

Background removal in x-ray photoelectron spectroscopy: Relative importance of intrinsic and extrinsic processes

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The shape of all major x-ray-excited peaks, including Auger transitions, from Cu, Ag, and Au are studied. The intensity contribution from inelastic (extrinsic) processes are removed. In all cases the primary excitation spectra thus determined are found to consist of a peak and a tail of (intrinsic) electrons which extends ~ 50 eV below the peak energy. Beyond this energy essentially all measured intensity is accounted for without the use of adjustable parameters. The ratio of intrinsic to extrinsic contribution to the measured intensity is of the same order as previously found for the simple metals.

I. INTRODUCTION

Quantitative chemical analysis of homogeneous solid surfaces by x-ray photoelectron spectroscopy (XPS) [or electron spectroscopy for chemical analysis (ESCA)] requires an understanding of various physical mechanisms.¹⁻⁴ For solids which may be considered homogeneous in the near-surface region, quantitative analysis essentially relies on knowledge of three factors: the photoionization cross section, the transmission function of the electron spectrometer, and the measured peak intensity for a given element. Much information is available both on photoionization cross sections,⁵⁻⁷ and on the analyzer transmission function as recently reviewed by Seah.⁸ The main problem in quantitative surface analysis by XPS therefore lies in the determination of peak intensity.

It is generally accepted that the peak height is an unreliable measure for the peak intensity because the width and thus also the height of a peak is highly influenced by chemical effects and by the resolution of the electron-energy analyzer. Therefore, peak areas are used. The determination of peak areas is by no means simple. Thus a peak will always be superimposed on a background of *extrinsic* inelastically scattered electrons. The problem therefore consists in removing this contribution from the measured intensity and thereby isolating the intensity originating from the photoionization of a single core level at the point of excitation in the solid.

It is expected that due to many-body effects, a photoionization peak in a solid is always accompanied by electrons with lower energy.⁹⁻¹⁸ These *intrinsic* electrons, which form a tail on the low-energy side of a peak, are part of the primary excitation spectrum. The effect has been shown to dominate the measured intensity in the near-peak (0-5 eV) region for several metals.^{12,13} For simple metals an analysis has shown¹⁵⁻¹⁸ that 20-50% of the measured intensity in the first plasmon peak is intrinsic in origin.

On the basis of a physical model for electron transport in solids,¹⁹ formulas for deconvolution of spectra were previously given.^{19,20} Later, analysis of experimental spectra showed that, in general, the inelastic background

intensity is quite small within the region of a peak.²¹

In the present work this approach is applied to XPS spectra in a wide energy region. Thus all major x-ray-excited peaks, including Auger transitions, from Cu, Ag, and Au are studied. In all cases, the energy distribution of primary excited electrons is found to consist of a peak and a tail which extends ~ 50 eV below the peak energy. Beyond this energy essentially all measured intensity is accounted for *without* the use of adjustable parameters. Finally, the possible sources of error in the applied model are discussed.

II. DECONVOLUTION MODEL

Let $j(E)$ denote the measured flux of emitted electrons at energy E from a homogeneous solid. Then the primary excitation spectrum is given by¹⁹

$$F(E) = j(E) - \lambda \int_E^\infty K(E'-E)j(E')dE', \quad (1)$$

where $K(E'-E)$ is the probability that an electron of energy E shall lose energy $E'-E$ per unit energy and per unit path length traveled in the solid, while λ is the mean free path for inelastic electron scattering. In the derivation of Eq. (1) it has been assumed that the cross section for inelastic scattering is identical for all electrons within the spectrum to be deconvoluted. In particular the dependence of K on the primary electron energy has been neglected, i.e., $K(E,T) \simeq K(T)$. Equation (1) takes into account the background produced by all multiple inelastic scattering events.

