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Electron-emission processes following $5p$ photoexcitation in fcc Yb

Giorgio Rossi and Andrzej Barski
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique,
Université de Paris-Sud, 91405 Orsay, France
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The electron-emission decay channel for photoexcited fcc Yb $5p_{3/2}$ and $5p_{1/2}$ core levels is observed by measuring the photoionization cross-section curves σ^* for the $4f$ subshell and valence-band electron states in the photon energy range 23–50 eV. *ONN* Coster-Kronig, $5p$-$5d$ resonant photoemission, and $5p$-$5d$ giant dipole autoionization decay channels produce well-resolved structures in the photoemission and σ^* curves. These processes shed light on the electronic structure of fcc Yb, which is largely hidden in conventional photoemission experiments.

Photoemission spectra of Yb have been recently studied in detail with different aims: determining the binding-energy position and surface shift of $4f$ electrons,[1] determining from the surface $4f$ emission shifts the surface crystallography of Yb films,[2] and, more recently, determining the electronic structure of Yb and Yb compounds.[3] The fact that the analysis of valence Yb states from photoemission has only recently been undertaken (after early low-energy ultraviolet photoemission spectroscopy studies[4]), is due to the fact that Yb photoemission spectra are dominated by the strong signal coming from the 14 localized $4f$ electrons (bulk and surface doublets), and only a region between 0.8 eV and the Fermi level is directly related to delocalized states. Furthermore, no clean single-crystal Yb surfaces have been available so far for angle-resolved photoemission spectroscopy (ARPES) investigations; therefore, the discussion of the Yb occupied states had to wait for an energy-dependent photoemission analysis. One fundamental problem in the understanding of the electronic structure of Yb is the amount of $5d$ admixture present in the occupied states. The atomic configuration of Yb is $5p^64f^{14}6s^25d^0$, but that of the following (trivalent) element Lu is $5p^64f^{14}6s^25d^1$, and also Yb can be found in the trivalent state at high pressure and low temperature.[5] These are strong indications of the presence of a $5d$ admixture in the electronic structure of Yb even in normal conditions (i.e., divalent fcc Yb), but neither band calculations nor experiments could actually give firm evidence of the d character of the valence states and its weight in the occupied density of states (DOS).[5]

From a cross-section analysis, and by finding a valence-band photoemission resonance over the $5p$ edges of Yb, we have very recently presented the first direct observation of occupied $5d$ states in Yb, and gave a relative quantification of the Yb-occupied $5d$ DOS as being of the order of 15% of the Lu-occupied $5d$ DOS.[3]

In fact, the $5p$-$5d$ photoemission resonance occurs at the same time as other resonant and nonresonant intense emission features turned on by the opening of the $5p$ core hole, which complicate the photoemission spectra.

We propose here the analysis of the electron-emission features that occur at energies close to the excitation thresholds for Yb $5p_{3/2}$ (24.1 ±0.1 eV) and Yb $5p_{1/2}$ (30.1 ±0.1 eV) and separate the solid state from the atomiclike effects. This analysis yields at the same time an explanation of the observed phenomena and additional knowledge on the Yb valence bands.

The experiments consisted of measuring the normal emission-electron energy distribution curves (EDC's) for Yb films at energies in the range 23–50 eV and trace from these the yield intensity curves for the observable valence-band region, -0.8 eV$-E_F$, and for the $4f_{13}$ final-state peaks. Once normalized for the many experimental and optical parameters that affect the photoemission intensity, the yield curves can be related to the true subshell photoionization cross section, and are here called σ^* according to the definition of Ref. 6. Preparation of the film and data collection were done in an ultrahigh vacuum environment (pressure during measurements $< 5\times10^{-11}$ Torr, during film condensation $< 10^{-9}$ Torr); the excitation source was the light from a thoroidal grating monochromator on the les Anneux de Collisons de l'Accélérateur Linéaire d'Orsay (ACO) storage ring at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique.

The measured cross sections for Yb $4f$ and the valence band are plotted, with a qualitative comparison to one-electron Hartree-Slater calculated atomic cross sections,[7] in Fig. 1. Both curves present sharp structure, not present in these simple atomic calculations, for energies exceeding the binding energies of $5p_{3/2}$ and $5p_{1/2}$ core electrons; otherwise they generally follow the atomic trends. The structure in the $4f\sigma^*$ and valence $(5d)\sigma^*$ have different delays with respect to the $5p$ thresholds, and have a different dependence on the spin-orbit component of the core hole, and we attribute them to different phenomena. We discuss the electron emission above the $5p_{3/2}$ threshold first. The opening of the $5p_{3/2}$ hole is expected to be followed by the usual decay channels: Auger transitions of the type $O_3N_{6,7}N_{6,7}$, $O_3N_{6,7}V$, O_3VV, direct $5p_{3/2}$ photoemission, and $5p$-$5d$ resonant photoemission of the $5d$ peak (valence band).

