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## Materials & Molecular Research Division

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July 1979

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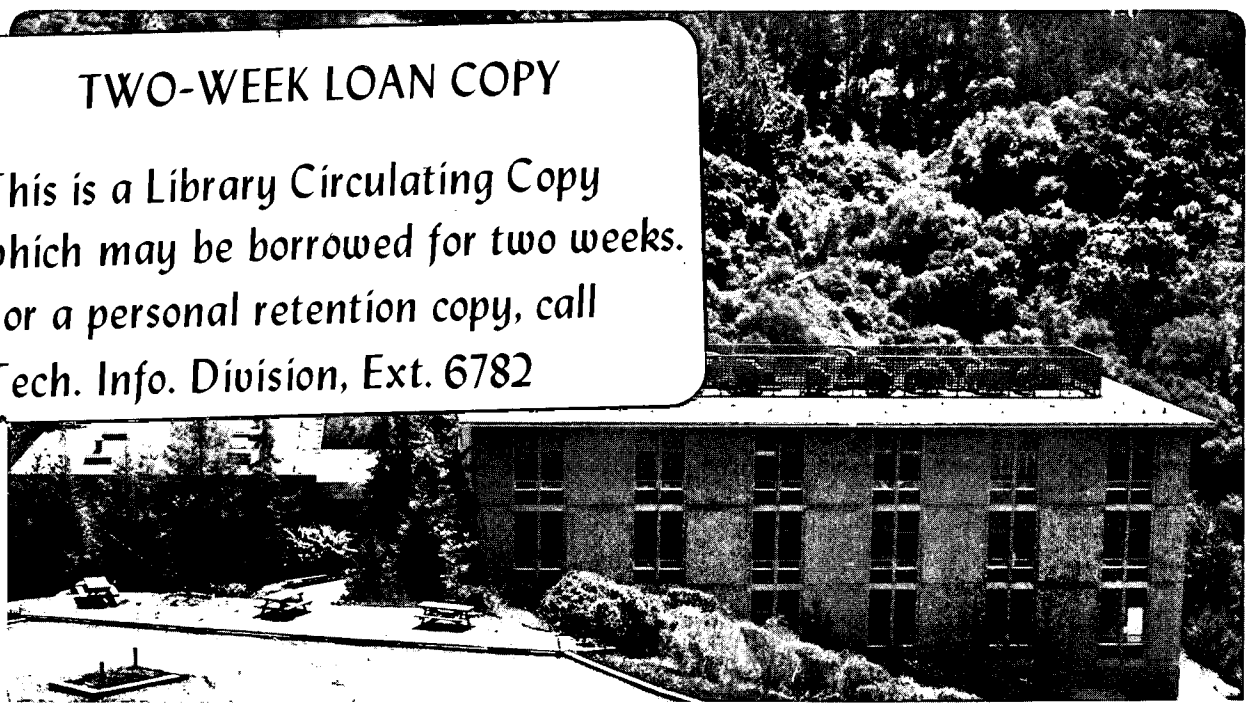

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# CONDENSED PHASE PHOTOELECTRON ASYMMETRY*

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ABSTRACT

Large directional asymmetries were observed in photoelectron distributions from core and valence levels in metals and adsorbate atoms. Intensities varied by factors up to 25 as the angle between $\vec{A}$ and $\vec{p}$ was varied. The energy dependence of asymmetry showed atomic behavior similar to that calculated for free atoms by Manson and co-workers, modified by a tendency for $\vec{p}$ to lie parallel to $\vec{A}$.

