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Photoemission from Yb: Valence-change-induced Fano resonance

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Photoemission and photon-absorption results on clean and oxidized Yb are presented that clearly reveal a difference in $4f$ occupancy between the clean ($4f^{14}$) and oxidized ($4f^{13}$) case. For the oxidized metal a resonance enhancement of the $4f$-electron emission is observed at the $4d$ threshold. The enhancement arises from autoionization decay following $4d \rightarrow 4f$ absorption transitions. The resulting line profile is shown to be well described by Fano's theory of interaction between a discrete and continuum state.

Resonance effects at the $4d$ and $3p$ thresholds for, respectively, rare-earth[1-5] and transition metals[6,7] are well established in absorption spectra. The decay processes following the absorption have, however, not yet been given much attention experimentally although the shape of the absorption structures depend[7] critically on the decay channel involved. Recent photoemission experiments on transition[8] and rare-earth[9-11] metals though indicate the possibility of gaining information about details of the decay processes by studying the enhanced electron emission arising from absorption and following decay.

We present photoemission and photon-absorption results on clean and oxidized Yb metal that unambiguously reveal (1) a strong $4f$-electron emission enhancement in the oxidized case, caused by autoionization decay following $4d \rightarrow 4f$ absorption transitions and giving rise to the characteristic line profile predicted by Fano[12] for interaction between a discrete and a continuum state, and (2) a difference in $4f$ occupancy between the clean ($4f^{14}$) and oxidized ($4f^{13}$) case which allows us to "turn on" the resonance absorption and enhanced $4f$-electron emission by exposing the clean metal to oxygen. Yb was chosen for this study because its localized $4f$ states are free of the itinerant-localized ambiguity of the transition-metal $3d$ states, and because $4d \rightarrow 4f$ absorption in the oxidized case produces a single resonancelike feature without interfering sharp multiplet structures.

The experiments were performed at the 4° line[13] of Beam Line I at Stanford Synchrotron Radiation Laboratory. A double-pass cylindrical mirror analyzer (CMA) was used as electron energy analyzer. It has an energy resolution[14] of 1.6% relative to the analyzer pass energy which normally was kept at 25 eV in the measurements to be presented.

Samples of Yb were prepared by *in situ* evaporation onto a metal substrate. During evaporation the pressure rose to $\lesssim 1\times10^{-8}$ Torr but a base pressure of $\lesssim 2\times10^{-10}$ Torr was obtained within a few minutes after an evaporation. Oxygen exposures were performed by exposing the clean film to pure oxygen, at partial pressures between 10^{-6} and 10^{-5} Torr.

The energy distribution of photoelectrons from the outermost levels of Yb metal excited by $h\nu = 150$ eV photons is shown in Fig. 1(a). The same spectral shape was observed over the entire energy range studied, 50–250 eV. In the metal, as in the free atom, Yb has a filled $4f$ shell. Upon photoionization of a $4f$ electron, the only possible final-state multiplets are $^2F_{7/2}$ and $^2F_{5/2}$, which gave rise[15] to the doublet structure in Fig. 1(a). Also shown in the figure are the fractional parentage coefficients[15,16] which should reflect the relative probability for excitation to the two final states. The energy separation between the multiplets in Yb were taken from Ref. 17. A rather good fit to the experimental result is obtained as seen in Fig. 1(a) in agreement with earlier[15,18] x-ray photoemission (XPS) studies.

After exposure of the clean metal to 100 langmuir (1 L = 10^{-6} Torr sec) of oxygen a very different spectrum is observed, as seen in Fig. 1(b). Further exposures to 500 and 5000 L produced virtually no additional modifications to the spectrum, except that the weak structure extending

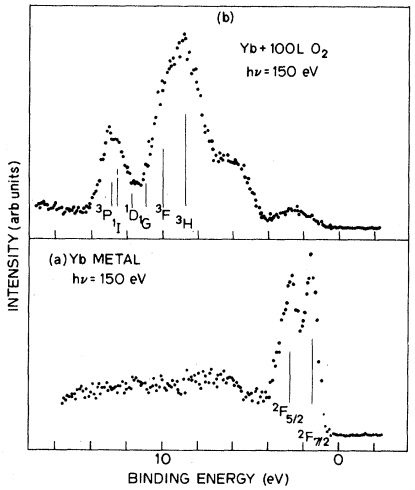

FIG. 1. Photoemission spectrum of the outermost levels in Yb for (a) the clean metal and (b) after an oxygen exposure of 100 L. The vertical bars that have been fitted to the data indicate the predicted energy separations of the different final-state multiplets (see text for details). The Au $4f_{7/2}$ level recorded on an *in situ* prepared Au sample has been used as reference level.

down to 2.5 eV below the Fermi level (E_F) became much weaker at an exposure of 500 L and was almost completely gone at an exposure of 5000 L. We ascribe this structure to metallic emission from atoms underneath the oxide layer. The shoulder seen around 6–7 eV below E_F has been identified as originating from O $2p$ states.