Auger transitions. The $O_3N_{6,7}N_{6,7}$ (i.e., the $5p_{3/2}$-$4f$-$4f$ Auger decay) final-state energy (energy of the ejected electrons) can be predicted by comparing the values of the $N_{4,5}N_{6,7}N_{6,7}$ super Coster-Kronig peaks[8] by substituting the $O_3(5p)$ initial hole energy for the $N_{4,5}(4d)$ initial hole energy. This allows the assignment of the emission structure between 6.5 and 8 eV kinetic energy that is measured for $h\nu$ larger than the $5p_{3/2}$ threshold, as shown in Fig. 2(a). The correspondent $O_2N_{6,7}N_{6,7}$ Auger is seen in Fig. 2(b) as it turns on at 12 eV kinetic energy for $h\nu$ exceeding the O_2 energy. These Auger signals have small final-state energies, so that they never overlap the emission features of the $4f$ and valence-band region; they do not influence, therefore, the cross-section plots. $O_3N_{6,7}V$ and O_3VV ($O_3O_{4,5}O_{4,5}$ and $O_3O_{4,5}P_1$) decays are expected to yield weak and broad

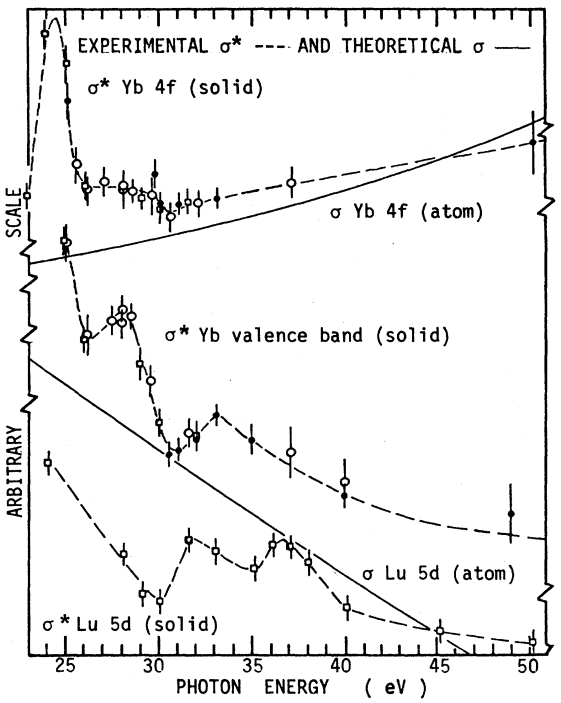

FIG. 1. Experimental photoionization cross-section curves σ^* measured with the method described in Refs. 6 and 3, for photon energies in the range 23–50 eV. From the bottom up is Lu $5d$ experimental σ^* and theoretical σ (Ref. 3); Yb valence band σ^* (emission between E_F and -0.8 eV; see Fig. 3); Yb $4f$, theoretical σ (Ref. 7) and experimental σ^*. The vertical scale is arbitrary, as well is the relative positioning of the curves on the vertical axis. Theoretical σ's are plotted to compare the shape of the curves, not to suggest quantitative analysis. The various symbols for the data points refer to measurements done with different electron beam fills in the ACO storage ring.

