Core-line asymmetries in the x-ray-photoemission spectra of metals

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Core-line asymmetries have been observed in the x-ray–photoemission spectra of a number of metals. They are ascribed to the interaction of the suddenly created potential of the photohole with the conduction electrons. A comparison of the experimental line shapes with those predicted by a theoretical calculation gives reasonable agreement. The procedure makes it possible to measure the term that quenches the x-ray absorption threshold singularity and shows that it can be substantial.

INTRODUCTION

High-energy probes such as x-ray-photoemission spectroscopy (XPS) and x-ray absorption and emission spectroscopy (XES) are valuable techniques for the study of the electronic structure of solids. It has, however, been realized for some time that in metallic systems these techniques are complicated by the interaction of the positive hole created in the process itself with the mobile conduction electrons.[1–5] As a result the spectra produced by these techniques do not, in general, represent simply the electronic states of the material under investigation, but may contain additional structure produced by this core-hole–conduction-electron interaction. This additional structure manifests itself as an enhancement (or quenching) of the absorption or emission at threshold in x-ray spectra[6] or as an asymmetry of core lines in XPS spectra.[7] Mahan[1] first formulated the theory for the x-ray-absorption problem and was able to show that the scattering of the conduction electrons by the hole potential results in a singularity at threshold. Nozières and DeDominicis[2] solved this problem exactly. Their results reveal that there are, in fact, two phenomena which contribute x-ray singularities, namely, the singular scattering of the electron excited to the Fermi energy and the singular readjustment of the Fermi sea to the core-hole potential. The relative strength and sign of these two contributions determines whether the intensity at threshold is enhanced or quenched.

The status of the experimental verification of these theoretical predictions has recently been summarized by Dow,[8] who concluded that so far none of the experiments supports the theoretical predictions in detail. This may be due to inadequate data treatment or to oversimplification in the application of theoretical predictions to actual metals.

Measurements of photoelectron line shapes,[9–11] or of x-rays originating from transitions between two core levels,[9] provide an alternate approach to this problem. In these experiments only one of the above effects is operative, namely, the readjustment of the Fermi sea to the suddenly created local hole potential. This effect is, of course, more important in XPS, in which the initial state has no core hole, than XES, in which both initial and final states have a hole, but with different potentials. The analysis and conclusions should therefore be clearest in XPS. The core-level line shape expected in photoemission due to the hole-conduction-electron coupling has been calculated by Doniach and Sunjic[9] using the results of Nozières and DeDominicis.[2]

The kinetic energy of a photoelectron can, in general, be written

$$E = h\nu + E_i - E_f - \varphi \ , \tag{1}$$

where E_i and E_f are the initial- and final-state energies of the system under investigation measured relative to the Fermi energy, and φ is the work function. E_f contains the contribution due to the readjustment of the Fermi sea. According to Ref. 2 the energy distribution in the immediate vicinity of the Fermi energy is given by

$$1/\zeta_0^{\alpha}\epsilon^{1-\alpha} \ , \tag{2a}$$

$$\alpha = 2\sum_l (2l+1)\left(\frac{\delta_l}{\pi}\right)^2 \ , \tag{2b}$$

where ϵ is the energy measured relative to the Fermi energy, ζ_0 is an energy of the order of the bandwidth, and δ_l is the phase shift at the Fermi energy of the lth partial wave. Using this result, Doniach and Sunjic[9] calculated the line shape of the photoelectron energy distribution, obtaining

$$I(\epsilon) = \frac{\Gamma(1-\alpha)}{(\epsilon^2+\gamma^2)^{(1-\alpha)/2}} \cos\left[\tfrac{1}{2}\pi\alpha + \theta(\epsilon)\right] \ , \tag{3a}$$

$$\theta(\epsilon) = (1-\alpha)\tan^{-1}(\epsilon/\gamma) \ , \tag{3b}$$

where Γ is the Γ function, and γ is the natural linewidth of the hole state corresponding to its lifetime. For $0 < \alpha < 1$ this expression gives a skew line shape tailing out toward greater binding energy. A fit of Eqs. (3) to experimental photoelectron energy distributions should therefore provide a rough estimate of the exponent α. The accuracy with which this can be achieved depends on the knowledge of the instrumental resolution function, but similar problems are, of course, also encountered in the analysis of x-ray singularities.

