

Solid-State Effects on the Valence-Band $4d$ -Photoionization Cross Sections at the Cooper Minimum

I. Abbati and L. Braicovich

Istituto di Fisica del Politecnico di Milano, I-20100 Milano, Italy

and

G. Rossi and I. Lindau

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

and

U. del Pennino

Istituto di Fisica dell'Università di Modena, I-41100 Modena, Italy

and

S. Nannarone

Istituto di Fisica dell'Università di Roma, I-00100 Roma, Italy

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Experimental evidence is presented for solid-state effects on the $4d$ photoionization around the Cooper minimum for a few transition metals: Ag, Pd, Mo, and Zr. The $4d$ parital cross section appears to be very sensitive to the d - d interaction; thus, the anti-bonding d states have a more atomiclike cross section than the bonding d states.

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As part of the development of a better understanding of atomic photoionization processes, the behavior of the cross section in the Cooper minimum (CM) region has been receiving increased attention.¹⁻⁵ Also, a field of current interest is the transition from atomic physics⁶⁻⁸ to solid-state physics and what implications that has for the photoionization processes and cross sections. In this Letter, we will address the latter problem and present unambiguous evidence for solid-state effects in the partial photoionization cross section of the $4d$ valence-band electrons in transition metals (Ag, Pd, Mo, and Zr).

The interest of CM effects is not limited to the basic questions of atomic to solid-state transition. The CM effect has recently been used in surface physics to obtain information about the local nature of the bonding between a transition metal ($4d$ or $5d$ electrons in the valence band) and a semiconductor substrate (in particular Si and Ge), i.e., in the research on transition-metal silicides and germanides.⁹⁻¹¹ The important aspect in this spectroscopy is that the transition-metal d cross section is sufficiently low in a certain photon excitation region that the Si (or Ge) sp valence states and their changes upon bonding to the transition metal can be observed.¹⁰

Spectroscopy of solids based on the CM effect raises several questions of fundamental interest:

(1) Do CM's always exist in solids composed of atoms having CM? (2) Is there, in general, a modification of the CM due to a solid-state effect? (3) Is there any correlation between such a solid-state effect and the nature of the $4d$ (or $5d$) wave functions in the solid? It thus seemed timely to try to answer some of these fundamental questions. It should be noted that the investigation of CM in solids can have a strong impact on the understanding of CM in atomic systems; solid-state experimental results can be used to test models in a great variety of situations as far as symmetry, shape of the wave functions, and relevant many-body effects are concerned.⁶

We selected four transition-metal elements along the $4d$ period in order to change some important parameters of the $4d$ initial states: the noble metal Ag (fcc), the near-noble element Pd (fcc), and two refractory elements at the beginning of the period characterized by strong d - d bonds and different crystal structures, Zr (hcp) and Mo (bcc). Our data give a comparison of the *shape* of the experimentally determined $4d$ photoionization cross sections (σ) in the photon energy range 70 to 200 eV.

The experiments were done on the "grasshopper" monochromator¹² at the Stanford Synchrotron Radiation Laboratory with use of a cylindrical mirror analyzer (CMA) for the photoelectron de-

tection. The Pd and Ag samples were obtained by evaporation of thick films (~ 100 Å) on clean inert substrates, while polycrystalline Mo and Zr rods were cleaned *in situ* by scraping with a diamond file. All the experimental details and the method used to measure the cross section σ will be described at length elsewhere.¹³

The measured σ (in arbitrary units) integrated over the acceptance angle of the CMA is related to the measured counting rate C by the equation

$$C = \sigma L \xi \Phi F(\chi, n, k, L), \quad (1)$$

where L is the electron escape depth (from Seah and Dench¹⁴), ξ is the efficiency of the CMA,¹⁵ Φ is the photon flux,^{13,15} and F accounts for the light reflection and refraction at the sample surface. F depends on L , the incident angle of the light χ , and the complex index of refraction $n + ik$ of the sample. The evaporated samples (Ag and Pd) could be measured at near-normal incidence, where the function F tends to unity in the extreme uv region.¹⁶ For the scraped samples (Mo and Zr), it was only possible, for technical reasons, to work at grazing incidence of the light ($\chi \cong 15^\circ$), and the optical correction factor F had to be calculated. The optical constants for Zr and Mo were obtained from a Kramers-Kronig transformation of the optical absorption data given by Weaver and Olson.¹⁷ Mo and Zr have rather flat absorption spectra¹⁷ in the relevant photon energy range $h\nu = 100$ to 200 eV, resulting in fairly small deviations in the F factor (less than 20%). The corrected σ for Zr and Mo (solid lines) is shown in Fig. 1, along with the experimental σ^* (dashed lines). The following should be noted:

(1) The measured σ can be divided into two distinct groups: The noble and near-noble metals (i.e., Ag and Pd) show a clear CM, whereas the σ for the refractory metals (i.e., Zr and Mo) vary slowly with $h\nu$ and retain only a shoulder, reminiscent of the CM effect but shifted to higher $h\nu$ by roughly 50 eV.

