# Autoionization decay following a strong 5*p*-hole–5*d*-electron interaction in fcc Yb metal

G. Rossi,* J. J. Yeh, I. Lindau, and J. Nogami
*Stanford Electronics Laboratories, Stanford University, Stanford, California 94305*

(Received 8 March 1984)

Photoemission from Yb metal reveals the existence of a strong autoionization decay above the $5p_{3/2}$ photoionization threshold. Intense emission at constant kinetic energy mimicking in shape the photoemission from the valence band and $4f$ states appears for photon energies larger than the $5p_{3/2}$ threshold. We relate this phenomenon with the atomic $5p$-$5d$ "giant resonance" of Yb, having a locally collapsed $5d$–screening-orbital state as an intermediate step for the autoionization.

The atomic ground-state electronic configuration of Yb is $5p^6 4f^{14} 5d^0 6s^2$. At the solid-state fcc Yb has a band structure formed by very close $6s$ (occupied) and $5d$ (empty) bands,[1] with a high density of $5d$ empty states at the Fermi level. Only a small degree of $s$-$d$ hybridization has been theoretically predicted, which gives a very small, fractional population of valence electrons of $5d$ character; the optical absorption of fcc Yb is dominated by interband transitions to $5d$ final states;[2] Yb is a divalent rare earth.

In this Rapid Communication we report a phenomenon found in the photoemission from Yb metal when a $5p$ core hole is formed, which is not found in Yb-Si compounds.[3] The phenomenon consists of the appearance of intense peaks in the electron energy distribution curve, which maintain constant kinetic energy (CKE) for excitation energies above the $5p_{3/2}$ threshold, as shown in Figs. 1 and 2. Figure 1 displays the as-measured curves from our synchrotron radiation angle-integrated photoemission experiment[4] performed on a clean, ultrahigh vacuum deposited Yb film. The spectra obtained with different photon energies in the range 15–31 eV are plotted versus the kinetic energy of the collected electrons. The bottom spectra (obtained with $h\nu$ values below the $5p_{3/2}$ threshold) show the electron states in the valence region of Yb: the final-state doublets $4f^{13}_{5/2,7/2}$ for the bulk and the surface atoms (shifted)[5] and the $6s$ density of states extending to the Fermi level.

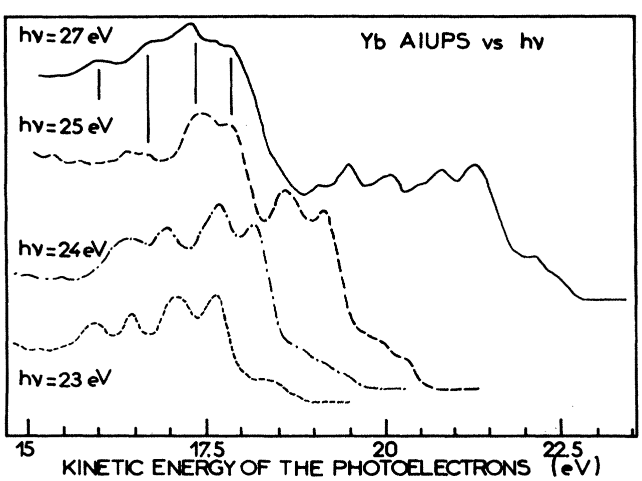


FIG. 1. Angle-integrated electron energy distribution curves (EDC's) for fcc Yb, at photon energies below and above the $5p_{3/2}$ threshold. For $h\nu > 24$ eV it appears the intense CKE emission.

At $h\nu = 25$ eV, an abrupt change of shape of the spectrum occurs, with the appearance of intense emission in the KE interval 15–18 eV; this intense emission remains for higher $h\nu$ values at CKE, as it is seen in the curve obtained with $h\nu = 27$ eV.[6]

Figure 2 allows a better look at the structure of the CKE emission that turns on at the $5p_{3/2}$ threshold ($24.1 \pm 0.1$ eV from *in situ* Mg $K\alpha$ x-ray photoemission spectroscopy). Two of the energy distribution curves (EDCs) of Fig. 1, one obtained with $h\nu < 5p_{3/2}$ threshold (24 eV) and one with $h\nu > 5p_{3/2}$ threshold (25 eV), are plotted versus the initial-state energy ($E_F$ was determined, *in situ*, by a Au standard), and the difference spectrum is obtained. We stress that any pair of EDC's having $h\nu > 5p_{3/2}$ and $h\nu < 5p_{3/2}$ threshold, respectively, yields the *same* difference curve at the *same* KE values, with minor shape differences being imputed to the changing background as a function of $h\nu$. The structure of the difference curve mimics the photoemission EDC of Yb, with four peaks of similar width and spacing as the photoemitted $4f$ final states and a weak edge at $19 \pm 0.1$ eV of KE.[7]

