Photoionization-cross-section studies of atomic and final-state effects on the Pb 5d core levels using synchrotron radiation

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Using monochromatized synchrotron radiation as the light source, the Pd-5d cross sections in Pb metal and the $5d_{5/2}$:$5d_{3/2}$ branching ratios in Pb metal, PbS, PbSe, and $PbCl_2$ have been studied from 22- to 90-eV photon energies. Constant-initial-state (CIS) spectra for Pb metal from 22 to 40 eV photon energies allow a direct comparison of the $5d_{5/2}$ and $5d_{3/2}$ cross sections. Superimposed on a smooth curve due to atomiclike behavior, the $d_{5/2}$ and $d_{3/2}$ CIS curves show differing structure that is probably related to transitions from the d levels to p-like states in the conduction band. The area ratios are chemically sensitive, and at higher photon energies contain structure which is probably due to scattering from neighboring atoms as seen in extended x-ray absorption fine structure.

I. INTRODUCTION

There has been considerable recent experimental[1-9] and theoretical[10,11] interest in the relative atomic photoionization cross sections of spin-orbit components (the branching ratio) from a given orbital, for example the Hg $5d_{5/2}:5d_{3/2}$ ratio in gas-phase Hg. The branching ratios deviate substantially from the statistical values of 2.0 and 1.5 for $p_{3/2}:p_{1/2}$ and $d_{5/2}:d_{3/2}$ ratios, respectively. Moreover, these ratios are strongly dependent on the incident-photon energy. Two reasons for such variations have been discussed by Walker and Waber[10] who made relativistic Dirac-Slater calculations of the partial photoionization cross sections for the $j = l \pm \frac{1}{2}$ components of atomic orbitals. The first contribution arises from the slightly differing kinetic energies of the outgoing electrons for the two spin-orbit components. If the partial cross sections are increasing with photon energy, the branching ratio will be larger than the statistical value; if they are decreasing, the ratio will be smaller than the statistical value. The second major contribution arises from the slightly different radial wave functions of the two components which lead to different dipole matrix elements. For example, in atomic Hg, the experimental $5d_{5/2}:5d_{3/2}$ branching ratio varies from over 2.0 at small kinetic energies[2] to 1.23 at intermediate energies[3] to 1.40 at high kinetic energies.[4] These values are in rather good agreement with the theoretical predictions,[10,11] but the lack of a large number of source energies in this case precludes any detailed comparison between theory and experiment.

In this study, we have obtained Pb $5d_{5/2}:5d_{3/2}$ branching ratios and constant-initial-state (CIS) spectra[12,13] in solid-state Pb compounds at closely spaced photon energies using the Wisconsin synchrotron source. We have found considerable "fine structure" on both the CIS curves and the branching-ratio versus photon-energy curves in the final-state energy range of 0–70 eV. This structure appears to be the first such observed for primary photoelectrons from core levels, and is related to final-state effects due to band structure[14-16] at low photoelectron energies, and scattering as seen in extended x-ray absorption fine structure[17-19] (EXAFS) at higher photoelectron energies.[20]

II. EXPERIMENTAL

The Tantalus I storage ring at the Synchrotron Radiation Center, Stoughton, Wisconsin, was employed as the photon source. Focusing and monochromatization of the radiation was achieved as described earlier,[21] and the overall resolution of the photoelectron spectrometer (the instrumental resolution, ΔE_i) was determined as given previously.[21,22] ΔE_i was $\leq 1\%$ of the photon energy (i.e., ≤ 0.4 eV at 40-eV photon energy). The one-meter Seya-Namioka monochromator was used for photon energies between 26 and 50 eV, while the two-meter grazing incidence monochromator was used for photon energies between 40 and 90 eV. The sample chamber pressure for the Pb, PbS, and PbSe spectra was less than 2×10^{-10} Torr, while the pressure for the $PbCl_2$ spectra was 5×10^{-9} Torr. The preparation of the samples, and the computer fitting techniques are given in previous papers.[23,24]