(2) The position of the maximum in σ is shifted to higher $h\nu$ in the refractory metals which also show a smoother onset of the cross section.

(3) The difference in the CM is attributed to a solid-state effect. The dependence on Z for the photoionization cross section of $4d$ electrons in the atomic case is weak, as might be expected since the $4d$ wave function does not change appreciably with the occupation number. This was clearly demonstrated by a recent Hartree-Fock-Slater calculation, using atomic wave functions,¹⁸ for the photoionization cross section of $4d$ elec-

trons in atoms with Z ranging from 39 to 54, which showed that there is only a small progressive shift of the peak of σ and of the CM towards higher $h\nu$ with increasing Z .¹⁹ The calculated σ for $5d$ electrons in atomic Au, Pr, W, and Ta also show similar CM effects.²⁰

(4) A full interpretation of the results shown in Fig. 1 will require a theoretical analysis which we hope our data will stimulate. At present, we can make some tentative suggestions related to the energy dependence around the CM. We will not discuss the changes in the onset of the cross section and the width of the maximum, both of which are known to be sensitive to many-body effects.²¹

The results shown in Fig. 1 suggest that the

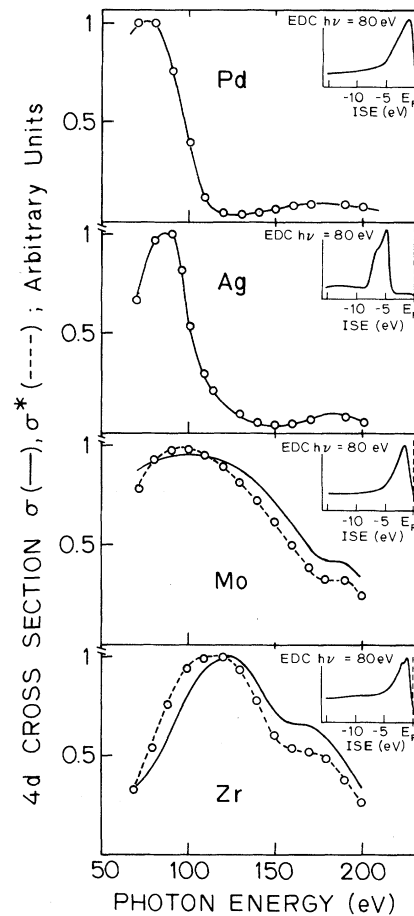


FIG. 1. Partially angle-integrated photoionization cross sections for the $4d$ subshell in Pd, Ag, Mo, and Zr in the $h\nu$ range 70 to 200 eV. The solid curves represent the cross section (see text). Insets: The angle-integrated electron energy distribution curves (EDC) for the four metals, as obtained with $h\nu = 80$ eV (ISE is the initial-state energy).

characteristics of the initial states are very important in determining the CM. In fact, there is a strong correlation between the two different kinds of behavior of the $4d$ cross sections and the nature of the d states in the two groups of elements, Ag and Pd versus Zr and Mo.

The refractory metals Zr and Mo have low occupation numbers for the d shell and only d -bonding states are present in the filled valence band, the corresponding antibonding states being empty and above the Fermi level.²² In the noble and near-noble metals, both the bonding and antibonding d states are occupied.

The strongest deformation of the wave function ψ , with respect to the free-atom case, takes place for states with strong bonding character and occurs mainly in the region beyond the radial node, i.e., in a region which is very important in determining the $4d$ CM. In fact, for Zr and Mo, the (atomic) ψ is a minimum at distances from the nucleus which are comparable to the ionic radii, whereas the minimum of the ψ for Ag and Pd is well within the ionic radii of these two elements.²² Distortions in the radial part of the wave function due to the solid thus occur in a region of d - d overlap which is more sensitive for changes for the refractory metals than for the noble and near-noble metals. This is a plausible explanation for the fact that the strongest solid-state effects on the CM are found for Zr and Mo.

