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Author

Kowalczyk, S.

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HIGH-RESOLUTION XPS SPECTRA OF Ir, Pt, AND Au VALENCE BANDS[†]S. Kowalczyk, L. Ley^{††}, R. Pollak[‡], and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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Structural features in the valence band XPS spectra vary from Ir ($Z = 77$) to Au ($Z = 79$) as expected on the basis of 5d6s band filling.

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X-ray photoelectron spectroscopy (XPS) spectra (hereafter denoted by $I(E)$) of the valence bands of several sixth-row elements have been reported earlier [1,2]. Those spectra were obtained from heated metal foils at resolutions of ~ 1 eV, in the presence of hydrogen gas. Although trends in $I(E)$ for the fcc-metals Ir, Pt, and Au were suggestive of band filling, detailed interpretation was precluded both by experimental limitations and by a lack of appropriate theoretical densities of states, $\rho(E)$, with which to compare $I(E)$. Several relativistic $\rho(E)$ calculations on Au have recently become available. Two of them [3,4] compare very well with the high-resolution (~ 0.6 eV) XPS spectrum of Au [5]. In this Letter we report the results of a high-resolution study of $I(E)$ for Ir, Pt, and Au that confirms the band-filling model for these elements.

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^{††}On leave from University of Bonn, Germany.

[‡]In partial fulfillment of Ph.D.

The experimental procedures have been described elsewhere [6]. Briefly, high-purity single crystals were spark-cut, mechanically polished, electro-polished, and introduced into a sample-preparation chamber at 2×10^{-7} Torr. They were then argon-ion bombarded (10 μ A, 1000 eV) at 8×10^{-5} Torr of argon and introduced into a Hewlett-Packard HP 5950A ESCA spectrometer at 8×10^{-9} Torr. In-situ monitoring of the carbon 1s and oxygen 1s lines showed these elements to be present in negligible amounts.

The raw spectra $I(E)$ are shown in Fig. 1, together with $I'(E)$, the spectra after correction for inelastic scattering. The similarity of $I'(E)$ for these three elements is striking and its variation from Ir to Pt to Au confirms band-structure expectations. To permit discussion of these $I'(E)$ within the framework of theoretical $\rho(E)$ predictions, we have truncated the $\rho(E)$ for Au, as calculated by Connolly and Johnson [2], to correspond to occupancies of 9 and 10 electrons in the 5d6s bands, thus simulating Ir and Pt, respectively. The results were broadened to simulate the experimental resolution [1,5], and the energy scales were expanded by 1.35 for Ir and 1.20 for Pt, to roughly match the experimental bandwidths. The resulting very approximate $\rho(E)$'s are also shown in Fig. 1.

Proceeding from Ir to Pt to Au, the band-filling phenomenon is quite evident. Four features, numbered in Fig. 1, are present in all three cases. These are: (1) A shoulder at 6.8 eV in Ir, 6.1 eV in Pt, and 7.0 eV in Au. (2) A peak at 3.8₅ eV in Ir, 4.3₅ eV in Pt, and 6.1 eV in Au. (3) A minimum at 3.0 eV in Ir, 3.3 eV in Pt, and 5.0 eV in Au. This feature is present in the calculated $\rho(E)$ for Au only if spin-orbit interaction is included. It may be less pronounced in Ir and Pt because for these lighter elements the ratio of

lattice interactions to spin-orbit interactions is larger. (4) Another peak component at 1.4_5 eV in Ir, 1.7_5 eV in Pt, and 3.5_5 eV in Au. The quoted energies are known to ± 0.1 eV.

A fifth feature--a second component of the second peak--appears at 0.8 eV in Pt and at 2.65 eV in Au. This part of $\rho(E)$ is at least partially unoccupied in Ir. The dip between features 4 and 5 is very shallow, especially in Au. In Au the 5d bands have become filled and dropped below E_F , as expected. The width of the occupied 5d bands as measured between the outermost inversion points of $I'(E)$ decreases systematically from 7.4 eV (Ir) to 7.1 eV (Pt) to 5.4 eV (Au). This is also expected. In auxiliary studies on liquid Hg ($Z = 80$) we found that the 5d states have assumed the character of a spin-orbit split core doublet, at 7.7 eV and 9.5 eV.

In summary, these high-resolution XPS spectra support the band-filling concept in considerable detail. It would be of interest to compare these $I'(E)$ spectra with $\rho(E)$ results from a systematic theoretical study of these three adjacent isostructural elements.