The energy distribution curves (EDC's) were obtained with a constant-pass energy of 40 V. Good-quality Pb-5d spectra were obtained in less than 10 min for photon energies between 26 and 70 eV. Above 70 eV, the quality of the spectra diminished substantially due to a decrease in synchrotron radiation intensity and a decrease in monochromator efficiency. For low kinetic energies ($\leq$15 eV), all spectra were taken with the samples biased by −3 V to measure accurately the low kinetic energy electrons. In the 40–50-eV photon range, spectra were taken with both monochromators to check the reproducibility. For Pb, PbS, and PbSe, it was possible with the ultrahigh vacuum conditions and very clean samples to obtain very good EDC's at photon energies as low as 26 eV. For $PbCl_2$, however, the very large secondary electron background made it impossible to obtain spectra below 32.5-eV photon energy, and the $PbCl_2$ spectra were generally of poorer quality. All kinetic energies are referenced to the vacuum level.[23]

CIS spectra of the Pb-metal 5d levels were obtained up to 40-eV photon energies using the Seya Namioka monochromator. In these spectra,[12,13] the photon energy and the electron analyzer voltage were swept automatically together, so that we follow the intensity of the 5d photoelectrons directly as a function of photon energy. CIS spectra were also taken at energies several eV away from the peak regions to ensure that any observed effects on the $d_{3/2}$ or $d_{5/2}$ CIS curves were not due to instrumental effects, Auger electrons, or other secondary electrons. The intensities were normalized electronically to the photon intensity using a Au diode. It was not possible to obtain such spectra with the grazing incidence monochromator above 45-eV photon energies, because we could not sweep photon energies continuously.

III. RESULTS AND DISCUSSION

A. CIS spectra

The CIS spectra of the Pb-$5d_{5/2}$ metal and $5d_{3/2}$ levels (with binding energies relative to the vacuum levels of $E_i = 22.0$ and 24.6 eV, respectively[23]) are shown in Fig. 1, curves C and B, respectively. The $d_{3/2}$ curve has been multiplied by 1.5 to facilitate comparison with the $d_{5/2}$ curve. The $5d_{5/2}$ curve shows maxima at 23.8, 27.3, and ~37 eV, with an inflection at ~30.5 eV (kinetic energies of 1.8, 5.3, ~15, and ~8.5 eV, respectively). The $5d_{3/2}$ curve shows maxima at 26.2, 29.8, and ~37 eV (kinetic energies of 1.6, 5.2, and ~13 eV, respectively).

An electron escape function[13] T_{eff} has been calculated (curve A, Fig. 1) from previously published optical constants,[25–27] a work function of 3.95 eV,[23] $E_{\text{Fermi}} = 9.7$ eV (relative to the zero of kinetic energy[28]) and escape depth estimates from the universal curve.[29] Since many of the above quantities are not well established, the T_{eff} curve is not expected to be particularly accurate, but it should have the correct qualitative shape. It is immediately obvious that the T_{eff} curve does not have a similar overall form to the $5d_{5/2}$ CIS curve, but the T_{eff} curve does indicate why the CIS curves rise to a maximum above threshold much faster than predicted for atomic gas-phase atoms.[8,10]

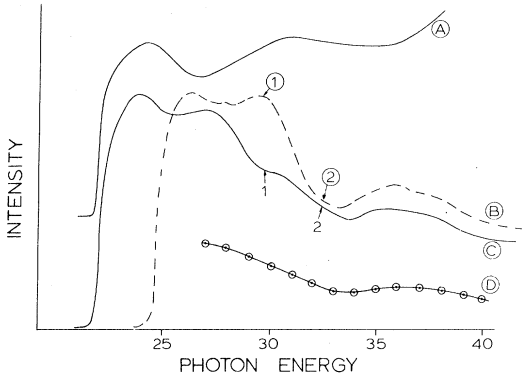

FIG. 1. CIS spectra of the Pb-metal $5d_{3/2}$ (curve B) and $5d_{5/2}$ (curve C) levels. The $5d_{3/2}$ curve has been multiplied by 1.5 to facilitate comparison of the two curves. Also included are an electron escape function T_{eff} (curve A), and a secondary electron background curve (curve D) measured from the EDC's. Points 1, circled 1, 2, and circled 2 are discussed in the text.

