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Yb 3d CORE-LEVEL PHOTOEMISSION OF YbN, YbP AND YbAs

T. GREBER, L. DEGIORGI, R. MONNIER, L. SCHLAPBACH, F. HULLIGER
and E. KALDIS

*Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zürich,
Switzerland*

On présente les résultats d'une étude expérimentale et théorique des spectres de photoémission des niveaux de coeur 3d de l'ytterbium pour la série YbN, YbP et YbAs. Les spectres expérimentaux sont obtenus à l'aide de la radiation $K\alpha$ émise par une anode de Si ($h\nu = 1740$ eV). Ils consistent en un pic principal correspondant à la configuration $3d^9 4f^{13}$ dans l'état final et un faible satellite $3d^9 4f^{14}$. Le degré de mélange des configurations $4f^{13}$ et $4f^{14}$ dans l'état initial en fonction de l'anion, ainsi que la forme détaillée des spectres, sont obtenus en combinant le formalisme à N corps de Gunnarsson et Schoenhammer [1], avec un calcul de structure atomique en couplage intermédiaire.

We present an experimental and theoretical study of the 3d core level spectra along the pnictides YbN, YbP and YbAs and determine the degree of valence mixing as a function of anion electronegativity. The experimental spectra are obtained using $SiK\alpha$ radiation ($h\nu = 1740$ eV). They show on the low binding energy side of the dominating $3d^9 4f^{13}$ multiplets a weak $3d^9 4f^{14}$ doublet. The theoretical lineshapes and satellite structures are obtained from a combination of many body techniques due to Gunnarsson and Schoenhammer [1] and standard atomic calculations in intermediate coupling.

This paper is an attempt at a systematic description of the ground state and of the 3d core level spectra of the pnictide series YbN, YbP, YbAs, following our recent success with one of them [2]. In the meantime, we have been able to quantify the uncertainties associated with the imperfect stoichiometries of our samples, which consistently show an excess of ytterbium, and this aspect should be kept in mind when we compare our experimental results with the theory, which assumes all Yb sites to be equivalent.

X-ray diffraction of the three pnictide samples showed a single phase NaCl-type structure and the lattice constants as given in table 1. The stoichiometry was determined by a chemical titration method after Kjeldahl for the Nitride and by X-ray fluorescence for the Phosphide and the Arsenide (see table 1). The XPS spectra were recorded in a VG Escalab under standard conditions ($p < 2 \cdot 10^{-8}$ Pa, $T < 300$ K).

$SiK\alpha$ radiation ($h\nu = 1740$ eV, Au $4f_{7/2}$ at 84.0 eV with 1.6 eV FWHM) had to be used to excite the Yb 3d core levels. The polycrystalline samples were cleaned in situ with a diamond file. The surface contamination was kept below 5 at%, as concluded from integrated intensity ratios normalized by atomic cross-sections from $MgK\alpha$ excited O 1s, C 1s and the respective N 1s, P 2p and As 3d levels. In the case

	$\text{Yb}_1\text{X}_{1-\epsilon}$ $\epsilon \pm 0.010$	$a_0 [\text{\AA}]$	$E_B(4f^{13})$ $\pm 0.03 \text{ (eV)}$	$E_B(4f^{14})$ $\pm 0.03 \text{ (eV)}$	$\frac{I(4f^{14})}{I(4f^{13}) + I(4f^{14})}$
YbN	0.031	4.782	1527.50	1522.98	0.062
YbP	0.025	5.544	1527.76	1521.66	0.071
YbAs	0.012	5.698	1527.81	1521.46	0.113

Table 1 - Experimental results, showing the off-stoichiometry ϵ , the lattice constant a_0 , the binding energy at the maxima of the $3d^9 4f^{13}$ respectively $3d^9 4f^{14}$ emissions (± 0.1 eV from spectrum to spectrum and ± 0.2 eV on an absolute scale), and the $4f^{14}$ spectral weight (± 0.001).

of the Arsenide, around 1527 eV binding energy (BE) [3] one has to take into account photoemission from the As 2s level. An extrapolation of theoretical cross-sections [4] indicates that the As 2s emission is one order of magnitude weaker than that from the Yb $3d_{5/2}$ levels and is smeared out due to a short lifetime ($2\Gamma \approx 3.5$ eV) [5].

We processed the experimental data as described in [2] to remove an inelastic background and contributions from $\text{SiK}\alpha_{3,4}$ radiation. Using a least square fit for two Gauss convoluted Lorentzian peaks in the BE range from 1528 to 1518 eV, we were able to extract the spectral weight of the $3d^9 4f^{14}$ contribution and the local maxima of the two multiplets.