Ideally it would be desirable to investigate the photoelectron line shape in simple metals such as Na, Li, Al, or Mg in order to facilitate a comparison not only with theory, but also with the results of the x-ray absorption and emission experiments. However, these simple metals are chemically very reactive and tend to form a surface layer of oxide or hydroxide. The photoelectron signal from such a surface layer unfortunately appears on the high-binding-energy side of the spectrum, as does the asymmetry produced by the electron-hole interaction. The separation of these two effects is consequently very difficult. We therefore decided to investigate the XPS core-level spectra of less reactive metals, even though the analysis may be more difficult because of the *d* character of the conduction electrons. Considering the available possibilities and keeping in mind the desirability of studying systematic trends, the 4*d* and 5*d* metals appear to be the most promising candidates. Ag and its adjacent elements as well as Au and its neighbors in the periodic table pose no significant experimental problems. Moreover, since the 3*d* core lines of the 4*d* metals and the 4*f* lines of the 5*d* metals are relatively narrow (1 eV or less), asymmetries should be readily detectable.

It should be noted that the core-hole–conduction-electron coupling produces another effect in the XPS spectra, namely, a series of plasmon satellites.[4,10,11] This effect is more difficult to observe because these satellites coincide with those created by the energy loss after photoemission. However, since the lowest plasma frequencies in all the metals investigated here are above 5 eV, the plasmon satellites do not interfere with the analysis of core-electron line shapes.

EXPERIMENTAL

Spectra of Rh, Pd, Ag, Ir, Pt, and Au were obtained with a Hewlett-Packard 5950A spectrometer. The samples were either evaporated films or foils which had been mildly argon-ion sputtered to remove surface contamination. For both types of sample, the only detectable impurities were carbon and oxygen, but their intensities were extremely low, especially in the evaporated samples. Keeping in mind that the 3*d* and the 4*f* lines of the 4*d* and 5*d* metals are among the strongest found in XPS spectra, there is no reason to suspect that they will be distorted in a measurable way by overlapping impurity lines. The measuring times were generally of the order of 5 min which proved sufficient to accumulate data of very high statistical accuracy.

In the spectra of all the metals mentioned, except Au, noticeable asymmetries of the line shapes are already visible in the raw data. However, attempts to fit the data directly with the functions in Eq. (3) using a nonlinear least-squares procedure were strikingly unsuccessful. The reason for this failure is readily traced to the instrumental broadening, which, in the case of Ag and Au, is greater than the natural width of the core-hole state. To overcome this problem, Eq. (3) would have to be broadened by convolution with the instrumental resolution function. However, to include this convolution in the least-squares routine requires excessive computer time. We therefore adopted the alternate procedure of deconvoluting the resolution function from the data prior to the fit.

The form of the resolution function was determined from the instrumental response at the Fermi edge of silver and copper. It was found to have a full width at half-maximum of 0.55 ± 0.05 eV and, to first order, a Gaussian shape. More detailed analysis of the Fermi edge, valence bands, and core levels indicates that the shape is slightly asymmetrical. The deconvolution was carried out using an iterative technique.[12,13] After deconvolution, the lines were fitted by Eq. (3). The present experimental results are summarized in Table I and Figs. 1(a)–1(f), which show both raw data and the deconvoluted spectra fitted by Eq. (3). We shall now briefly discuss the results for the various elements:

Au: The lines show no detectable asymmetry in the raw data, and the analysis substantiates this observation. The final linewidth of ~0.4 eV [full width at half-maximum (FWHM)] is compatible with the original data, but larger than the value obtained at low counting rate, which indicates a life-

