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UV photoionization cross section in low-*d*-occupancy transition metals determined with inverse photoemission

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The photon energy dependence of the photoionization cross section in a solid has been measured in the UV region ($10 < h\nu < 25$ eV) using an experimental method based on inverse photoemission. Measurements have been performed on low-*d*-occupancy transition metals (Ti, Zr, Hf, V, Nb, and Ta). The observed trend is in good qualitative agreement with the available atomic calculations, at variance with measurements around the Cooper minimum region ($50 < h\nu < 200$ eV), where strong modifications with respect to the isolated atom have been observed in previous experiments based on direct photoemission.

The valence electron states of condensed materials can be directly probed with photoemission spectroscopy: the filled states below E_F can be probed with direct photoemission[1] (PES) and the empty states above E_F with inverse photoemission (IPES).[2] In both spectroscopies the excitation process relies upon the interaction between the photon field and the valence electrons. In direct photoemission, a photon is absorbed by the valence electron whereas in inverse photoemission a photon is emitted during the radiative decay of the energetic electron injected in the solid. These two processes are connected by a time-reversal relationship.[3]

A key parameter in PES and IPES is the photoionization cross section (σ), particularly its photon energy dependence, $\sigma(h\nu)$, which constitutes a unique description of the orbital character of the electron states involved in the excitation process. As far as the isolated atom is concerned a great effort, both theoretical and experimental, has been devoted to the investigation of $\sigma(h\nu)$. Moving from the isolated atom to the solid, the valence wave functions are distorted by the formations of the bond and therefore a modification of $\sigma(h\nu)$ is expected. However, in spite of its relevance, the available information on this subject is relatively scarce. To our knowledge no calculations have been performed on the role of solid-state effects on $\sigma(h\nu)$ except for the particular case of $h\nu = 1487.6$ eV (Ref. 4) and for Silver above threshold.[5] From an experimental point of view $\sigma(h\nu)$ has been measured for *d* states of various transition metals in the photon energy region of the so-called "Cooper minimum," i.e., for $h\nu$ between 50 and 200 eV.[6] The available data show that, in this spectral region, $\sigma(h\nu)$ remains strongly atomiclike in noble and near-noble metals whereas it undergoes strong modifications in low-*d* occupancy transition metals. For photon energies below a few tens of eV, the spectral region in which $\sigma(h\nu)$ has its largest values and undergoes its strongest variations, no data have been published until now.

The present paper describes measurement of the photon energy dependence of the photoionization cross section in the energy range between 10 and 25 eV for *d* states in low-*d*-occupancy transition metals. The experimental technique adopted is new since it is based on inverse photoemission, at variance with the measurements performed until now, all based on direct photoemission. This technique, as discussed below, offers a relatively simple way of extracting information on $\sigma(h\nu)$ from the IPES spectra[7] by avoiding certain difficulties involved with the calibration of the photon flux intensity in direct photoemission experiments. The major goal of this work is to present the experimental values of $\sigma(h\nu)$; a deeper understanding will be possible only when detailed calculations of $\sigma(h\nu)$ in the solid state will be available.

The IPES apparatus is described in more detail elsewhere.[8] Briefly (Fig. 1), a beam of monoenergetic electrons is sent onto the sample (*S*) and the photons produced by their radiative decay are dispersed with a grating (*G*) on a flat field where a multichannel detector (MCP) allows one to collect up to 12 simultaneous spec-

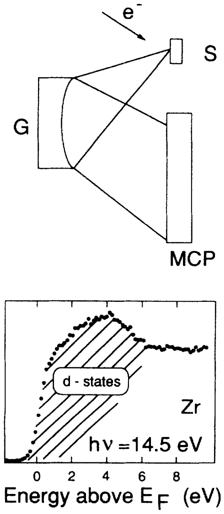

FIG. 1. In the upper part it is shown the experimental layout of the inverse photoemission apparatus used in the present investigation. In the lower part it is shown a typical isochromat spectrum from bulk polycrystalline Zr. The dashed portion of the spectrum is mostly determined by *d*-derived states.

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tra. The data presented here have been collected in the so-called "isochromat" mode by scanning the electron energy and by keeping the photon energy constant in each spectrum. The large angular spread of the electron beam assures that the spectra must be regarded as k integrated. The metallic sample were polycrystal cut from high-purity commercial rods. The clean surfaces were prepared *in situ* in the vacuum system (base pressure 1×10^{-10} Torr) by scraping with a diamond file. A typical example of an isochromat spectrum from a Zr sample is shown in the lowest part of Fig. 1; our experimental data consist in a collection of spectra like this, each characterized by a different photon energy. The photon energy range covered by our grating is between 10 and 25 eV. The dashed area in the spectrum of Fig. 1 indicates the d-derived portion of the spectrum, which is proportional to the photoionization cross section and to the instrumental efficiency:[9] $I(h\nu)\propto\sigma(h\nu)\times\eta(h\nu)$.