Let $Q(R)dR$ be the number of electrons emitted, in the direction of the analyzer, per unit time and per unit solid angle, after having traveled a path length R , dR in the solid. Then the deconvolution formula, Eq. (1), is exact on the condition that $Q(R)$ is independent of R . For homogeneous solids $Q(R)$ is a constant if angular scattering of electrons can be neglected. When angular scattering is taken into account one expects^{22,23} the path-length distribution of emitted electrons to be exponentially decreasing with R ,

$$Q(R) \propto e^{-R/L} \quad (2)$$

where L is the characteristic attenuation length. Then a deconvolution formula, which is quite similar to Eq. (1), is valid,^{20,23}

$$F(E) = j(E) - \frac{\lambda L}{\lambda + L} \int_E^\infty K(E' - E) j(E') dE'. \quad (3)$$

Note that in Ref. 20 an exponential distribution of electron emitters was considered, i.e., in the present notation $Q(R) \propto e^{-R/(L \cos\theta)}$. For this reason a $\cos\theta$ appears in Eq. (14) of Ref. 20.

In the following we study the consequences of these deconvolution formulas for experimental spectra of Cu, Ag, and Au. The inelastic scattering cross section $K(E, T)$ is evaluated within dielectric response theory^{24,25} as discussed in detail previously.^{20,21,25} Values of λ are taken from the calculations by Tung *et al.*²⁶ and by Powell,²⁷ respectively.

III. EXPERIMENTAL

Polycrystalline high-purity Cu, Ag, and Au samples were cut, polished, and introduced into a UHV chamber with a base pressure in the 10^{-11} Torr range. After Ar sputter cleaning the surface contamination was below the 1% level. Mg $K\alpha$, or Al $K\alpha$, radiation was used to excite the core electron and the energy distribution of emitted photoelectrons was detected with a VG Instruments hemispherical electron energy analyzer (VG-CLAM). The analyzer was operated in the constant pass energy mode and measured intensity distributions were corrected for the analyzer transmission function which in this mode is proportional to $E^{-0.45}$ where E is the kinetic energy of the detected electrons.^{8,28}

IV. RESULTS AND DISCUSSION

Figures 1–3 show the results of the analysis. The upper curves are the measured spectra after subtraction of a constant background and after correction for the analyzer transmission function. These spectra were now deconvoluted by the use of Eq. (1) as described in Sec. II. This results in the lower spectra. Also shown are the difference spectra, which correspond to the background signal of inelastically scattered electrons. Values of λ were taken from Tung *et al.*²⁶ A recent calculation by Powell²⁷ gives values of λ which for Ag and Au are, to within a few percent, identical to (although systematically slightly higher than) the values used here. The λ values for Cu, however, are $\sim 20\%$ higher.²⁷ Therefore, in Figs. 1(a) and 1(b), we have also shown (by the dashed curves) the inelastic background signal resulting from the application of the λ values by Powell.²⁷ In the deconvolution procedure no adjustable parameters were used. Note that in all cases, essentially all intensity far away from a peak is consistently removed. Also note that all peaks extend ~ 50 eV below the peak energy.

Minor adjustments of the applied λ value would bring the calculated background intensity on the low-energy side of all peaks to an almost perfect agreement with experiment. This was, however, not attempted since the aim of this work is to test the present model for background subtraction without use of adjustable parameters.