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The photoelectric effect is driven by an interaction of the form $\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}$, where $\vec{A}$ is the vector potential associated with the photon field and $\vec{p}$ is the photoelectron momentum. This suggests an angular dependence in the distribution of photoelectrons relative to the direction of $\vec{A}$. For a dipole process in a free atom, this angular distribution should vary as[1-3]

$$\frac{d\sigma}{d\Omega} = [\frac{\sigma}{4\pi}][1 + \beta(\varepsilon)\ P_2(\cos\alpha)], \qquad (1)$$

where $\alpha$ is the angle between $\vec{A}$ and $\vec{p}$ and $\varepsilon$ is the photoelectron's kinetic energy. The energy-dependent asymmetry parameter $\beta(\varepsilon)$ is sufficient to describe photoelectron angular distributions from free atoms. Extensive calculations of $\beta(\varepsilon)$ in atoms are now available, and a number of measurements of $\beta(\varepsilon)$ have been made with rare-gas samples.[4]

The situation in condensed phases is very different. For ordered systems the crystallographic or molecular axes, rather than only the direction of $\vec{A}$, tend to dominate photoelectron angular distributions for energies near threshold, and Eq. (1) is no longer directly applicable. The extent to which Eq. (1) may be explicitly applicable to condensed phases is a question that has received little attention until now.[5] In this Letter we report the first results of a comprehensive study undertaken to elucidate this important question. We have observed large asymmetries in photoemission from

both core and valence levels, at energies well above threshold. Derived $\beta(\varepsilon)$ values show strong qualitative similarities to Manson's calculations[4] on free atoms.

Experiments were conducted on the 4° branch of Beam Line I at SSRL. A hemispherical analyzer with two-circle rotation capability allowed the independent variation of $\alpha$ and $\theta_e$, the angle between $\vec{p}$ and the sample normal, through the range $0 \leq \alpha, \theta_e \leq \pi/2$. To minimize systematic errors $\theta_e$ was held fixed at $\pi/4$ while the sample and analyzer were rotated together, thereby covering the range $48° \leq \alpha \leq 90°$. The important combination of s-polarization with $\alpha = 90°$ was thereby included. Ultrahigh vacuum techniques (ion sputtering, Auger spectroscopy) were employed, and the monochromatized photon beam intensity was monitored by a gold photoyield detector. Data were collected in the photon energy range $40 \text{ eV} \leq h\nu \leq 252 \text{ eV}$. The Fresnel equations[6] were used to calculate changes in $\vec{A}$ at vacuum-metal interfaces: The changes were small in the energy range covered. Three systems were studied: Pt metal, atomic Se on a Pt surface, and polycrystalline Ag. In each case the metal surface was ion-bombarded to clean it and reduce the local order. The levels for which data are presented below are Se 3d, Pt 4f, Ag 4s, Ag 4p, and the Ag valence band ($4d^{10}5s$).

The trend of the data was very striking. In several levels the peak intensity for $\vec{A} \perp \vec{p}$ was dramatically smaller--by factors up to 25--than for other values of $\alpha$. Selected

illustrative spectra are shown in Fig. 1. This was the major result that we sought to establish, and the experimental geometries were selected with this purpose, rather than covering the whole angular range of $\alpha$ to obtain more precise values of $\beta$. We also chose to emphasize the energy dependence of the asymmetry, rather than the angular dependence of $d\sigma/d\Omega$, which can be assumed to have the general form of Eq. (1), by Yang's theorem.[3] Nevertheless, the data could be used to test this form. The intensity-vs-angle data, also shown in Fig. 1, support the $P_2(\cos\alpha)$ form.

The most interesting result, however, is the detailed manner in which $\beta(\varepsilon)$ qualitatively follows expectations based on atomic calculations. Results for the Se 3d and Pt 4f subshells are shown in Fig. 2. The contrasting behavior of these two curves can be understood by comparison with free-atom calculations, also shown in Fig. 2 for nearby elements. Kennedy and Manson[7] have calculated $\beta(\varepsilon)$ for Kr 3d; their Hartree-Fock "length" result is shown in Fig. 2, as are the Hartree-Slater (HS) $\beta(\varepsilon)$ curve for Au 4f given by Manson[4] and the HS curve for $\sigma(\varepsilon)$ calculated by Combet Farnoux.[8] It happens that these two curves are generically rather similar if considered over the entire range of $\varepsilon$. The initial 3d and 4f states are radially nodeless, and the oscillations in $\beta(\varepsilon)$ arise through an increase in the ratio $\sigma(\ell \rightarrow \ell+1)/\sigma(\ell \rightarrow \ell-1)$ with $\varepsilon$, combined with variation of the total phase shift with $\varepsilon$ for the two final-state