This is the new observation: a very intense emission resembling a replica of the valence band and $4f$ photoemis-

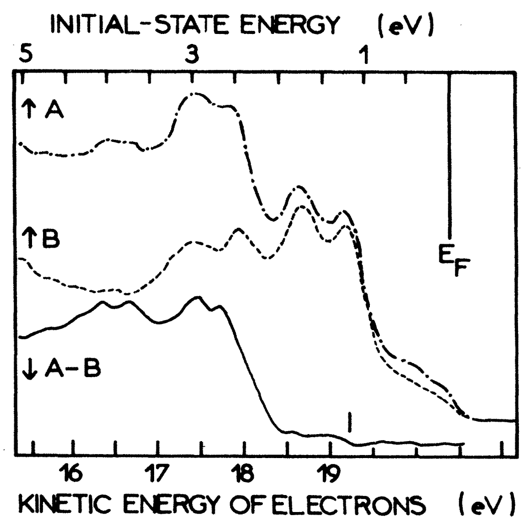


FIG. 2. EDC's for $h\nu$ values smaller and larger than the $5p_{3/2}$ energy ($h\nu = 24$ eV dashed, and $h\nu = 25$ eV dash-dotted curves) plotted vs initial state energy. The difference curve (solid) reveals the structure of the CKE emission that resembles a replica of the valence band and $4f$ photoemission.

sion, turns on as a CKE feature when a $5p$ core hole is formed in metallic Yb (but not in Yb-Si compounds), as if a very efficient monochromatic excitation channel opening above the $5p$ threshold would supply $23.6 \pm 0.1$ eV to the valence and $4f$ electrons (calculated from the KE of the "replica" spectrum). The normalized $4f$ photoemission yield[8] over the $h\nu$ range of the experiment is given in Fig. 3, and compared with our one-electron HFS calculation of the cross section for photoionization of the atomic $4f$ electrons.

The observed effect is not explained by the usual core-bound-state transitions found in resonant photoemission[9] nor by a simple combination of $O_{2,3}O_{4,5}P_1$ and $O_{2,3}O_{4,5}N_{6,7}$ Auger core-valence-valence (CVV) transitions, because of the unavailability of significantly occupied $O_{4,5}$ ($5d$) band states. Also, the sharpness of the CKE peaks exclude the presence of two band-like final-state valence holes; as in a regular CVV Auger decay, those, in fact, would yield a broad emission due to the convolution of the valence and $4f$ states. Further, although indirect, information comes from the *absence* of the CKE "replica" structure in the photoemission from Yb/Si reacted interfaces and compounds;[3] this imposes the need to regard this phenomenon as different from an obvious Yb CVV Auger. Finally the very large intensity of the CKE "replica" emission, which is comparable to that of the photoemission by the same states at the near threshold $h\nu$ values studied, requires a very efficient decay channel for the $5p$ hole.

In a phenomenological framework it is tempting to explain the CKE emission as being excited by the decay of an electron in the $5p$ hole from a sharp intermediate state lying just below $E_F$ (within 0.55 eV below $E_F$ according to our data) which would supply $\sim 23.6$ eV of energy to a $4f$ or valence electron. We propose such state to be a locally collapsed $5d$ state efficiently overlapping the $5p$ hole; i.e., a localized $5d$ impurity state (with the impurity being the Yb atom with one $5p$ core hole) that acts as screening orbital for the $5p$ hole, being populated by one electron. Screening orbitals (or equivalently core excitons) have been proposed to explain the line shapes of core-level photoemission peaks in adsorbate and bulk systems.[10,11] A collapsed $5d$ atomic-like state overlapping the $5p$ hole would allow resonant $5p$-$5d$ dipole transitions at the $5p$ threshold, and as a screening orbital could localize an electron from the valence band at higher $5p$ excitation energies. With our assumption of a localized $5d$ intermediate state, the CKE emission is then explained as the consequence of autoionization of the "impurity" Yb atoms, via the decay of one electron from the intermediate state to the initial $5p$ hole and emission of a $4f$ or valence electron. This would be a resonant process for energies just above the $5p$ threshold because of the expected strong $5p$-$5d$ dipole, and a $5p$–screening-orbital–$4f$ or $5p$–screening-orbital–valence Auger decay for higher excitation energies. The relevant fact is that the $5d$ screening orbital would contribute one full electron to the $5p$ decay process, and its final-state hole would be virtual, not contributing therefore to the line shape of the CKE emission that indeed resembles a one-hole final state emission.