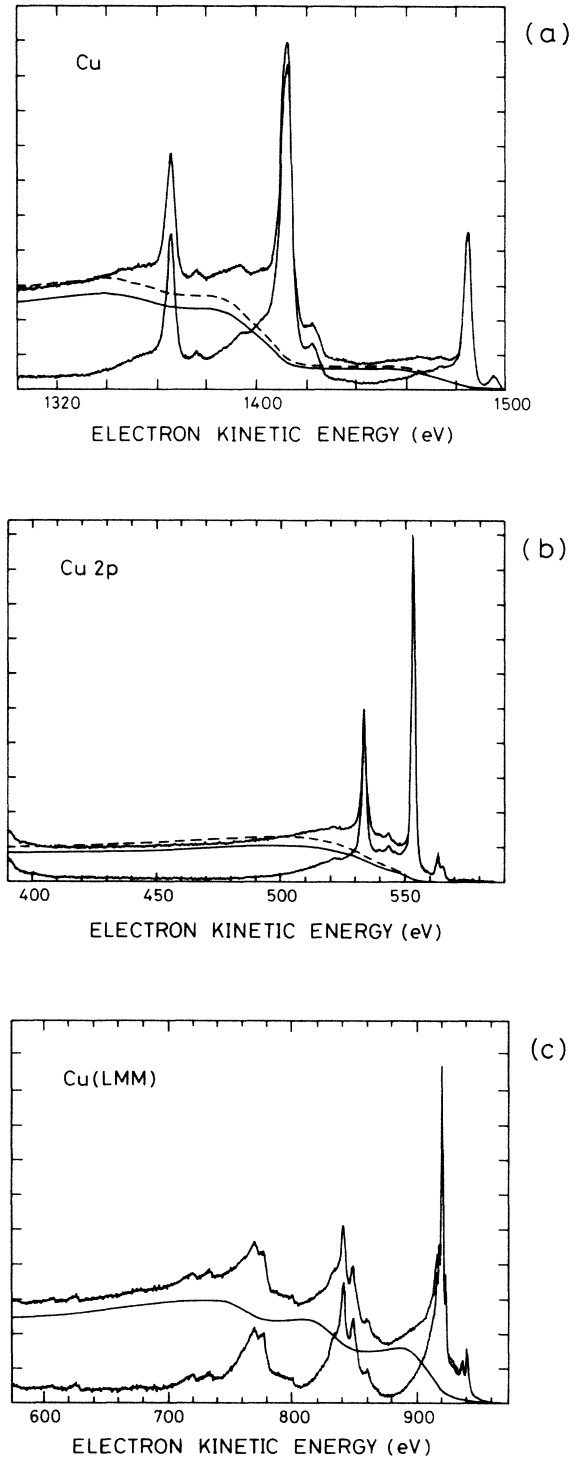


FIG. 1. Experimental Al $K\alpha$ -excited photoelectron spectra of copper (upper curves) and the primary excitation spectra as determined by Eq. (1) (lower curves). The difference curves are the background signal of inelastically scattered electrons. The inelastic scattering cross section $K(E, T)$ (Ref. 21) for $E = 1400$, 550, and 915 eV and the corresponding inelastic mean free paths $\lambda = 21.0$, 10.5, and 15.5 Å (Ref. 26), respectively, were used. For the spectra in (a) and (b) the inelastic background corresponding to $\lambda = 25.0$ and 13.0 Å (Ref. 27) are also shown (dashed curves).