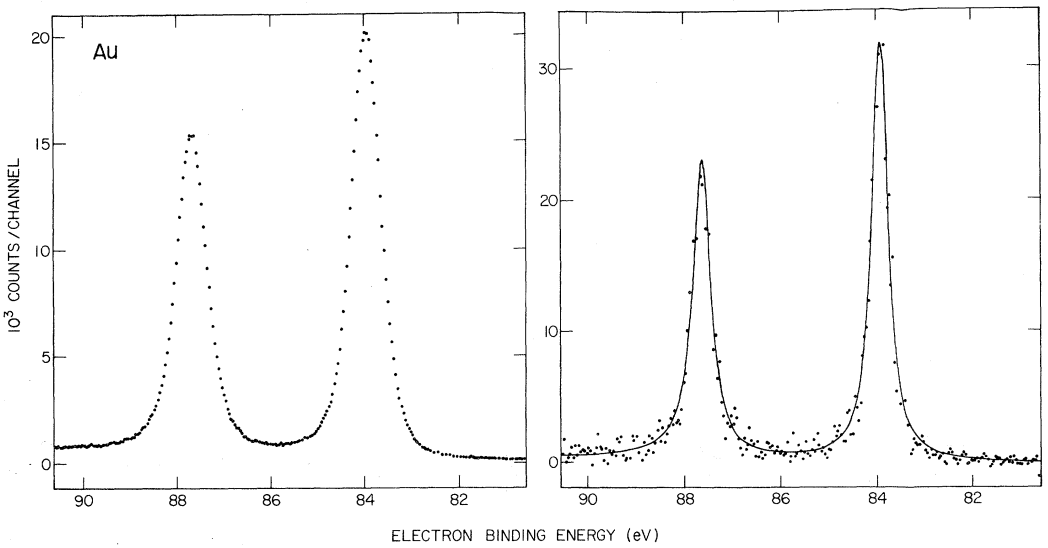
TABLE I. Experimental results; energies are measured relative to the Fermi energy, linewidth 2γ and asymmetry parameter α from a fit to Eq. (3) after deconvolution.

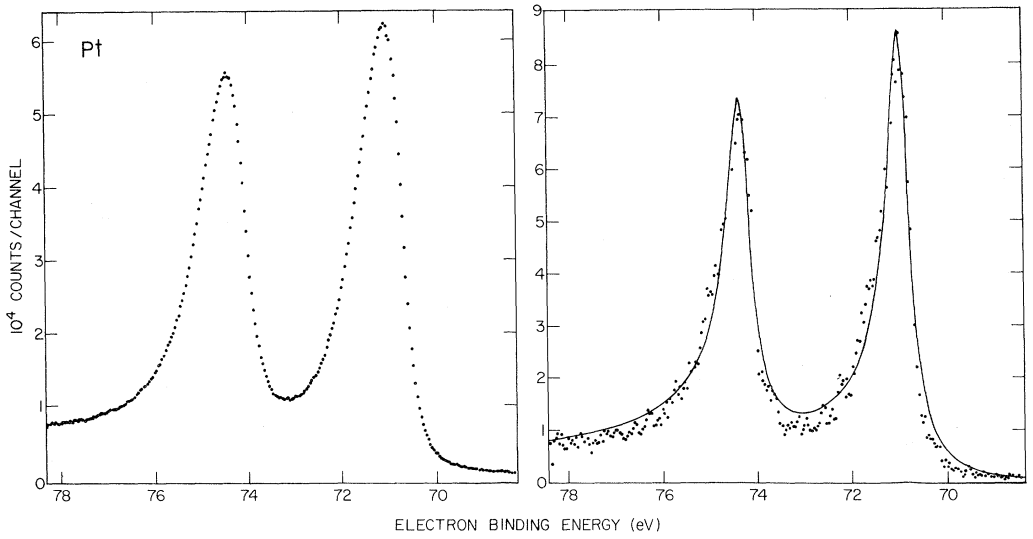
Element	Level	Energy[a] (eV)	2γ[b] FWHM (eV)	α[c]
Rh	$3d_{3/2}$	311.9	0.80	0.20
	$3d_{5/2}$	307.2	0.60	0.10
Pd	$3d_{3/2}$	340.6	0.66	0.25
	$3d_{5/2}$	335.2	0.74	0.11
Ag	$3d_{3/2}$	374.3	0.40	0.07
	$3d_{5/2}$	368.2	0.38	0.03
Ir	$4f_{5/2}$	63.7	0.46	0.13
	$4f_{7/2}$	60.7	0.40	0.12
Pt	$4f_{5/2}$	74.7	0.53	0.19
	$4f_{7/2}$	71.3	0.50	0.19
Au	$4f_{5/2}$	87.7	0.43	0.00
	$4f_{7/2}$	84.0	0.40	0.02

