 0.2 eV from the BIS data. In the case of the isostructural compound $EuPd_3$, however, a deviation of about 0.7 eV is observed,[16] which is probably connected with the larger radius of the Eu atom. These observations show that Miedema's scheme may not be applicable to systems, where electronic and structural properties are strongly dependent on compound formation.

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