If one $4f$ electron were lost to a bonding orbital upon oxidation, we would have a $4f^{13}$ configuration in the ground state and the possible final-state multiplets, upon photoionization of one $4f$ electron, would be ^3H, ^3F, ^3P, and ^1S, ^1D, ^1G, ^1I. By using the energy separations observed[17] between these multiplets in Tm^{3+} (which has a $4f^{12}$ configuration) and Cox's fractional parentage coefficients,[16] a good fit to our data is obtained as shown in Fig. 1(b). (For the triplet states the location of the centroid of the multiplet, taken over the different J values, is represented by the bars shown in the figure.) No fine structure corresponding to the separate multiplets in the two peaks[18] is observed, however. This is probably due to some broadening effect in the oxidized film inasmuch as our instrumental resolution [$\gtrsim$0.5 eV full width at half maximum (FWHM)] should have been sufficient to resolve some of these structures.

The preceding assignments are further supported by our measurements of the absorption coefficient in the vicinity of the $4d$ threshold using the partial electron yield technique.[19,20] In this technique, electrons of a fixed energy (typically a few eV) are collected while scanning the photon energy, thus obtaining a measure[20] of the photon-absorption coefficient. In Fig. 2 the partial yield spectra of the clean and oxidized Yb sample are shown. In the clean film the Yb atoms have an electron configuration of $4d^{10}4f^{14}$, so the $4d$ electron excited in the absorption process has no unfilled $4f$ level to occupy. The oscillator strength for transitions into a continuum state should be weak in the vicinity of the $4d$ threshold so no drastic change in the absorption coefficient is expected to occur. The spectrum for the oxidized metal, however, does undergo a dramatic change at the $4d$ threshold, implying that the initial $4f$ occupancy for the oxidized metal is definitely less than 14. Furthermore, a single absorption line is observed, as is expected to arise[4] from the transition $4d^{10}4f^{13} \rightarrow 4d^9 4f^{14}$, again implying that the Yb atoms have $4f$ occupancies of $4f^{14}$ in the metal but $4f^{13}$ in the oxide. This has been suggested previously[4,21] although the earliest absorption data[1] indicated the presence of Yb^{3+} ions also in the metal. We also note that the relative binding energies of the O $2p$ and Yb $4f^{13}$ states are consistent with the oxidation process stopping at Yb^{3+} (the $4f^{13}$ states lie below the upper part of the O-$2p$ density of states).

In order to detect possible decay of the $4d^9 4f^{14}$ state via autoionization processes, the electron emission from the outer levels was studied near the $4d$ threshold. In Fig. 3 the spectrum of the outer levels is shown when excited with different photon energies between 177 and 195 eV. Enhanced emission of both the peak at 12 eV and the one at about 9 eV below E_F is observed although the most dramatic effect seen is a change in their relative strengths. The enhanced emission arises from autoionization decay processes of the type

$$4d^9 4f^{14} \rightarrow 4d^{10} 4f^{12} + \text{electron}, \qquad (1)$$

which have been termed super Coster-Kronig transitions by McGuire.[22] The different enhancement behavior of the various multiplets indicate

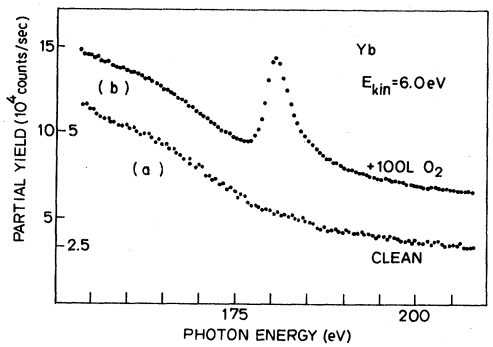

FIG. 2. Partial electron yield spectrum of Yb in the $4d$-absorption threshold region for (a) the clean metal and (b) after an oxygen exposure of 100 L.