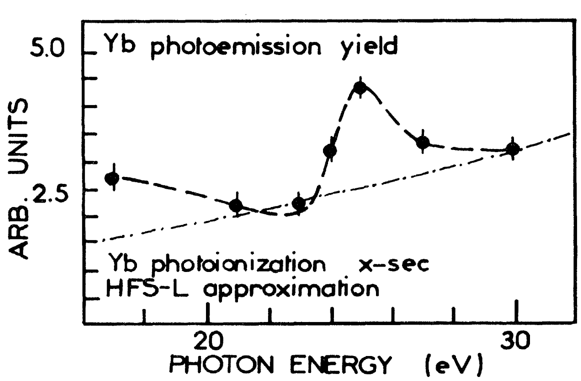


FIG. 3. Photoemission yield (normalized CIS) for the $4f$ states in fcc Yb as compared with the calculated photoionization cross section for atomic Yb $4f$ orbitals (Hartree-Fock-Slater-Length approximation). The resonance at the $5p_{3/2}$ threshold is the result of the coupling of photoionization and the discussed autoionization decay.

The distinction suggested of resonantly enhanced autoionization and Auger decay is mostly semantic, but allows to connect our discussion with the known resonant processes of atomic Yb. The excited states of Yb I lie in the continuum of Yb II and Yb III so that autoionization and Auger decays may follow the excitation of a $5p$ electron in atomic Yb.[12] In particular, due to the presence of easily collapsed $5d$ empty orbitals (the next element is Lu, which is $4f^{14}6s^2 5d^1$), "giant" $5p$-$5d$ resonances are responsible for sharp peaks in the Yb I $5p$ absorption spectrum at excitation energies between 27 and 28 eV.[12–14] The decay of the excited states of Yb I can yield series of ejected-electron peaks corresponding to final states like $5p^6 6s$, $5p^6 6p$ or $5p^6 4f^{13} 6s^2$, at energies between 17 and 20 eV KE.[12]

In other words a strong $5p$-$5d$ dipole, resonantly enhanced by the collapse of the $5d$ wave function under the potential of the $5p$ hole[14] makes autoionization with ejection of a loosely bound electron a highly favorable process.

Our suggested explanation of the data implies that the formation of a localized $5d$ impurity-state screening orbital is an effect, at the solid state, that is related to the atomic collapse of the $5d$ wave function.[15] A weak $5d$ band character and the presence of a high density of empty ($5d$) states at $E_F$ would be the prerequisites for the process to occur. In this respect it is illuminating the fact that in Yb silicides the CKE "replica" emission does not appear. As expected from the electronic structure of the transition metal silicides, Si-$3p$–metal-$nd$ valence states hybridize to form bonding bands. A full (hybrid) band character is then expected for the Yb $5d$ states in the Yb-Si compounds, not allowing the local collapse of an atomiclike orbital. We add that the ordinary CVV Auger transition (with $C = 5p$) in these silicides has so little intensity that it is basically lost in the background of the spectra.[3] The CKE "replica" emission is therefore expected to be important only in systems electronically similar to metallic Yb, like Eu[16] and possibly some rare-earth compounds with empty $d$ bands at the Fermi level.

In summary, we observe a strong emission at CKE, above the $5p$ threshold in Yb metal, that mimics the distribution of the valence and $4f$ states. We associate this phenomenon with the existence of a localized $5d$ state attracted by the $5p$ core hole which acts as an intermediate state for autoionization decays (the Auger process is also an autoionization), reminding the related atomic processes. The superposition of the autoionization decay and the photoionization gives a resonance line shape to the Yb $4f$ photoelectron yield.

A more detailed and quantitative understanding of the observed phenomenon will only become possible after more experimental and theoretical work is done; in particular, variations of the intensity of the CKE emission with $5p$ core hole lifetime (i.e., excitation energy) could be important.