Clearly, it is straightforward to extract the photon energy dependence of σ from the spectra as soon as the photon energy dependence of the instrumental efficiency is known. It must be observed that $\eta(h\nu)$ only depends on the instrumental apparatus and not on the particular sample under investigation. In order to determine $\eta(h\nu)$ two equivalent calibration procedures can be used, as described in Refs. 10 and 11. The photon energy dependence of η determined with these two experimental procedures is in good agreement with the one expected by taking into account the reflectivity of the gold coating of our grating, its blaze angle, and the spectral response of the microchannel plate used for photon detection. In the following therefore it will be assumed that $\eta(h\nu)$ is given. A more detailed discussion of the problems involved with the procedure adopted in determining $\sigma(h\nu)$ can be found in Ref. 11.

Figures 2 and 3 show the experimental values of $\sigma(h\nu)$ (dots) for d-derived states in two columns of the Periodic Table. The original spectra are not shown here for space reasons but an overview can be found in Fig. 1 of Ref. 12. In these spectra the extension of the d-related signal on the energy scale has been assumed to be equal to the corresponding width of the d-projected DOS (density of states) calculated within a single-particle approximation.[13] In order to extract the d-related signal from the spectra, the details of the background subtraction procedure are not particularly relevant since the trends shown in Figs. 2 and 3 do not critically depend on it. The incertitude in $\sigma(h\nu)$ related to the background subtraction fall within the error bars. Each series of experimental points is compared with the atomic calculations of Ref. 14 (solid line). The absolute intensity of the cross section is not accessible with our experimental technique and therefore the intensities have been normalized in a convenient way in order to compare their photon energy dependence. More precisely, in Figs. 2 and 3 the theoretical cross sections are shown with their true value whereas the experimental values have been multiplied by a constant factor. In this way, even if the absolute values of the experimental cross section is not known, it is possible to appreciate the relative changes of $\sigma(h\nu)$.

Generally speaking, the data shown in Figs. 2 and 3 in-

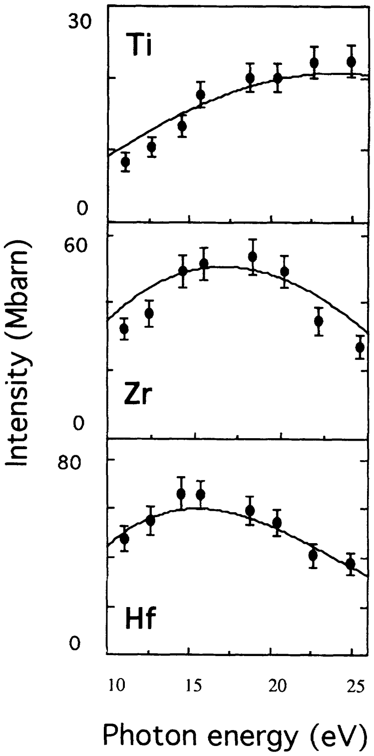

FIG. 2. Experimental values (dots) of the photon energy dependence of the photoionization cross section for Ti, Zr, and Hf. The solid line shows the single-particle calculations for the isolated atom by Yeh and Lindau (Ref. 12).

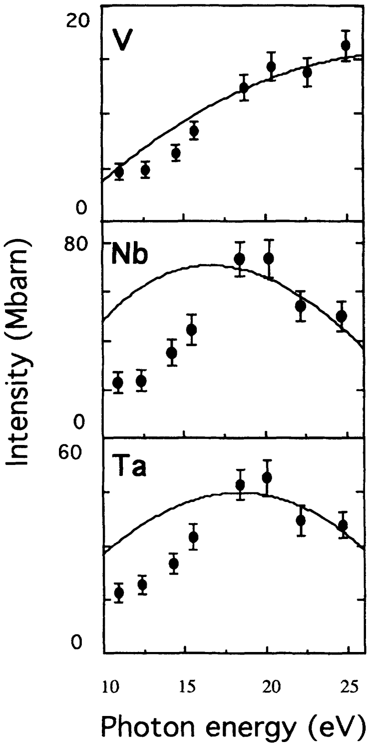

FIG. 3. Experimental values (dots) of the photon energy dependence of the photoionization cross section for V, Nb, and Ta. The solid line shows the single-particle calculations for the isolated atom by Yeh and Lindau (Ref. 12).

dicate that the experimental trend is in qualitative agreement with the atomic calculations. This is nontrivial since, for Zr and Mo, a strong distortion of the experimental cross section has been observed in the Cooper minimum region (50–200 eV) with respect to the atomic calculations.[6] In particular, it is interesting to observe that the agreement is particularly good as far as the position of the maximum of the cross section is concerned. On the other hand, in the low $h\nu$ region discrepancies are observed for V, Nb, and Ta (Fig. 3). In the following discussion, mostly focused on the similarities between experimental data and theory, it will be shown how a simple model can explain the relatively lower sensitivity, in the UV, of $\sigma(h\nu)$ to the modification of the wave function with respect to the Cooper minimum region. Finally, we will try to point out the possible reasons of the observed discrepancies.