Both the primary Pb 5d electrons and the secondary electrons (the background in the EDC's in Fig. 2) contribute to the CIS curves; and thus at low photon energies when the background is large, the CIS curves do not measure the 5d cross sections directly. However, above ~40 eV when the secondary background is very small [Fig. 2(b)], these CIS curves are very nearly determined by the primary cross sections. There are three strong pieces of evidence which indicate that the secondary contribution is not the cause of the structure in curves B and C. First, $5d_{3/2}$ and $5d_{5/2}$ background curves obtained from the EDC's [see Fig. 1, curve D for the $5d_{5/2}$ curve] show a smooth progression with a slight maximum at ~37 eV. The $5d_{3/2}$ background curve, while substantially more intense, has the same qualitative form. Second, the CIS curves taken at initial-state energies slightly removed from 22.0 and 24.6 eV gave smooth curves showing only a small maximum at ~37 eV. This peak at ~37 eV in the CIS and background curves is probably due to Auger electrons ($5d\,6p^2$ transitions), which from the valence p band

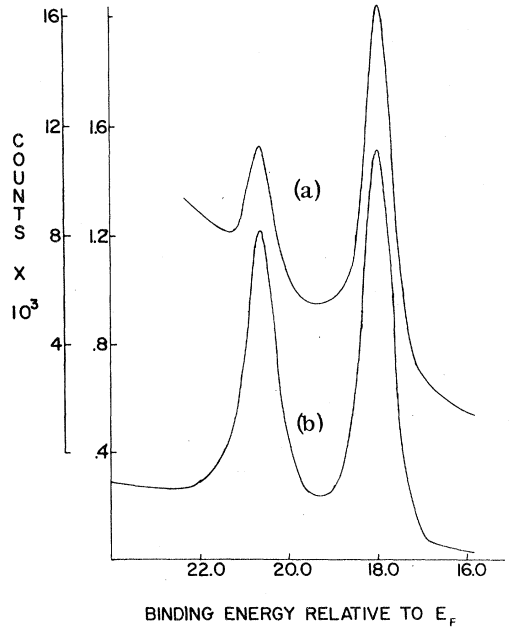

FIG. 2. EDC's of the Pb 5*d* levels in Pb metal taken with photon energies of (a) 32.5 eV and (b) 53.3 eV. The total instrumental resolutions are 0.4 and 0.5 eV, respectively.

spectra of Pb metal,[30] should give broad maxima at kinetic energies between ~10 and ~18 eV. Third, the $5d_{5/2}:5d_{3/2}$ branching ratios (due to primary electrons only) obtained from the EDC's (see above) show structure which is entirely consistent with the CIS curves.

The structures in the CIS curves up to 34 eV can thus be attributed to changes in primary *d* photoelectron cross sections. This structure, and in particular the difference in $d_{3/2}$ and $d_{5/2}$ structure, appears to be the first observed for primary photoelectrons. However, this structure is probably due to similar final-state band-structure effects which have been observed for the reflectance spectra of PbSe and PbTe,[16] and the constant-final-state spectrum of BiTe.[15] Unfortunately, the band structure for Pb metal has been calculated only up to 8 eV above the Fermi level,[28,31,32] so we cannot quantify specific final-state effects at present.

It would be desireable to extend these CIS curves to much higher photon energies to obtain direct measurement of the *d* cross sections. However, we cannot go above 45-eV photon energies with the present monochromator and obtain good statistics. Clearly, this method for obtaining cross-section information is extremely useful, as also shown by recent gas-phase partial-ionization cross-section measurements.[33]

B. Branching ratios

We have obtained the $5d_{5/2}:5d_{3/2}$ branching ratios for Pb metal, PbS, PbSe, and $PbCl_2$ (Fig. 3) from the EDC's. Two such spectra of the Pb 5*d* levels (Fig. 2) show an obviously large difference in the $d_{5/2}:d_{3/2}$ ratio. The reproducibility of the ratios (Table I) is better than ±0.02 for photon energies above 40 eV, but decreases to ±0.1 at lower photon energies. The general trend in area ratios is similar to that predicted and observed for the atomic Hg 5*d* levels[3,10]: the very large ratios at low kinetic energy decrease to ~1.3 eV for higher kinetic energies and then often increase slightly.