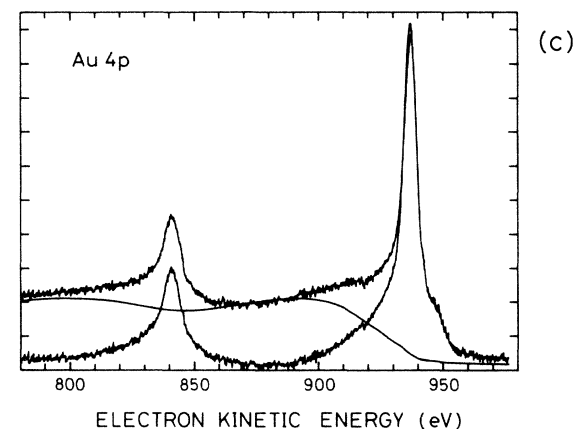
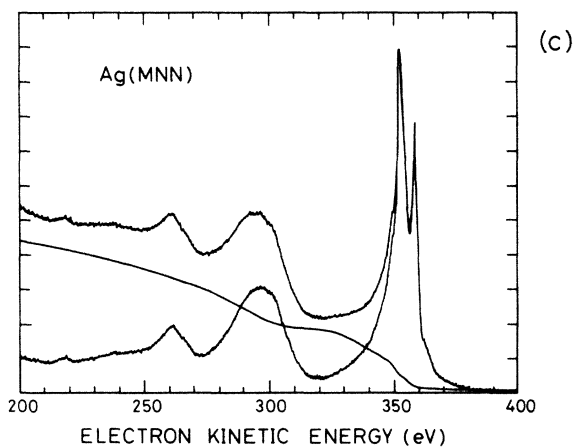
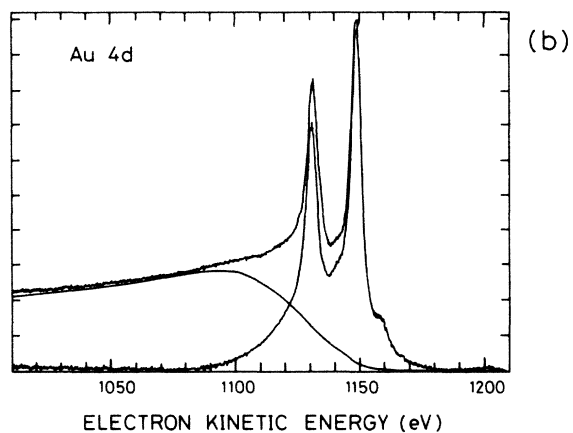
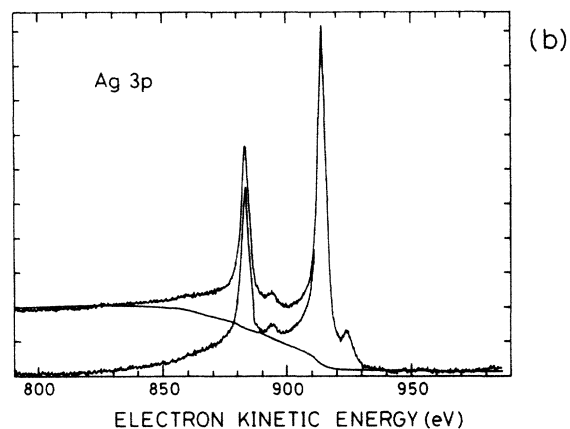
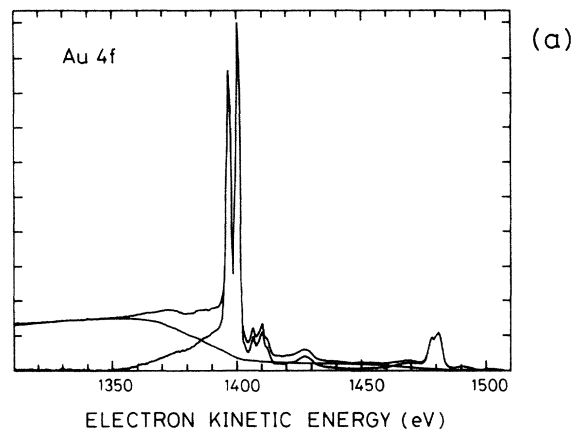
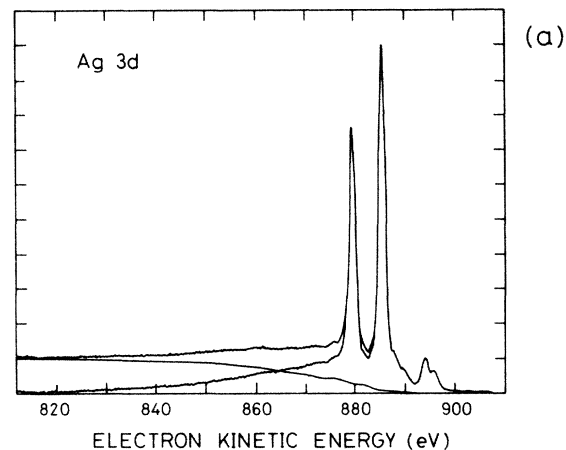


FIG. 2. Experimental photoelectron spectra of silver (upper curves) and the primary excitation spectra as determined by Eq. (1) (lower curves). The difference curves are the background signal of inelastically scattered electrons. In (a) and (c) Mg $K\alpha$, while in (b) Al $K\alpha$ x rays were used to excite the core electrons. The inelastic scattering cross section $K(E, T)$ (Ref. 21) for $E = 880, 900$, and 330 eV and the corresponding inelastic mean free paths $\lambda = 14.9, 15.0$, and 7.8 Å (Ref. 26), respectively, were used.

FIG. 3. Experimental Al $K\alpha$ excited spectra of gold (upper curves) and the primary excitation spectra as determined by Eq. (1) (lower curves). The difference curves are the background signal of inelastically scattered electrons. The inelastic scattering cross section $K(E, T)$ (Ref. 21) for $E = 1400, 1145$, and 950 eV and the corresponding inelastic mean free paths $\lambda = 21.5, 17.1$, and 14.0 Å (Ref. 26), respectively, were used.