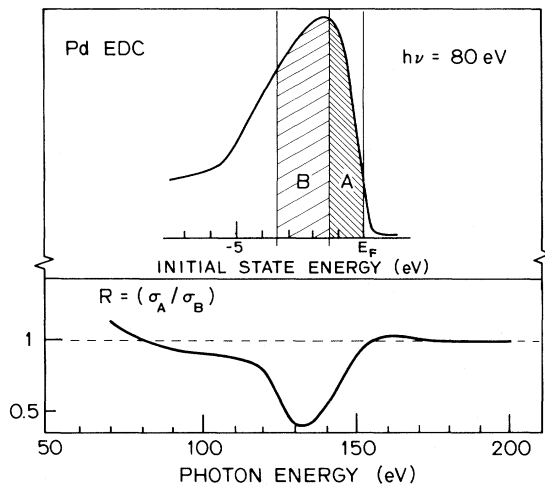


FIG. 2. Top panel: Angle-integrated EDC for Pd metals as obtained with $h\nu = 80$ eV. The states in region A (between -1.2 eV and E_F) are mostly $4d$ antibonding, while the states in region B (-3.5 to -1.2 eV) are $4d$ bonding. Bottom panel: Ratio of the counting rates (see text) for (region A)/(region B) of the Pd $4d$ band in the $h\nu$ range 70 to 200 eV.

The analysis of further experimental results supports this picture, namely that the nature of the initial states plays a key role in determining the solid-state CM. The $4d$ valence states of Pd can be divided into two energy regions which have different energy dependences for the cross section σ . This is demonstrated in Fig. 2 where the valence-band photoemission spectra for Pd taken at a photon energy of 80 eV is shown. The area ratio between the σ of the two indicated regions A and B is also plotted. The shallow valence states between ~ -1.3 eV and E_F contain a strong antibonding contribution. It is then interesting to compare the σ for these states to the σ for the deeper-lying bonding states (here taken as the states between -3.3 and -1.3 eV).

The difference of the two σ is strong in the CM region, 120 to 150 eV, with the shallow antibonding states having a more pronounced CM than the deeper bonding states. This shows that the d states with some antibonding character are more "atomiclike" in their σ behavior. This observation is also consistent and analogous to that reported by Carlson *et al.*²³ for the CM behavior in bonding and nonbonding lone-pair orbitals of

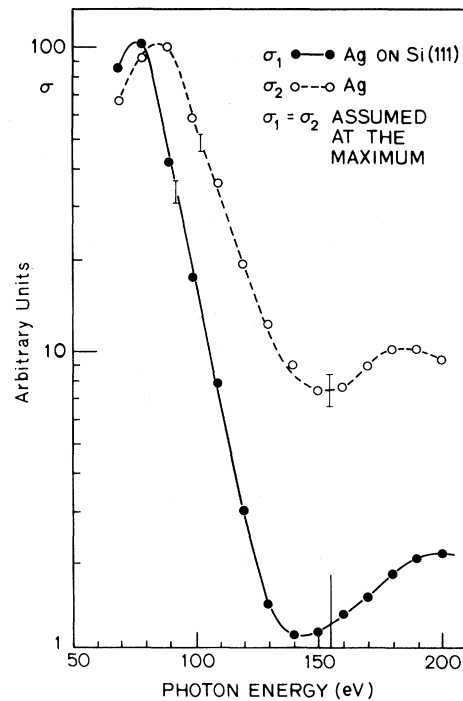


FIG. 3. Partially angle-integrated photoionization cross sections for Ag $4d$ for metallic Ag (dashed line) and for semi-isolated Ag atoms on the Si(111) 2×1 surface.

molecules (e.g., CCl_4).

One further result that supports our explanation can be obtained from the $4d$ cross-section data for bulk Ag and for semi-isolated Ag atoms (Ag atoms deposited at submonolayer coverages onto a Si substrate). The comparison is given in Fig. 3 and shows a dramatic difference in the $4d$ cross section. The result for bulk Ag is in qualitative agreement with the CM reported earlier by Wehner *et al.*,¹⁸ i.e., it agrees very well in energy position but differs slightly in the overall shape, probably because of the different correction factors discussed earlier. The CM is roughly a factor of 8 stronger for the semi-isolated Ag atoms on the Si surface than for bulk Ag (see Fig. 3). From this, we can infer that the $4d$ wave function is atomiclike in the absence of d - d interactions. In fact, the result for the semi-isolated Ag atoms compares favorably with the atomic calculation for Ag $4d$.¹⁹

Summarizing, we have presented the results of the first systematic investigation on solid-state effects on the partial photoionization cross section of a valence-band shell around the Cooper minimum. We have shown that the Cooper effect is severely reduced in orbitals with strong bonding character, and we propose that this phenomenon is primarily a consequence of the distortion of the radial part of the wave function in the overlap region in the solid state. We have also indicated how the cross-section behavior can be used as a diagnostic tool to probe the degree of localization of the valence state, i.e., the transition from atomic to solid-state physics.

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