channels, which affects the interference term between the two channels. The photoemission cross-sections $\sigma(\varepsilon)$ also show the behavior expected theoretically, as indicated in Fig. 2. It is clear, however, that our measured $\beta(\varepsilon)$ are systematically higher than the corresponding atomic curves, a result consistent with larger plane wavelike character in the conduction-band final state. We conclude that for the 3d level of adsorbate Se atoms and the 4f level of Pt metal the $\beta(\varepsilon)$ curves are at least qualitatively predicted by free-atom theory. A more stringent test was desirable, however, because these are both nodeless core levels.

Silver metal provides this test. The 4s, 4p, and valence band ($4d^{10}5s$) functions all possess radial nodes, and Cooper minima[9] in $\sigma(\varepsilon)$ are expected for the 4p and 4d subshells. The energy of the Cooper minimum for Ag 4p should lie too near threshold[4] for us to detect in this experiment, but the 4d subshell should show the effect at $\varepsilon \sim 10$ Ry. Indeed, the experimental $\sigma(\varepsilon)$ values (Fig. 3) bear out this expectation. The $\beta(\varepsilon)$ results for both 4d and 4s also show a systematic qualitative resemblance to the atomic calculations (Fig. 3), again with a shift to higher values of $\beta$. The theoretical $\beta(\varepsilon)$ curves for Xe 4d and $\sigma(\varepsilon)$ for Xe 4s and 4d in Fig. 3 are the Hartree-Fock "length" results of Kennedy and Manson.[7] It is expected that $\beta(\varepsilon) = 2$ for the 4s subshell for all $\varepsilon$ from rather general arguments[10] except for correlation and/or relativistic effects very close to

threshold. The resemblance between experiment and theory is striking for both the 4s and 4d subshells. The 4p peak was very wide because of final-state effects,[11] and we were unable to derive precise intensities from our data. Qualitatively, the 4p results tend to support the above conclusions, with $\beta(\varepsilon)$ values being typically in the range 1.1 - 1.5.

The main conclusion of this work is that intermediate-energy photoemission in solids shows $\beta(\varepsilon)$ behavior with atomic character, modified by a tendency toward higher asymmetry; i.e., toward $\beta = 2$. These experiments encompass adsorbate core levels, metal core levels and valence bands, s, p, d, and f subshells, and cases with and without Cooper minima. Further studies are in progress to characterize condensed-phase photoelectron asymmetry through a wide range of subshells, elements, and materials. Aside from its intrinsic interest, this phenomenon should be useful in characterizing orbital symmetries and in identifying the origins of photoemission lines. Its implications for X-ray photoemission (ESCA) spectra are considerable. In particular, quantitative comparisons of peak intensities are very sensitive to the angle $\alpha$ (or its equivalent for "unpolarized" X-rays). Finally, photoelectron analyzers intended for use with synchrotron radiation from horizontal storage rings should be designed to accept electrons in directions other than those for which $\vec{A}\cdot\vec{p} = 0$; e.g., the vertical.

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FIGURE CAPTIONS

Fig. 1 Upper panels: the Ag 4s photoemission peak at $h\nu$ = 225 eV, from polycrystalline silver, with $\alpha = \angle\vec{A},\vec{p}$ = 48° and 90° (left); peak intensity for 48° $\leq \alpha \leq$ 90°, fitted to Eq. (1) with $\beta$ = 1.92 (right). Lower panels: similar results for the silver valence-band peak (Ag 4d).

Fig. 2 Variations of photoemission cross-sections ($\sigma$) and asymmetry parameters ($\beta$) with electron kinetic energy. Data are denoted by circles and connected by curves in experimental (left) panels, for Se(Z = 34) as adsorbate atoms and Pt(Z = 78) as metal. Theoretical curves for Kr(Z = 36) and Au(Z = 79) as free atoms were taken from Refs. 7, and 4 and 8, respectively. The experimental $\sigma$ values are only on a relative scale. The $\sigma$ variations are close to theory, while $\beta$ shows an upward shift and in Pt a decreased amplitude of variation with energy.