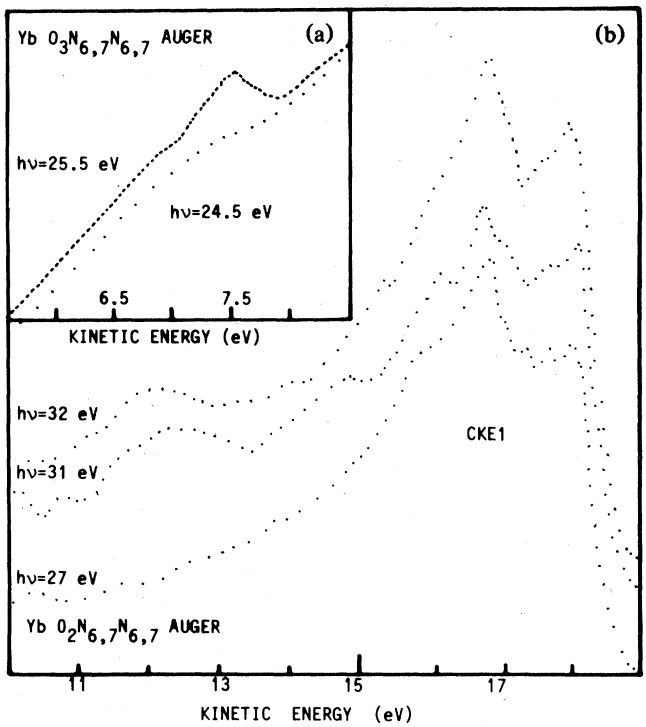

FIG. 2. (a), (b) Yb $O_{2,3}N_{6,7}N_{6,7}$ Auger transitions as they turn on when the photoexcitation energy exceeds the O_3 ($5p_{3/2}=24.1$ eV) and O_2 ($5p_{1/2}=30.1$ eV) energy. In panel (b), along with the $O_2N_{6,7}N_{6,7}$ Auger, seen is the intense CKE1 emission that turns on at the O_3 threshold (see text and Fig. 3).

structures, since the occupation of the $O_3(5d)$ states is very small, and the line shape of such transitions should reflect the convolution of a broad and flat density of states. We cannot recognize such structures in our data or cross sections, but it should be kept in mind that they may have a role in the quantitative analysis of the cross sections. In fact, none of the conventional Auger transitions can explain the strong peaks in the cross sections above the $5p$ edges, nor the emission structures that appear in the EDC's.

Resonant photoemission. d-like valence states can be final states for bound-to-quasibound transitions from p-symmetry core levels; at threshold energies for the np core levels, the direct nd valence-band photoemission can interfere with the np-nd excitation, yielding a resonance of the final-state emission peak.[9]

This phenomenon is well known for transition metals and has been shown recently to be present for the Lu $5p$ edges (Ref. 2, data shown also in Fig. 1). The peak of the resonance in the d-band cross sections is related to the maximum in the empty d-band DOS, and can therefore be delayed by a few eV with respect to the np threshold, depending on the electronic structure of the metal. In analogy with the case of Lu, we interpret the peaks of the Yb valence-band cross section as due to $5d$ photoemission resonances, corresponding to a maximum in the distribution of the $5d$ empty DOS at ~ 3.5 eV above E_F (to be compared with 6 eV as deduced from bremsstrahlung isochromat spectroscopy[10]). The resonance is equally well seen on the $5p_{3/2}$ and $5p_{1/2}$ core edges, and represents indeed the most direct proof of the presence of $5d$ character in the top of the occupied valence DOS of divalent Yb.

The $5d$ photoemission resonance explains well the shape of the valence-band cross section, but does not explain the structures of the $4f$ cross section. The $4f$ photoemission peaks lie deeper in energy than the measured valence-band peak, and should be little influenced by the resonant behavior of the valence-band photoemission due to the expected decrease of the $5d$ DOS at higher binding energies. On the other hand, a very sharp feature in the $4f\sigma^*$ appears right at threshold energy for the $5p_{3/2}$ core excitation, and a much weaker one appears at threshold for the $5p_{1/2}$ excitation; they require a different explanation.

Giant 5p-5d autoionization. The presence of a very intense constant-kinetic-energy (CKE) structure in the Yb electron-emission spectra for excitations exceding the $5p_{3/2}$ energy was signaled for the first time in Ref. 11. The nature of the emission, shown with dashed areas in the photon energy-dependent EDC's of Fig. 3, was discussed as being related to an autoionization decay process which involves the initial $5p_{3/2}$ state, an intermediate atomiclike state, and the final states centered around 17.5 eV of kinetic energy. The mechanism was invoked in order to explain the existence of such a CKE structure at that constant final energy, the fact that its width and shape resembles a replica of

the direct photoemision from the $4f$ and valence states, and the occurrence at the $5p_{3/2}$ threshold. The present new data give better detail, extend to higher energy than those of Ref. 11, and cover the $5p_{1/2}$ edge. The CKE1 (i.e., related to the $5p_{3/2}$ hole) indeed turns on strongly at threshold and changes completely the Yb photoemission line shape; at higher photon energies it is well recognized as a constant energy structure, still very intense for excitation energies as high as 50 eV and higher, indicating that the origin of this structure must be considered as Auger-like, at least at high excitation energies. As a matter of fact, some very recent electron excited high-resolution Auger spectra by Sancrotti[12] show peaks that we attribute to the CKE1, CKE2, and *ONN* transitions.