A complete description of our procedure for calculating the 3d core level spectra in ytterbium compounds with non integer valency has been given in ref. [2], to which we refer the reader for details. In short it consists in the following two steps: first we determine the respective weight of the $4f^{13}$ and $4f^{14}$ configurations in the ground state of the system by comparing the integrated experimental photoemission intensities for the corresponding peaks with the computed ones. For that, we use the many-body treatment of the degenerate Anderson impurity model proposed by Gunnarsson and Schoenhammer [1]. Second we derive the complex lineshape of the "4f¹³ peak" by distributing the intensity over the different multiplets of the final state $3d^9 4f^{13}$ configuration, taking into account the fact that the initial (\equiv ground) state has pure $^2F_{7/2}$ character. The multiplet calculation is done in intermediate coupling and includes the dipole matrix element for the transition of the 3d electron to a continuum np (or equivalently nf) state.

Theory and experiment are compared in Fig. 1 for the three compounds. In order to reproduce the measured satellite-to-main peak intensity ratios, the calculations required 0.94, 0.94 and 0.88 holes in the Yb 4f shell for YbN, YbP, and YbAs. From the off-stoichiometry alone, and assuming a trivalent anion and an electron trapped at each anion vacancy, the weight of the $4f^{13}$ component would be: 0.938 ± 0.020 , 0.950 ± 0.020 , and 0.976 ± 0.020 respectively, instead of 1. This strongly suggests that in the perfectly stoichiometric compounds only YbAs would show clear cut mixed valent behaviour, YbP is a borderline case, and Yb in YbN is certainly integer valent, with a pure $4f^{13}$ configuration.

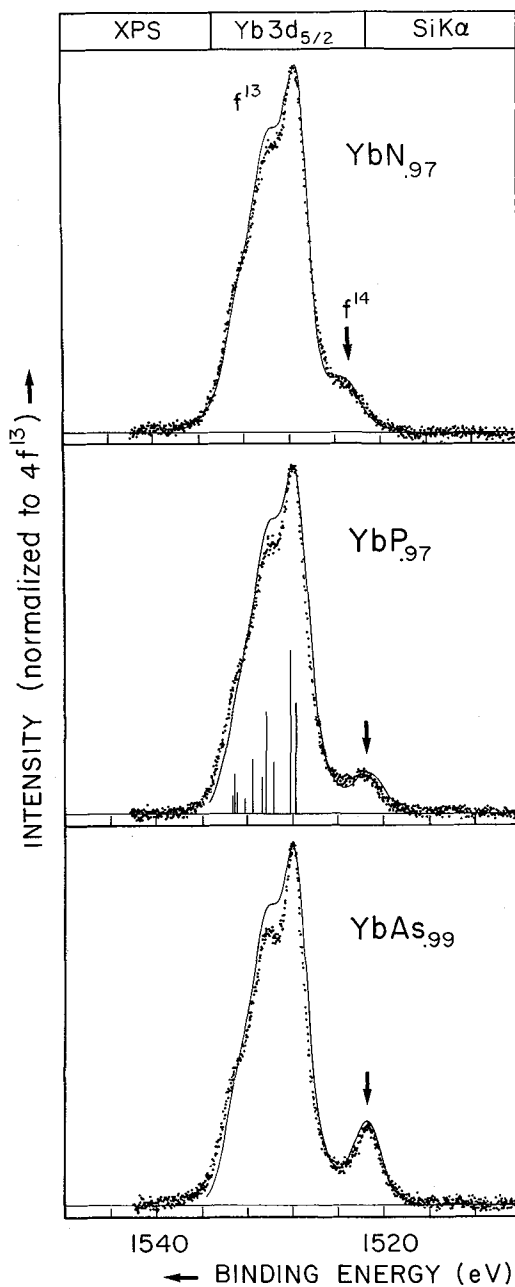


Fig. 1 - Processed XPS data, in comparison with theoretically calculated spectra, showing the Yb $3d_{5/2}$ levels of YbN, YbP and YbAs. The arrows indicate the position of the weak $3d^9 4f^{14}$ contribution in the final state. In the case of the phosphide the theoretical $3d^9 4f^{14}$ multiplets and their weights, which are used for all three cases, are displayed.

An interesting outcome of the calculations is that the value of the model-parameter U_{fC} , which describes the repulsion between the core hole and the one in the 4f shell, is much lower in the nitride (7 eV) than in the phosphide and in the arsenide, where it lies at 9 eV and 8.6 eV respectively. We have no estimate to which extent the lattice contraction from the arsenide to the nitride, deviations from stoichiometry or other effects account for this variation of U_{fC} .

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