In a very crude model $\sigma(h\nu)$ is proportional to the square of the matrix element which connects, via a dipole operator, the initial atomic wave function with a free-electron final-state wave function. This model, absolutely inadequate for any quantitative estimate, is nevertheless useful in pointing out the most relevant physics involved in determining the energy dependence of σ. In the upper part of Fig. 4 it is shown the energy dependence of σ calculated by assuming as an initial state the atomic Zr $4d$ wave function.[15] In the lower part of Fig. 4 this wave function is shown with dots. The final state has been assumed to be a free-electron spherical wave with $l=3$, i.e., having f character. With this assumption we neglect the transition to a final state having p character $(\Delta l=-1)$ the other channel $(\Delta l=+1)$ being dominant. The most significant considerations on Fig. 4 are the following.

(1) At threshold (point A) σ approaches zero. In the lower part of Fig. 4 the wave function corresponding to a kinetic energy of the photoelectron of 1 eV is shown. Clearly, the overlap with the initial-state wave function is negligible.

(2) For a kinetic energy corresponding to the maximum of $\sigma(h\nu)$ (B) the overlap between the initial and final states is strong, as curve B shows. In other words, the maximum in the cross section is somehow related to the atomic wave function in its region closer to the nucleus.

(3) For a kinetic energy well above the maximum (C) the rapid oscillations of the final-state wave function chop the initial-state wave function in portions having alternate sign whose sum approaches zero.

Upon the formation of the solid the atomic wave function is distorted mostly in its outer region. The region closer the nucleus, where most of the electronic charge is concentrated, is less affected. As discussed above, the maximum in $\sigma(h\nu)$ corresponds to the strongest overlap between the initial and final states which, as Fig. 4 clearly shows, occurs in the region closer to the nucleus, i.e, the one which is less affected by the formation of the bond. On the basis of this argument it is reasonable to understand the experimental observation that $\sigma(h\nu)$ in the UV is not dramatically distorted as occurs at higher energies. In the Cooper minimum region, on the other hand, the absolute value of the cross section is very small due to the cancellation of several terms having different sign and this makes the cross section more sensitive to the modification of the initial-state wave function. Regarding the model adopted in order to obtain the curves shown in Fig. 4 we stress again that its purpose is simply to point out that in the UV region $\sigma(h\nu)$ is mostly determined by the inner part of the atomic wave function. This model cannot be used in order to discuss the discrepancies observed in Figs. 2 and 3.

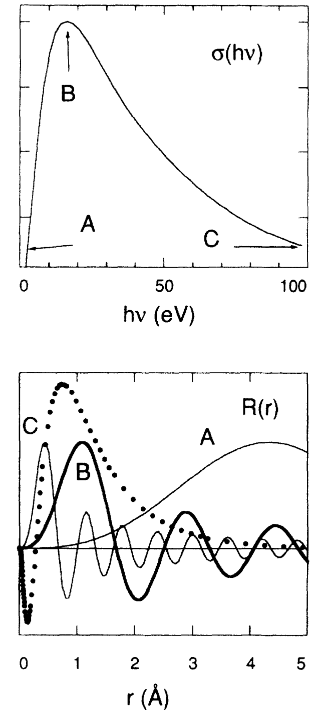

FIG. 4. In the upper part it is shown the photon energy dependence of the photoionization cross section for Zr $4d$ states calculated by taking as a final state a free-electron wave with $l=3$. In the lower part are shown the initial-state atomic wave function (dots, Ref. 13), and the radial wave function corresponding to kinetic energies of the photoelectron equal to 1 eV (curve A), 17 eV (B), and 100 eV (C).

These considerations, purely qualitative, allow one to understand the most relevant physical factor involved in determining our experimental results presented here. These results indicate that the photoionization cross section of d states in bulk metals have a photon energy dependence which is qualitatively in agreement with the atomic calculations performed within a single-particle scheme. In order to gain a better understanding of this result, it would be necessary to compare the experimental data with calculations of $\sigma(h\nu)$ in which the electron states involved in the transition are considered as many-electron Bloch states. This would make it possible to assess the role of band-structure effects such as those connected with the joint density of states, whose relevance is probably non-negligible for low $h\nu$'s. Furthermore, the perturbation introduced by the spectroscopic tool itself, i.e., the addition of an electron in an inverse photoemission experiment, should be included in these calculations. This goal is probably too ambitious at present but we hope that data such as those presented here will stimulate theoretical investigations on this subject.

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