Of greater interest is the spectral structure in Fig. 3. The initial sharp structures in the Pb-metal ratios are readily understood with the help of the CIS curves (Fig. 1, curves *B* and *C*). After a sharp decrease in area ratio between 27 and 30 eV due to the onset of the $d_{3/2}$ peak, the initial minimum at 30 eV {8.0-eV kinetic energy relative to the $d_{5/2}$ peak [Fig. 3(a)]} occurs when the $d_{3/2}$ CIS curve is a maximum and the $d_{5/2}$ CIS curve is at a minimum (Fig. 1, points 1). The branching ratio then increases to a maximum at 32.5 eV (10.5-eV kinetic energy) at which energy the $d_{3/2}$ curve has decreases much more rapidly than the $d_{5/2}$ curve (Fig. 1, points 2). Then, the ratio decreases due to the $d_{3/2}$ curve increasing relative to the $d_{5/2}$ curve.

As noted earlier, the branching ratios could not be obtained directly from the CIS spectra, because of the larger secondary background under the $d_{3/2}$ curve. For example, at 32.5 eV, the area ratio obtained from the CIS curves is 1.40, while the observed branching ratio is 2.9. As must be the case, however, the CIS and EDC curves give results in good agreement when the background (*B*) is included in the EDC intensities. Thus, the ratio of $(d_{5/2}+B_{5/2}):(d_{3/2}+B_{3/2})$ from the EDC in Fig. 2(a) of 1.46 is in good agreement with the 1.40 obtained from the CIS curves.

Similar sharp changes in branching ratio occur for $PbCl_2$, PbS, and PbSe up to ~20-eV kinetic

TABLE I. Reproducibility of the Pb $5d_{5/2}:5d_{3/2}$ area ratio for Pb metal.

Photon energy (eV)	Ratios[a]
30.0	1.88, 1.92, 2.02, 2.07, 2.26
40.0	1.59, 1.63, 1.64
74.2	1.32, 1.33, 1.34

[a] These and all other ratios have not been corrected for amplitude distortion in solids. Below 65-eV photon energies, this correction should be ≤ 0.01, but at 90 eV might be as large as 0.04.