At any rate, the interesting physics that emerges from this phenomenon is the existence of a strong *intra-atomic* relaxation happening in a solid, that more efficient (faster) than the conduction-band relaxation.

In this respect, we note that in a mixed valent alloy of Yb ($YbAl_3$) a different, strong effect (not well characterized, due to insufficient data) induced by the $5p$ core hole was found,[17] consisting in a $4f^{13}$-$4f^{14}$ valence change as an intra-atomic relaxation mechanism. It thus appears that photoemission in proximity of shallow core-level thresholds, like the $5p$ in rare earth, can be accompanied by highly efficient competitive intra-atomic relaxation processes that deserve study and may shed light on the complex problem of solid-state relaxation upon electron emission.

G. Rossi wishes to thank many colleagues for stimulating discussions. The experiment was supported by National Science Foundation Grant No. DMR-79-13102 and was performed at the Standford Synchrotron Radiation Laboratory which is supported by U.S. Department of Energy, Office of Basic Energy Sciences, and National Science Foundation, Division of Material Research.

---

*New address: Laboratoire pour l' Utilisation du Rayonnement Electromagnêtique, Universitè de Paris-Sud, Batiment 209 C, 91405 Orsay, France.

[1] *Ab initio* relativistic augmented plane wave (RAPW) band calculations for fcc Yb show a small energy gap between filled and empty bands, but small adjustments of the potential are enough to make the bands overlap, as a consequence a very small amount of $s$-$d$ mixing, if any, is present in solid Yb. de Haas–van Alphen and magnetoresistance data are also ambiguous about the semimetallic or metallic character of fcc Yb. For a review, see S. H. Liu, in *Handbook of the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978).

[2] J. A. Endriz and W. E. Spicer, Phys. Rev. B 2, 1466 (1970).

[3] Photoemission data, strictly comparable to those presented in this Rapid Communication, for Yb/Si reacted interfaces will be presented elsewhere; an account of the XPS results on those samples is found in G. Rossi, J. Nogami, J. J. Yeh, and I. Lindau, J. Vac. Sci. Technol. B 1, 530 (1983).

[4] Light from a Seya-Namyoka monochromator was impinging the sample surface at grazing incidence, in a $5\times10^{-11}$-Torr environment. The electron emission was collected with a cylindrical mirror analyzer whose axis was normal to the sample surface. The Yb film was $\sim 500$ Å thick onto a UHV scraped polycrystalline Yb substrate.

[5] On the surface shift of Yb $4f$ see, for example, F. Gerken, J. Berth, R. Kammerer, L. J. Johansson, and A. Flodstrom, Surf. Sci. 117, 468 (1982).

[6] The upper $h\nu$ cutoff of the beam line was 31 eV. The CKE features can also be seen in the spectra at $h\nu = 40$ eV by H. Ishii, T. Honyu, H. Ohkuma, and S. Yomaguchi, ISSP, University of Tokyo, Activity Report of the Synchrotron Radiation Laboratory (unpublished), p. 71.

[7] The exact spacing and intensity ratio of the CKE peaks depends on the $h\nu$ dependent background of the subtracted spectra.

[8] G. Rossi, I. Lindau, L. Braicovich, and I. Abbati, Phys. Rev. B 28, 3031 (1983).

[9] See, for example, D. Chandesris, J. Lecante, and Y. Petroff, Phys. Rev. B 27, 2630 (1983).

[10] O. Gunnarsson and K. Schonhammer, Phys. Rev. Lett. 41, 1608 (1978).

[11] J. C. Fuggle, M. Campagna, Z. Zolnierek, and R. Lässer, and A. Platau, Phys. Rev. Lett. 45, 1597 (1980); F. Ulrich Hillebrecht, J. C. Fuggle, P. A. Bennet, Z. Zolnierek, and C. Freiburg, Phys. Rev. B 27, 2179 (1983).

[12] R. A. Rosenberg, S. T. Lee, and D. A. Shirley, Phys. Rev. A 21, 132 (1980).

[13] D. H. Tracy, Proc. R. Soc. London Ser. A 357, 485 (1977).

[14] G. Wendin, in *Vacuum Ultraviolet Radiation Physics* (Pergamon, Vieweg, 1974).

[15] J. F. Herbst and J. W. Wilkins, Phys. Rev. B 26, 1689 (1982).

[16] Unpublished work by the authors.

[17] W. F. Egelhoff and G. G. Tibbets, Phys. Rev. Lett. 44, 482 (1980).