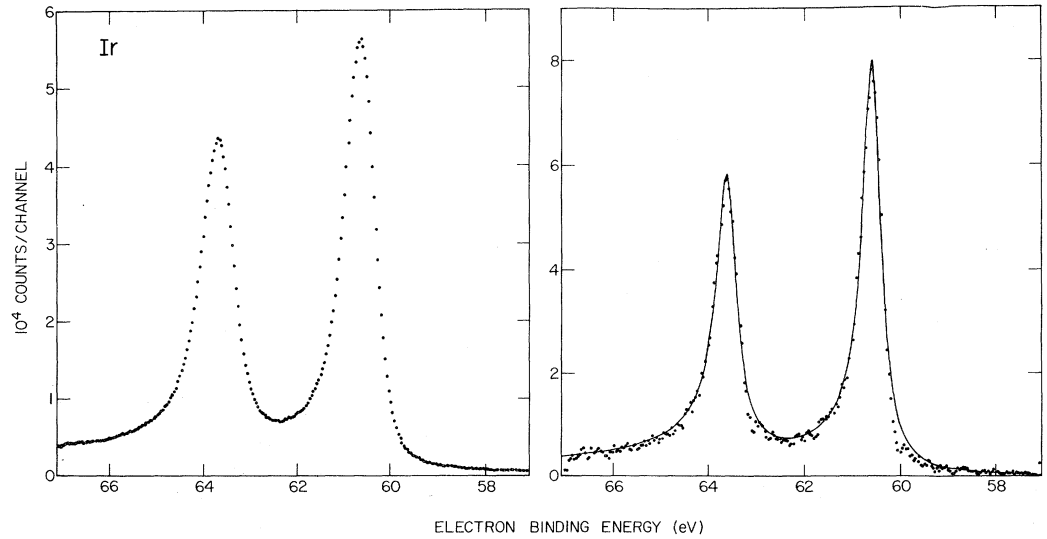
[a]Estimated uncertainty ± 0.1 eV.

[b]Linewidths may contain residual instrumental broadening.

[c]Estimated uncertainty ± 0.03.


Au
10^3 COUNTS/CHANNEL
ELECTRON BINDING ENERGY (eV)


Pt
10^4 COUNTS/CHANNEL
ELECTRON BINDING ENERGY (eV)


Ir
10^4 COUNTS/CHANNEL
ELECTRON BINDING ENERGY (eV)