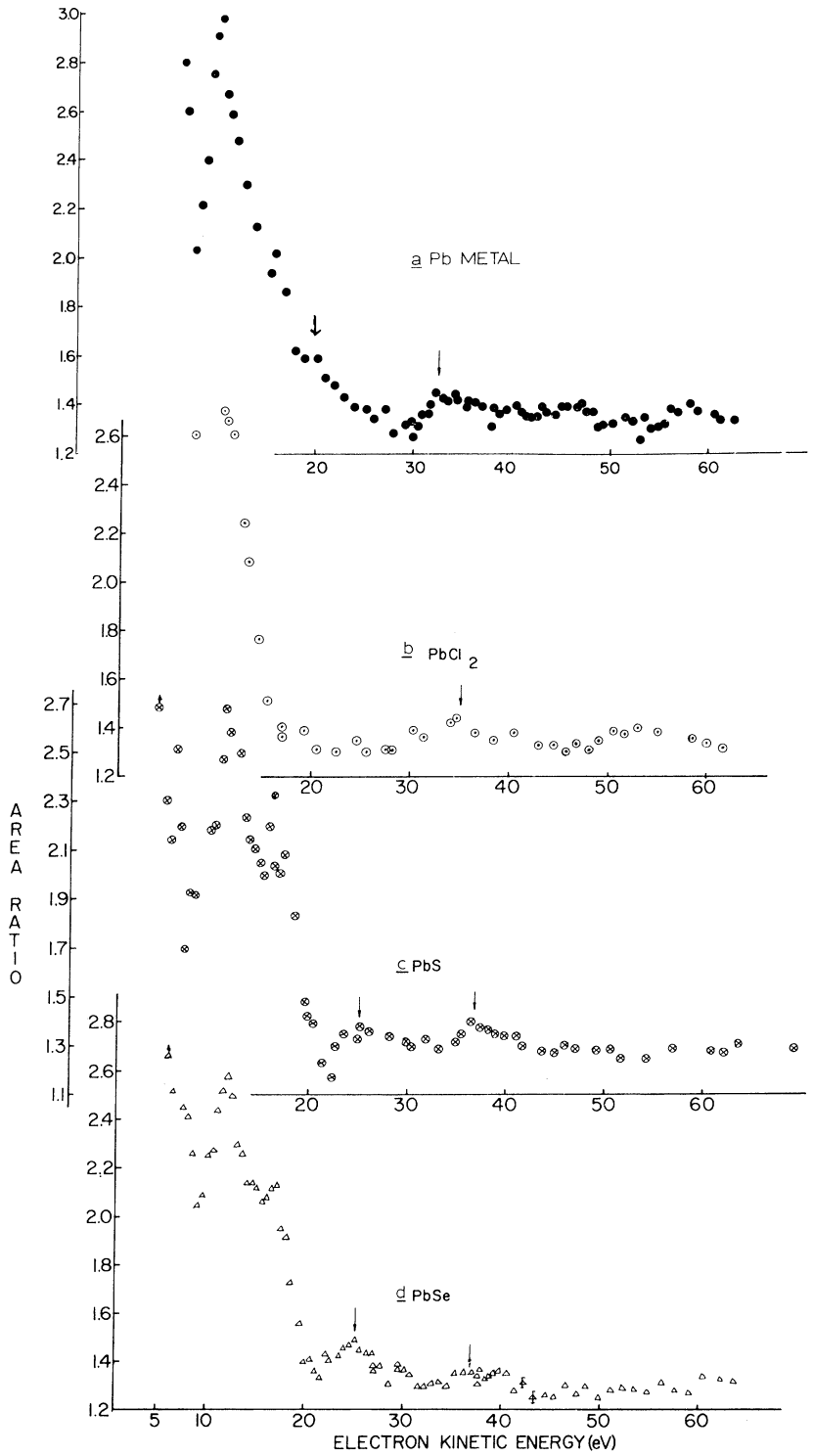

FIG. 3. $5d_{5/2}$: $5d_{3/2}$ branching ratios vs electron kinetic energy (for the $5d_{5/2}$ electrons) for Pb metal, $PbCl_2$, PbS, and PbSe. The kinetic energies are referenced to the vacuum level.

energies, and these changes are probably once again due to final-state band-structure effects. Again, the band structures[34,35] are not known far enough above the Fermi level to quantify our interpretation.

Additional small peaks are apparent on the branching ratio plots. In Pb metal, there is a distinct peak at ~32-eV kinetic energy, an inflec-

tion at ~20 eV and other possible peaks (for example at 47 eV) which are not as apparent. Similar effects are seen for $PbCl_2$, PbS, and PbSe, with the PbS and PbSe spectra being very similar. In PbS and PbSe there are distinct peaks at ~25- and ~38-eV kinetic energy, and in $PbCl_2$, there is a distinct peak at 35-eV kinetic energy.

Because band-structure effects should not be significant above ~20-eV kinetic energy, it seems very likely that the above peaks are related to scattering of photoelectrons by neighboring atoms, as is normally observed in EXAFS (Refs. 17–20). Here we are considering the ratio of two closely spaced cross-section curves, both having sinusoidal EXAFS structure. The ratio of these closely spaced (relative to the sinusoidal period) curves will give rise to a slightly displaced periodic dependence having the same period as the initial cross-section curves.

Although we cannot quantify our suggestion due to our limited data, unknown phase shifts, and backscattering amplitudes, there is qualitative evidence, based on bond lengths, which supports our suggestion. Thus, the positions of the above small peaks (20–25 and 30–40 eV) are consistent qualitatively with the large known bond lengths[36] in these compounds [3.50 Å for Pb-Pb, 3.02 Å (average) for Pb-Cl, 2.97 Å for Pb-S, and 3.06 Å for Pb-Se]. For example, Br-O having a similar bond length of 3.14 Å gives EXAFS maxima at similar energies, ~22 and ~50 eV above threshold.[18] [The EXAFS period increases rapidly with decrease in bond length. For example, Cu-O, with a bond length of 1.97 Å gives its first maximum ~60 eV above threshold (compared to ~22 eV for Br-O).] Moreover, the trend in our maxima appears to be consistent with the trend in bond lengths in the Pb compounds. Assuming, that the ~30-eV peaks correspond to the same maximum in the four compounds, it is apparent that Pb metal (with the longest interatomic distance) gives a peak at substantially lower energy than the other three compounds with smaller (and very similar) bond lengths.

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