Fig. 3 Comparison of $\sigma$ and $\beta$ results for silver (Z = 47) metal with theoretical values for atomic Xe(Z = 54), from Ref. 7, with format similar to Fig. 2. The 4s peak shows $\beta \sim 2$, while for the 4d peak both the Cooper minimum in $\sigma$ and the modulation of $\beta$ are qualitatively reproduced, though the latter is

attenuated, perhaps in part by admixture of s character in the valence band.

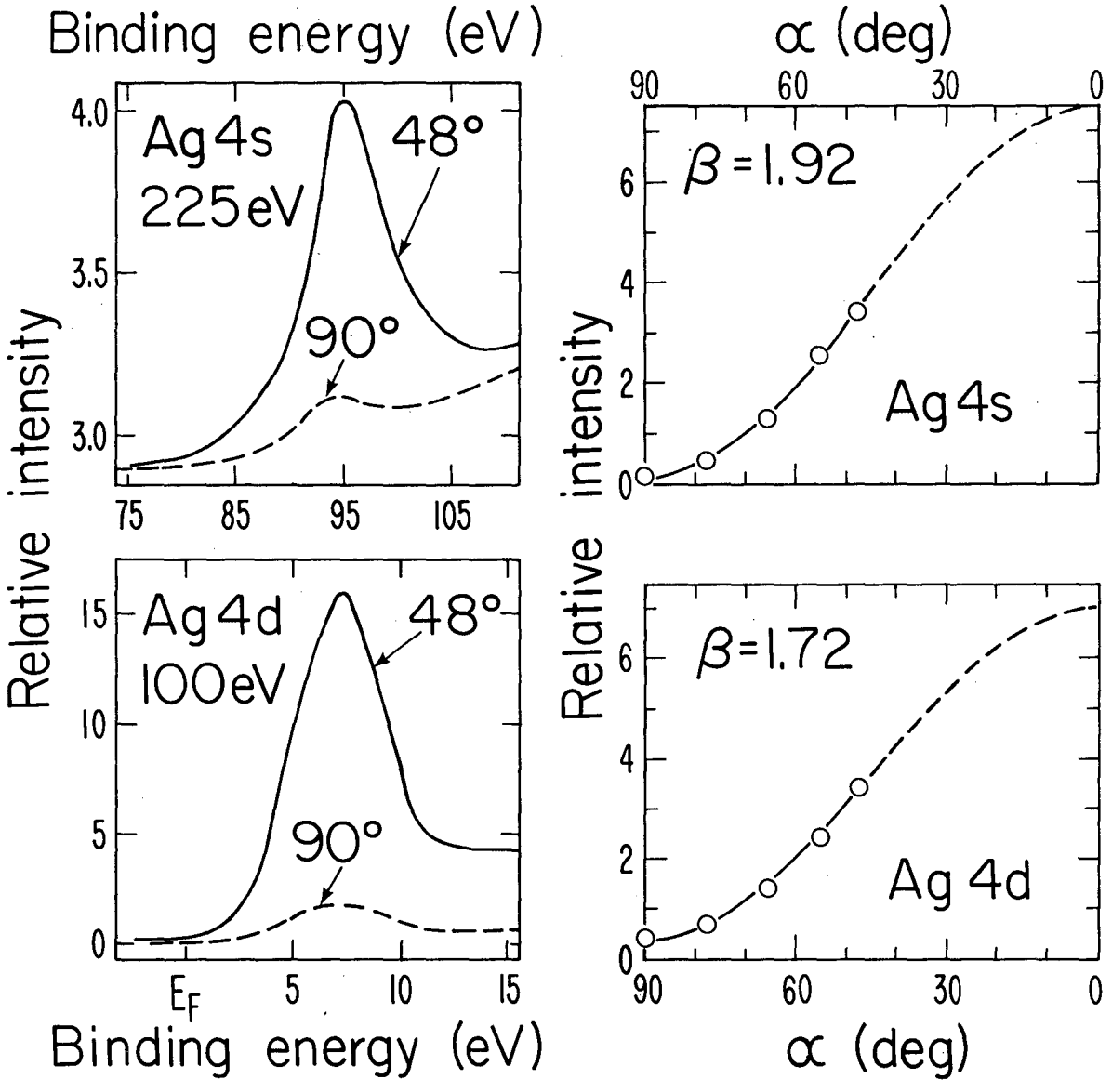


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Figure 1