The remaining intensity in all primary excitation spectra in the range of 0–50 eV energy distance to a given peak is to be expected. Thus, electrostatic screening of the core hole created in the photoionization process causes any peak to be accompanied by a tail of intrinsic electrons on the low-energy side.^{9–18} For comparison, it was previously found,^{15–18} that for simple metals, 20–50% of the measured intensity in the first plasmon peak has an intrinsic origin, i.e., is part of the primary excitation spectrum.

The data in Figs. 1–3 show a quite similar behavior for Cu, Ag, and Au. For these metals a single plasmon excitation energy cannot be defined. However, the most probable energy loss in a single scattering event in these metals is 10–30 eV.^{21,29} At this energy distance to a peak, Figs. 1–3 show that the ratio of intrinsic to extrinsic contributions to the measured intensity is of the same order as previously found for the simple metals.^{15–18}

Finally, a list of possible sources of error in the present analysis is discussed.

(1) The inelastic scattering cross section $K(E, T)$ is evaluated within dielectric response theory based on the assumption that the total cross section from all valence electrons can be expressed as a sum of simple Drude terms.^{21,24,25} The limit of small momentum transfers ($k \rightarrow 0$) was taken from electron transmission experiments at high energies. This may be an oversimplification since the detailed k dispersion (assumed to be free-electron-like for each Drude term) is not known.

(2) The bulk and the near-surface regions are assumed to have identical inelastic electron scattering properties. This, of course, is not strictly true. However, surface excitations will not add to the overall inelastic background intensity.¹⁷ Rather, some bulk contribution should be subtracted from and a corresponding surface contribution added to the calculated background intensities in Figs. 1–3. Therefore surface excitations may, especially for peaks in the low-energy region, introduce minor changes in the shape of the calculated background intensities close to a peak but will not affect the general qualitative results of the analysis.

(3) The deconvolution formula, Eq. (1) is only strictly valid on two conditions.¹⁹ First, it has been assumed that the cross section $K(E, T)$ is a constant function of T , independent of E within the spectrum to be deconvoluted.

Since we only consider the region of small relative energy loss $T \ll E$, this will to a good approximation be fulfilled. Further, $\int_0^E K(T) dT$ and the fact that only the product λK enters in Eq. (1) cause the formula to be less sensitive to variations in $K(E, T)$ with E .^{30,32}

The second assumption in the derivation of Eq. (1) is that the path-length distribution of emitted electrons $Q(R)$ is a constant independent of the path length R . As noted in Sec. II, elastic electron scattering is expected to result in an exponentially decreasing path-length distribution [Eq. (2)]. Then the prefactor on the integral is changed to $\lambda L / (\lambda + L)$ [Eq. (3)]. Since, in the present deconvolution of spectra λ was consistently used, one would expect the calculated background intensity to be too high. This seems not to be the case. Two possible explanations for this are (a) according to Ref. 23 one expects $L \approx 5\lambda_1$ where λ_1 is the transport mean free path for elastic electron scattering. Since, in typical cases, $\lambda_1 > \lambda$ (Ref. 31) the effect will be small. (b) As discussed above, a recent calculation by Powell²⁷ gives λ values, which for Ag and Au are a few percent higher while those for Cu are $\sim 20\%$ higher compared to the values²⁶ used here. Therefore the prefactor may already be chosen slightly lower than the actual value of λ .

(4) The transmission function of the electron spectrometer could deviate slightly from the $E^{-0.45}$ dependence assumed here. The effect is expected to be largest for peaks at low energies.

V. CONCLUSIONS

The background signal in all major x-ray excited peaks, including Auger transitions, from Cu, Ag, and Au were studied. The contribution from inelastically scattered (extrinsic) electrons was removed without the use of adjustable parameters. The resulting primary excitation spectra consist in all cases of a peak and a tail of (intrinsic) electrons which extends ~ 50 eV below the peak energy. Beyond this energy essentially all measured intensity is accounted for. The ratio of intrinsic to extrinsic contributions is of the same order as previously found for the simple metals. Possible sources of error in the analysis were discussed.

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