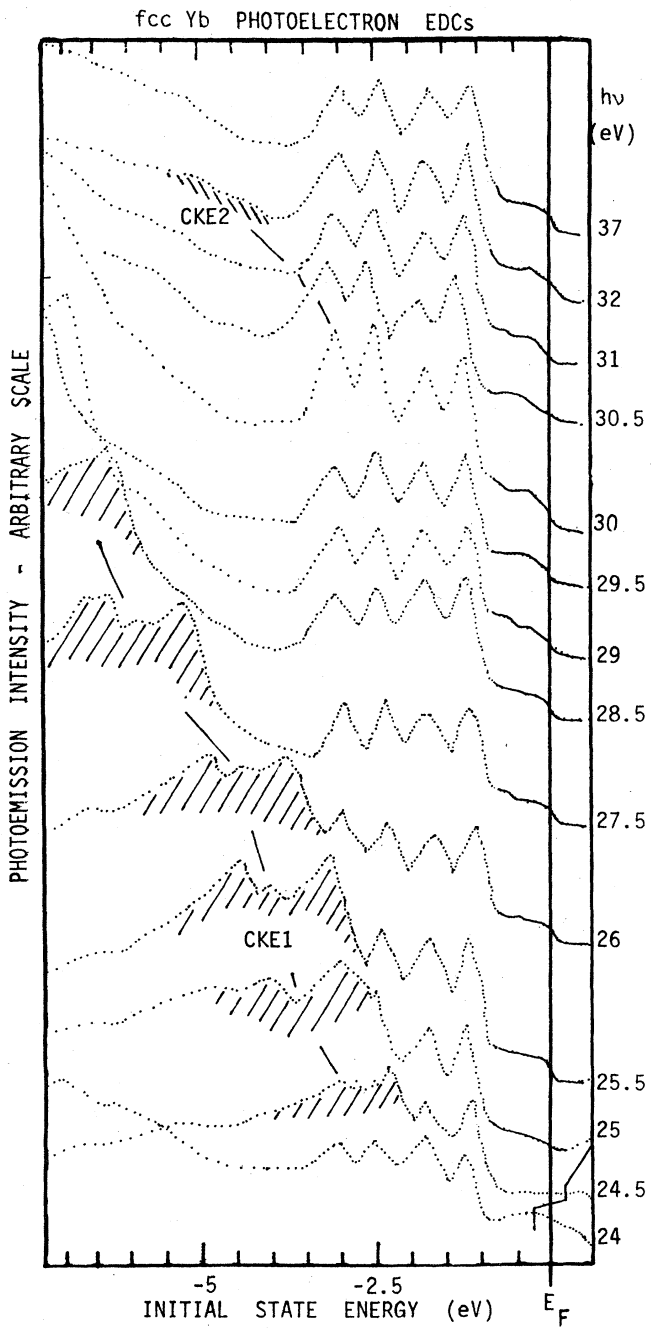

FIG. 3. Photoelectron EDC's for fcc Yb films, for $h\nu$ values between 24 and 37 eV. The region fitted by a solid line is the part of valence band whose cross section is reported in Fig. 1. The structures at -1.2 and 2.5 eV are the $4f$ final-state doublets, and at 0.6 higher binding energy the relative surface shifted components. The CKE1 and CKE2 labels are explained in the text. A peak excited by second-order light sweeps through the Fermi-level region in the two bottom curves ($h\nu = 24$ and 24.5 eV); it is signaled by a thick mark.

It remains that the CKE1 peak intensity and shape cannot be due to an OVV-like Auger transition, and requires the role of a localized intermediate state for the decay process, having energy close below the Fermi level (-0.55 eV from energy balance of the emission features), with high overlap to the initial $5p_{3/2}$ hole, and with zero width (atomiclike).

Such a state can be understood as a d-like screening orbital pulled below E_F by the core hole potential, having an efficient overlap with the $5p$ open core so as to allow an atomiclike $5p$-$5d$ giant resonance; in this process shallow electrons would be emitted with a constant amount of energy supplied by the screening orbital-$5p$ recombination. This means that the $5d$ band can collapse into an atomiclike state around the $5p$-ionized Yb atom, and the new virtual state (or impurity state if we consider the $5p$-ionized Yb atom as an impurity within the Yb metal) contributes to O_3–screening orbital–$N_{6,7}$ or O_3–screening orbital–V Coster-Kronig transitions.