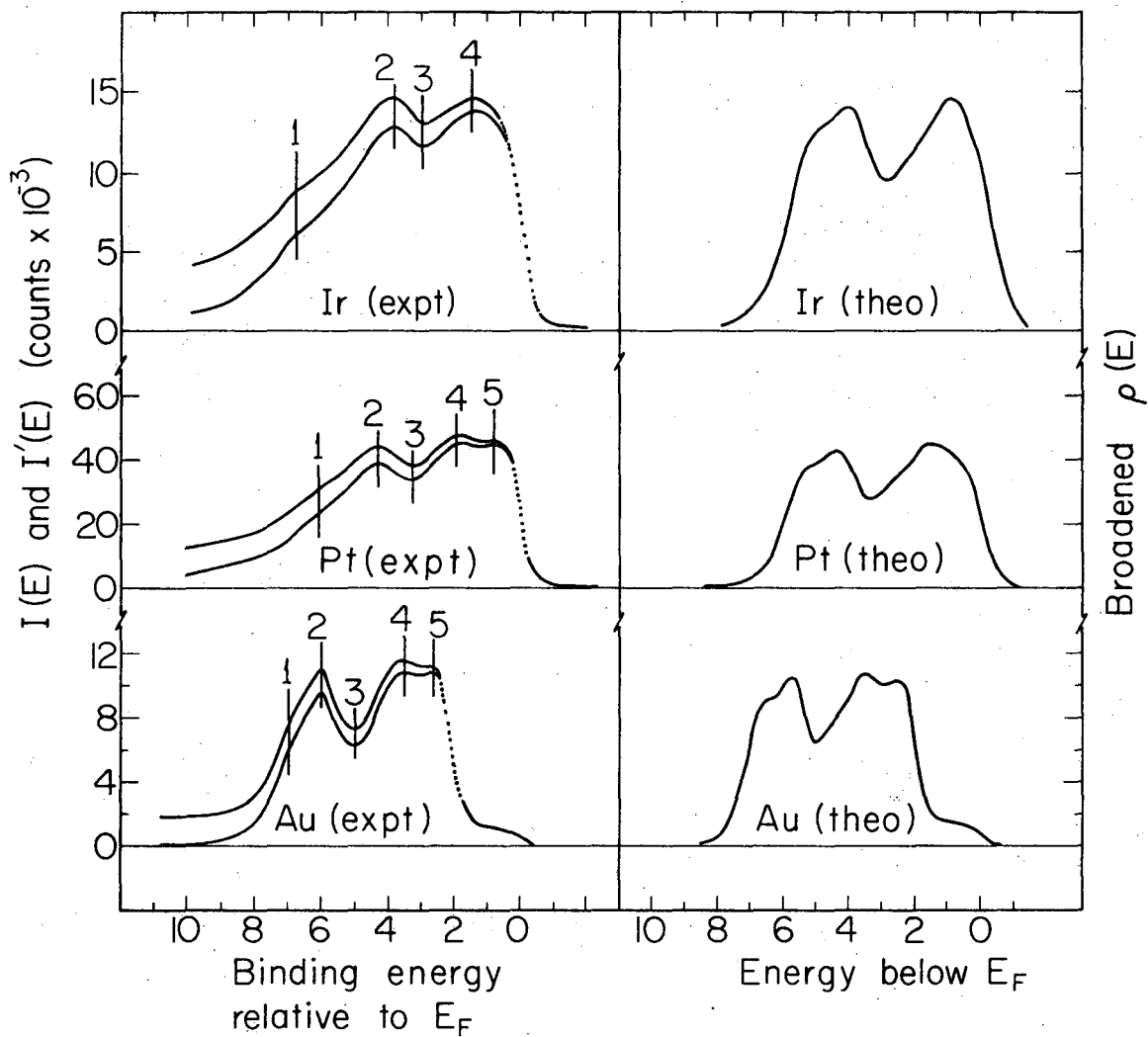
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References

1. C. S. Fadley and D. A. Shirley, J. Res. Nat. Bur. Standards 74A (1970) 543.
2. Y. Baer, P. F. Hedén, J. Hedman, M. Klasson, C. Nordling, and K. Siegbahn, Physica Scripta 1 (1970) 55.
3. J. W. D. Connolly and K. H. Johnson, MIT Solid State and Molecular Theory Group Report No. 72, p. 19, 1970 (unpublished); and private communication.
4. N. E. Christensen and B. O. Seraphin, Phys. Rev. B4, 3321 (1972).
5. D. A. Shirley, Phys. Rev. B5 (1972) 4709.
6. R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Letters (to be published).

Figure Caption

Fig. 1. Left panels and left ordinate: experimental XPS spectra of 5d6s bands of Ir, Pt, and Au. Upper curve in each case shows raw spectrum $I(E)$; lower curve is the corrected spectrum $I'(E)$. Data were all taken digitally. They are shown as points only for the leading edges of the 5d bands, where data density permits. Right panels and right ordinate: Theoretical densities of states obtained by broadening Connolly and Johnson's $\rho(E)$ results. For Ir and Pt this $\rho(E)$ was truncated and the energy scale expanded.



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Fig. 1

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