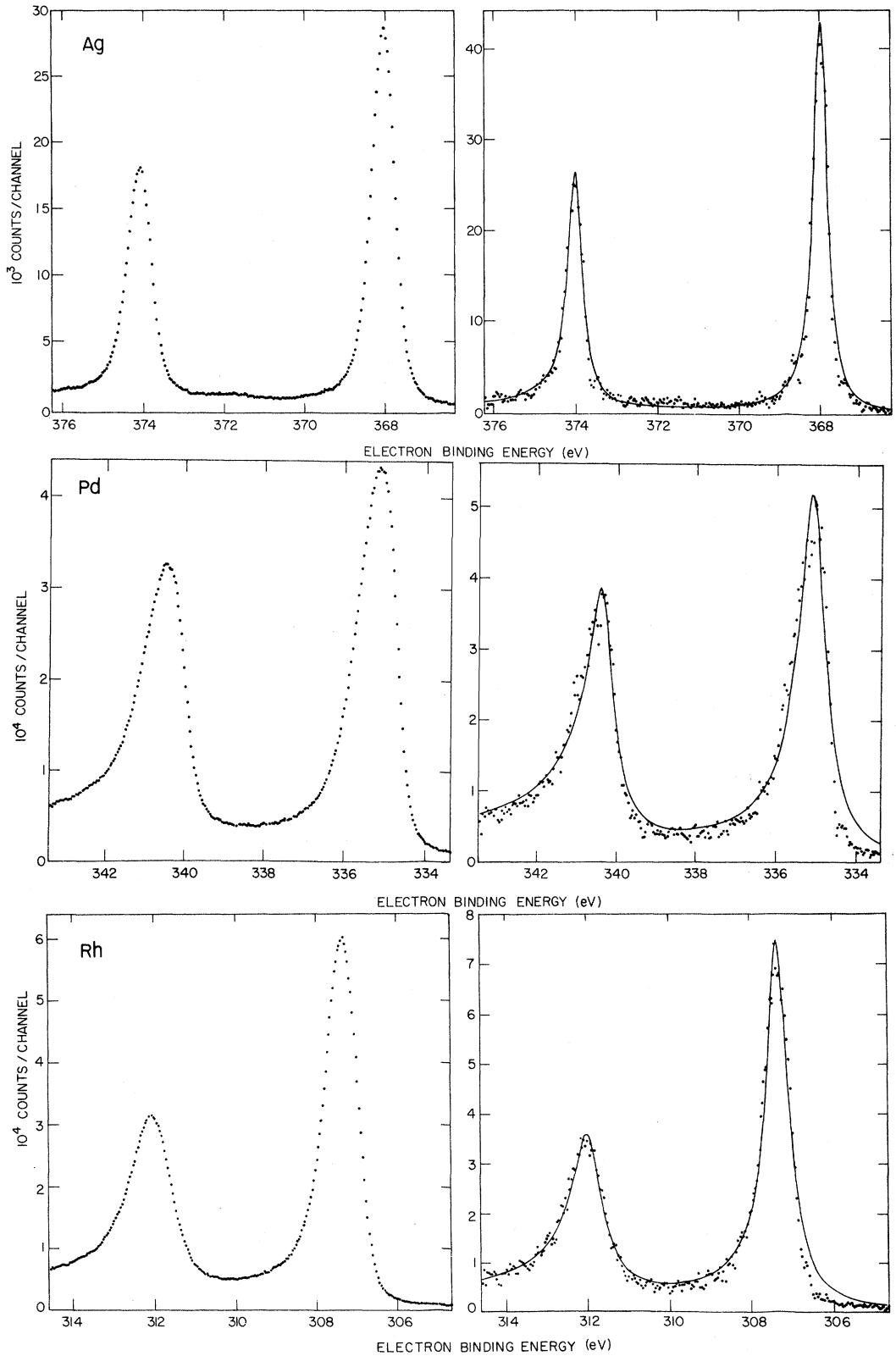


FIG. 1. X-ray photoemission spectra of the 4*f* lines of Au, Pt and Ir and the 3*d* lines of Ag, Pd, and Rh. The left-hand panel shows the original data, the right-hand panel the results of deconvolution (points) and least-squares fitting with Eq. (3) (line).

time width as small as 0.25 eV.

Pt: The results on this metal exhibit a minor problem in that the deconvoluted spectra show a slight shoulder on the high-binding-energy side. It should be mentioned that in spectra of sputtered samples, which had a higher impurity signal, this additional line was much stronger. In view of the weakness of the C and O signal on the evaporated Pt sample it seems unlikely that the additional line is a Pt compound. We are inclined to believe that it represents Pt atoms which are affected by surface contamination. Apart from this problem the fit of Eq. (3) is quite good and the asymmetry index α is the same for both lines.