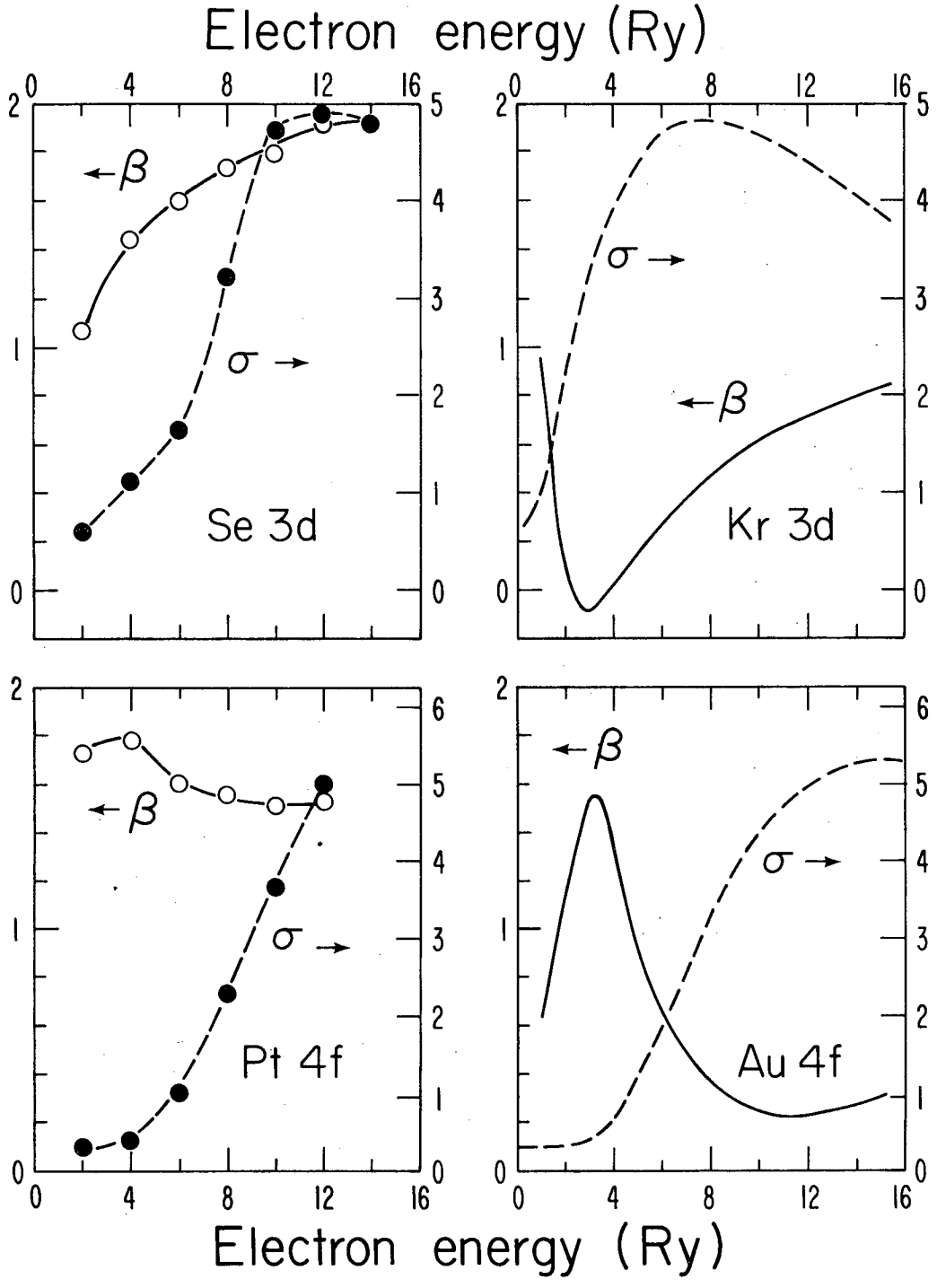


Figure 2

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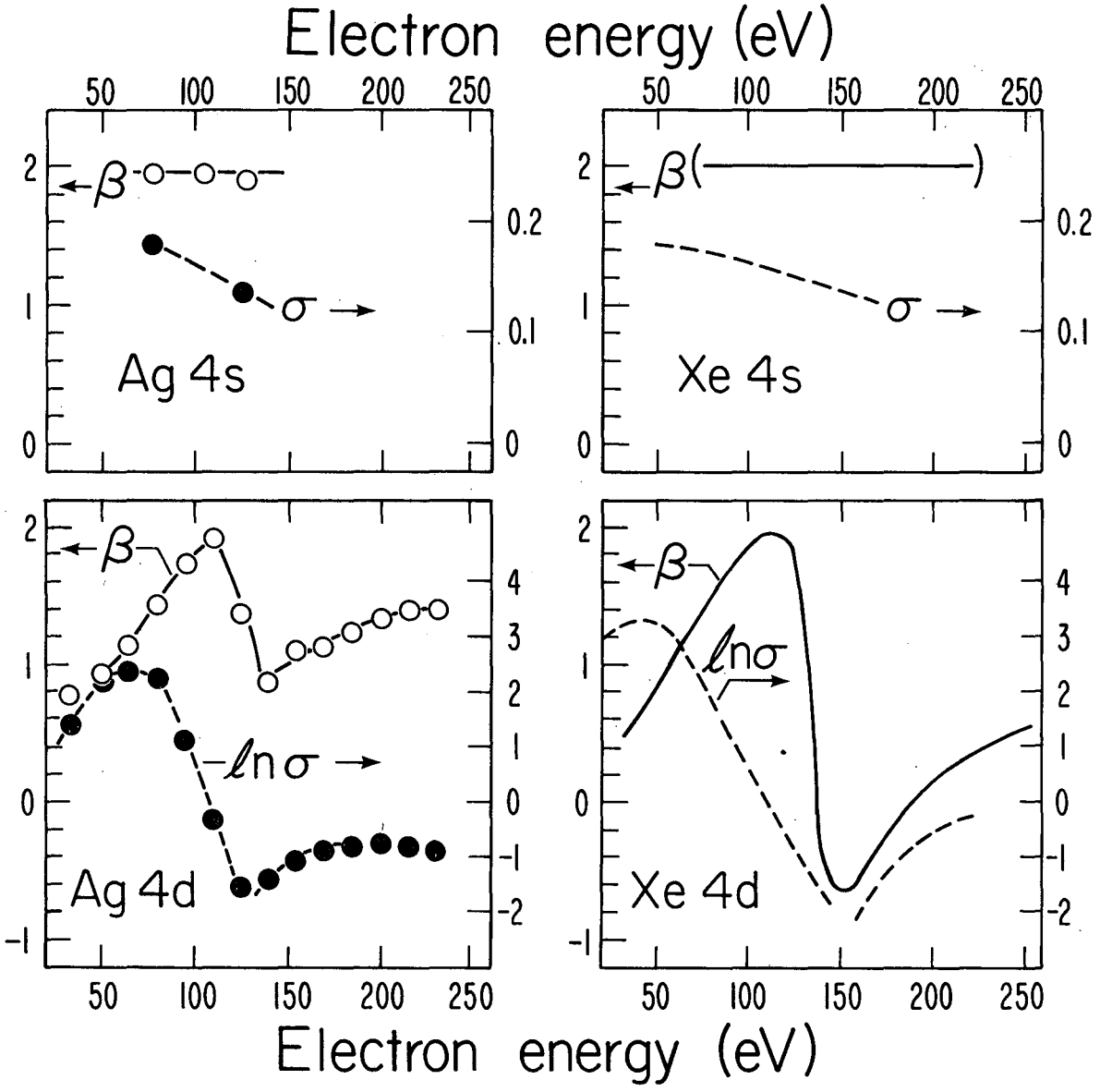


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Figure 3

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