The resonant behavior close to threshold is understood as the direct trapping of the $5p_{3/2}$ photoelectron into the $5d$ screening orbital. This accounts for the sudden onset of the CKE1 transition at the $5p$ energy. The fact that the CKE1 intensity remains high at higher energies indicates that the mechanism is still favorable when off resonance, with the intermediate screening orbital state being filled with a conduction electron. This phenomenon must be considered as different from a regular Auger, since its existence is strictly bound to the possibility of collapsing a $5d$ screening state which does not exist in the ground state of Yb and the $5p$-$5d$ giant dipole, which greatly enhances the cross section for this channel. A further proof of this peculiarity comes when comparing the emission features of Yb intermetallics at the Yb $5p$ edges. Yb/Si mixed interfaces and silicides have been studied[13] in similar experiments and shown the *ONN* Auger transitions (with chemical shifts and line-shape changes as expected for different environments of the Yb atom) while they *do not show the CKE1 and CKE2 structures,* this being a consequence of the rehybridization of the Yb *sd* charge with the Si *sp* charge. Charge transfer from Yb to Si probably pushes the d-like states away from the E_F region, making impossible the $5d$ collapse and consequently the autoionization decay. The first intense peak in the $4f$ cross section is therefore due to the turning on of the CKE1 structure that seeps through the $4f$ photoemission peaks as the $5p_{3/2}$ threshold is reached and passed. The second feature of the $4f\sigma^*$ at 30.5 eV is also understood as the correspondent phenomenon induced by the opening of the $5p_{1/2}$ hole, as it is well seen causing an apparent branching ratio between the bulk and surface shifted $4f_{5/2}$ and $4f_{7/2}$ doublets in the EDC's of Fig. 3, and labeled CKE2.

The important difference between the two CKE structures is their intensity, which is very different and does not scale simply with the initial-state multiplicity, i.e., with the dipole selection rules of the process. This phenomenon can be compared to the branching ratio for the deexcitation of the

$Yb_I(^2P_{3/2})$ and $Yb_I(^2P_{1/2})$ atomic configurations.[14]

In ejected electron spectroscopy of atomic Yb (Refs. 15 and 16) the photoexcitation of the $5p_{3/2}$ threshold is followed by autoionization decays of the type

$$Yb_I 5p^5(^2P_{3/2})4f^{14}6s^25d^* \rightarrow Yb_{II}5p^64f^{14-x}6s^{2-y} ,$$

where $x \neq y$, $x,y = 0, 1$ with ejection of a shallow electron ($4f$ or $6s$ or $5d$). Rossi, Yeh, Lindau, and Nogami suggested the analogy between these processes and the CKE1.[11] The CKE2 atomic analog would then be the autoionizations of the excited configuration,

$$Yb_I 5p^5(^2P_{1/2})4f^{14}6s^25d^* ,$$

but this yields very little[16] or no intensity[15] in atomic spectroscopy. This fact is accounted for by the presence of an intense nonradiative transition,

$$Yb_I 5p^5(^2P_{1/2})6s^25d^* \rightarrow Yb_{II}(^2P_{3/2}) ,$$

which represents a Coster-Kronig conversion of the $5p_{1/2}$ hole into a $5p_{3/2}$ core hole state of the Yb ion.[14,15] The intensity ratio of the CKE1 and CKE2 structures can therefore be understood on the basis of their atomic analogs. Similar arguments have been proposed to explain the asymmetry in the $5p$ opitcal-absorption branching ratio measured for most rare-earth and alkali-earth elements.[17]

Summarizing, we have shown and discussed the complexity of the electron-emission features of photoexcited divalent Yb when the photon energy approaches and reaches the $5p$ core ionization thresholds. Auger, resonant photoemission, and giant autoionization decays are well distinguishable if the experimental determination of the energy-dependent EDC's line shape and of the subshell photoionization cross sections is done and jointly analyzed. The results of the present study are quite rich, in fact, the evidence of photoemission resonances is a proof of the presence of a sizable density of $5d$ states in the upper part of the valence band of divalent Yb; the presence of the giant autoionization phenomenon proves that the $5d$ band can locally collapse when a high density of empty $5d$ states is present at the Fermi level,[18] as it is the case in divalent Yb, and as it is not the case in Yb silicides. These features can be exploited for a deeper analysis of the electronic structure of Yb intermetallics, and may be found to be of special importance for having access to otherwise hidden characters of the Yb valence band.

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