Ir: The results for this metal are quite satisfactory. The fit to the deconvoluted data is very good and the asymmetry parameters obtained for both lines are equal, giving confidence in the procedure and the results obtained.

Ag: The data for this material show only a small asymmetry, but there is an appreciable difference between the asymmetry parameters for the two lines. Since the asymmetries are small the difference may, however, not be significant. In general the Ag results are gratifying.

Pd: The results show a major problem and are far from satisfactory. The deconvoluted spectra indicate that each line actually consists of two components, perhaps representing bulk and surface. In addition the asymmetry parameter α differs by a factor of 2 for the two lines.

Rh: A visual inspection of the data for this metal shows quite acceptable results. The only disturbing feature is the factor of 2 difference in α for the two lines.

DISCUSSION

The results summarized in the table reveal some noteworthy trends. For both the $4d$ and $5d$ series α is highest for those metals (Pt and Pd) which show the strongest tendency towards magnetism. They have the highest density of states and strongest electron-electron correlations. On the one hand, within the simple picture that α represents the scattering of Fermi-energy electrons by the hole potential, the observed trend, as well as the small values of α found for Au and Ag, is, readily understandable. On the other hand, it is difficult to compare the experimental values of α quantitatively with the theoretical predictions given by Eq. (2b), since three phase shifts must be considered. They obey the Friedel sum rule

$$\sum_l (2l+1)\delta_l = \tfrac{1}{2}\pi Z,$$

have maximum values corresponding to screening by a single type of electron, e.g., $\delta_2^{\max} = \frac{1}{10}Z\pi$, but otherwise depend on additional theoretical input.

For a comparison of the data for the noble metals with Eq. (2) we will use phase shifts derived from the study of dilute alloys of Cu. Since core-level ionization leaves one unscreened nuclear charge, the phase shifts should be similar to those for an atom with next higher Z, i.e., Zn in Cu. The phase shifts obtained for that case,[14,15] $(\delta_0, \delta_1, \delta_2) = (0.247, 0.294, 0.064)$, yield a value of $\alpha = 0.069$. This is close to the smallest value of α (~ 0.055) realizable for $Z = 1$, which occurs for phase shifts not too far from those for Cu. The present results for Ag and Au are in reasonable accord with these estimates.

For the transition metals Pd and Pt, α assumes values of 0.11 and 0.19 (we discount the larger values for the Pd $3d_{3/2}$ line, which also has an anomalous width). The larger values of α presumably reflect the greater importance of d-electron screening since the density of states at the Fermi energy has dominantly d character in those metals. As our initial assumption we will take the p-wave phase shift to be 0. Values of α greater than 0.1 are then found for the following combinations of phase shifts (subject to the constraint that δ_2 not exceed 0.19, the value appropriate for 0.6 of a d hole). Phase shifts of (0.6, 0, 0.19) yield an α of 0.11; (0.8, 0, 0.15) yields 0.15, and (1.0, 0, 0.11) yields 0.22. These values of α span the experimental observations. If δ_1 is allowed to assume small positive values, e.g., 0.1, the d phase shifts are significantly reduced, but the corresponding values of α still run from 0.10 to 0.21. In other words, the observed values of α in these transition metals are compatible with reasonable values for the phase shifts.

The asymmetry parameters for Rh and Ir can clearly be obtained with phase shifts of the same magnitude. The major unexplained phenomenon lies in the different values of α for the two lines of Rh. (We tend to discount a similar effect in Pd because of the strong surface signal and the reversed linewidth ratio.)

The data presented are consistent with the effect predicted by Nozières and DeDominicis,[2] which tends to quench x-ray singularities and produces skew line shapes in XPS. More quantitative analysis awaits further experiments and an analysis in terms of real band structures. As already pointed out by Doniach[16] hole-electron scattering will also influence the valence band shape obtained in photoelectric measurements. Spectroscopic measurements based on the determination of electron energy distributions therefore do not yield a direct image of the density of states, but are distorted by final-state effects which are inherent in the measuring process.

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