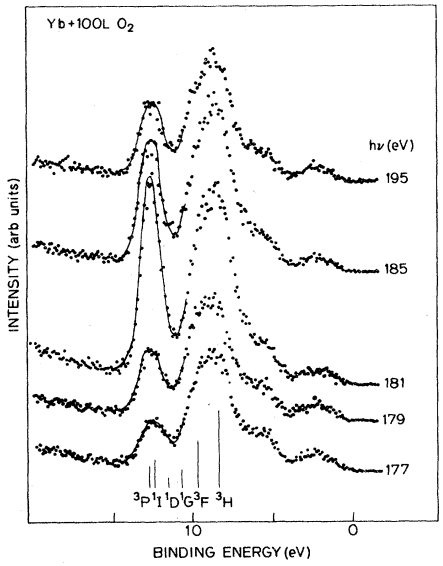

FIG. 3. Photoemission spectrum of the outermost levels of Yb in the oxidized case excited with different photon energies in the vicinity of the $4d$-absorption edge. The spectra have been normalized with respect to variations in incident photon flux with stored beam current.

that selection rules govern the decay process. Simple symmetry arguments[23] pertaining to decay of the initial state $4f^9 4f^{14}(^2D)$ into final states $4d^{10}4f^{12}\epsilon l(^2D)$ do not, however, exclude any of the final-state multiplets and particularly not ^3P or ^1I. Thus, we can state with certainty only that the decay process selectively enhances the ^3P and ^1I states more than the ^3H, ^3F, and ^1G states.

The final state arrived at after the decay can be exactly the same as the one obtained after direct photoemission of a $4f$ electron from the ground state

$$4d^{10}4f^{13} \rightarrow 4d^{10}4f^{12}\epsilon l \quad (l = g \text{ or } d). \tag{2}$$

Interference occurs between the direct $4f$-photoemission process and the process of $4d$ absorption and accompanying decay since the two processes involve the same initial and final states. This has been shown to give rise to a characteristic line profile for the cross section variation in the vicinity of the resonance.[12,24] Fano[12] predicts a line shape for this type of process which obeys the equation

$$\sigma(h\nu) = \sigma_a \frac{(q+\epsilon)^2}{1+\epsilon^2} + \sigma_b , \tag{3}$$

where $\epsilon = (h\nu - E_0)/\Gamma$, E_0 is the resonance energy, Γ is the half-width of the line, and q is the line profile index. The cross sections σ_a and σ_b correspond to transitions to states of the continuum that, respectively, do and do not interact with the discrete autoionizing state.

In order to directly compare experimental data with this expression we utilized the technique of constant-initial-state (CIS) spectroscopy.[19] The initial state is selected by setting the analyzing energy to the photon energy minus the binding energy (referred to the vacuum level) of the electronic level to be studied. The results obtained when setting the initial state in the $^2F_{7/2}$ multiplet for the clean metal, and in the ^3P and ^1I multiplets for the oxidized case are very much like the partial yield spectra shown in Figs. 2(a) and 2(b). The dotted and solid curves of Fig. 4 show, respectively, the line shape obtained from the ratio of the two CIS curves (oxide and metal), and the excellent fit to the data achieved with a curve of the form $(q+\epsilon)^2/(1+\epsilon^2)$ for the parameter values $\Gamma = 1.7(\pm 0.2)$ eV, $q = 2.4(\pm 0.2)$, and $E_0 = 180.5(\pm 0.3)$ eV. The uncertainties are estimated from visual inspection of the fit. The emperical parameters Γ and q are related[12,24] to the Coulomb $V_E = \langle 4d, \epsilon l | v_c | 4f, 4f \rangle$ and dipole $P = \langle 4d | r | 4f \rangle$, $M = \langle 4f | r | \epsilon l \rangle$ matrix elements by $\Gamma = \pi | V_E |^2$ and $q = P/\pi M V_E$. We have not calculated these matrix elements but the determined values appear reasonable when compared to the parameter values previously obtained[9] on Ce ($\Gamma = 1.3$ eV and $q = 2.4$).

In summary, we have presented photoelectron energy distribution and photo-absorption coefficient data for clean and oxidized Yb metal. Dramatic differences between the clean and oxidized cases are observed, especially in the vicinity of the $4d$ absorption threshold, which implies that the ground-state electron configuration is $4f^{14}$ in the metal and $4f^{13}$ in the oxide. The enhancement of $4f$ electron emission that is "turned on" by oxidation provides a definitive example of a Fano

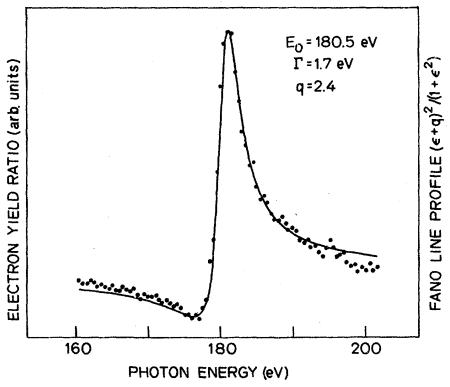

FIG. 4. Experimentally obtained line profile around the $4d$ threshold (dotted curve) and a best fit of a Fano-type line profile (solid curve) to the data. See text for details.

line profile as obtained from autoionization decay of a discrete state in a solid.

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