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Photoionization cross section of d-core levels in solids: A synchrotron radiation study of the spin-orbit branching ratio

G. Margaritondo,* J. E. Rowe, and S. B. Christman
Bell Laboratories, Murray Hill, New Jersey 07974

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The partial photoionization cross section of In $4d$, Sn $4d$, Pb $5d$, and Bi $5d$ in different materials has been investigated in the photon energy range $\hbar\omega = 20$–60 eV. The experiment consisted of measuring the intensity ratio between the two spin-orbit components, R, as a function of $\hbar\omega$. A large deviation of R from its statistical value of 1.5 has been found which exhibits a strong dependence on $\hbar\omega$. The R vs $\hbar\omega$ dependence is quite similar in different materials and for different d core levels. Closer than ~ 6 eV to the photoionization threshold this dependence is mostly due to the rapid changes with $\hbar\omega$ of the partial atomic photoionization cross section σ. Further away from threshold the R-σ relation is more complicated, but atomic effects still prevail over solid-state effects.

I. INTRODUCTION

The synchrotron radiation emitted by the University of Wisconsin Storage Ring has been employed to study the partial photoionization cross section σ of d core levels in solids. The investigations have been carried out in the photon energy range $\hbar\omega = 20-60$ eV on the In $4d$ level in InSb, InSe, and In metal, on the Sn $4d$ level in SnS_2, on the Pb $5d$ level in PbI_2, and on the Bi $5d$ level in BiI_3 and Bi_2Te_3. We have concentrated on measurements and interpretation of the branching ratio between the partial cross sections of the $j = 3/2$ and $j = 5/2$ spin-orbit components of the $4d$ or $5d$ doublet. We have found a large deviation of R from its statistical value $(l+1)/l = 1.5$. The actual value of R depends on the photon energy and the variation of R is quite rapid close to the photoionization threshold. This is primarily due to the dependence on $\hbar\omega$ of the atomic-d-level partial cross section[1,2] although some small solid-state effects[3,4] cannot be excluded in the measured R vs $\hbar\omega$ behavior. From our results it appears feasible to use the R vs $\hbar\omega$ behavior to study the photoelectric cross section of core levels at photon energies close to the photoionization threshold. Indeed, a direct study of the σ vs $\hbar\omega$ behavior is made difficult in that energy region by the large number of inelastically scattered secondary electrons.

Deviation of R from its statistical value has been reported by several authors for p and d core levels in solid and gases.[4-15] We have employed synchrotron radiation to study R for the first time over an extended photon energy region in the case of Cs $5p$.[15] Afterwards, synchrotron radiation measurements of R for extended $\hbar\omega$ ranges have been reported by several authors for the Xe $5p$,[8,13] Xe $4d$,[10,13] Cd $4d$,[14] and Hg $5d$[14] doublets in the gas phase and by Bancroft, Gudat, and Eastman[4] for the Pb $5d$ level in Pb metal and in Pb compounds. In all the above investigations R exhibited an $\hbar\omega$-dependent deviation from its statistical value. This deviation was particularly strong in the spectral region close to the photoionization threshold.

Relativistic Dirac-Slater model calculations of R have been reported for the first time by Walker *et al.*[1,2] In general, R is related to the statistical factors and to the partial cross sections, $\sigma_{j=l+1/2}$ and $\sigma_{j=l-1/2}$, of the two spin-orbit components as follows:

$$R(\hbar\omega) = [(l+1)/l][\sigma_{j=l+1/2}(\hbar\omega)/\sigma_{j=l-1/2}(\hbar\omega)] \,. \tag{1}$$

For d core levels $(l+1)/l = 1.5$ and the cross-section ratio in Eq. (1) becomes

$$\frac{\sigma_{j=l+1/2}}{\sigma_{j=l-1/2}} = \left(1 - \frac{\Delta}{E_{f,3/2}}\right)^{-1/2} \frac{\frac{2}{5}|\langle\frac{5}{2}|V|E_{f,5/2},\frac{3}{2}\rangle|^2 + \frac{1}{35}|\langle\frac{5}{2}|V|E_{f,5/2},\frac{5}{2}\rangle|^2 + \frac{6}{7}|\langle\frac{5}{2}|V|E_{f,5/2},\frac{7}{2}\rangle|^2}{\frac{1}{3}|\langle\frac{3}{2}|V|E_{f,3/2},\frac{1}{2}\rangle|^2 + \frac{1}{15}|\langle\frac{3}{2}|V|E_{f,3/2},\frac{3}{2}\rangle|^2 + \frac{3}{5}|\langle\frac{3}{2}|V|E_{f,3/2},\frac{5}{2}\rangle|^2} \,, \tag{2}$$

where $\langle a|V|b,c\rangle$ is the radial dipole matrix element between a bound state with $j = a$ and an ionization state with energy b and $j = c$. The two final-state energies in Eq. (2) are $E_{f,3/2} = E + \hbar\omega$ for transitions from $|3/2\rangle$ and $E_{f,5/2} = E + \Delta + \hbar\omega$ for transitions from $|5/2\rangle$, where E is the energy of the state $|3/2\rangle$, Δ is the spin-orbit splitting between the bound states, and all energies are measured from the ionization limit. Walker *et al.*[1,2] have observed that there are two major causes for strong deviations of R from its statistical value. One is the small difference between the two final-state energies for transitions at a given $\hbar\omega$ involving either a $|l-1/2\rangle$ or a $|l+1/2\rangle$ bound state. This is reflected in Eq. (2) by the two different final-state energies, $E_{f,3/2}=E+\hbar\omega$ and $E_{f,5/2}=E+\Delta+\hbar\omega$. The second major cause is the difference between the radial wave functions of the two initial states $|l-1/2\rangle$ and $|l+1/2\rangle$ in Eq. (2). The first cause should prevail whenever the σ's are rapidly changing functions of $\hbar\omega$ and in particular close to the photoionization threshold. In that case, as we quote from Ref. 1, "if the partial cross section is rising the ratio of cross sections is greater than statistical, while if the partial cross section is falling the ratio will be less than statistical." In other words, $R-(l+1)/l$ qualitatively behaves like the photon energy derivative of σ. [In a crude rigid-shift model one would have $R-(l+1)/l=d(\ln\sigma)/d\hbar\omega$.]

Studying the R vs $\hbar\omega$ behavior is then a way to investigate how the partial cross section changes with $\hbar\omega$.[16] An important feature of this method is that measuring R does *not* imply absolute measurements of partial cross sections. Thus it is reasonably easy to measure R at photon energies close to threshold, where *absolute* measurements of partial cross sections are made difficult by the large background of inelastically scattered secondary electrons. Solid-state effects in $\sigma(\hbar\omega)$ and therefore in $R(\hbar\omega)$ cannot be excluded *a priori*—for example, the final states in Eq. (2) are Bloch-like low-energy-electron-diffraction states rather than pure atomic ionization states. However, our experimental results demonstrate that for the d core levels under investigation atomic effects prevail in the R vs $\hbar\omega$ behavior.

This article will be structured as follows. The experimental procedure will be illustrated in Sec. II. The results will be discussed in Sec. III in light of previous d-doublet branching ratios measured in solid[1,5,12] and gaseous systems.[6,7,9,10,13,14] The main points of the discussion will be summarized in Sec. IV.

II. EXPERIMENTAL METHODS

The experiments have been carried out at the University of Wisconsin Synchrotron Radiation Center employing a beam line equipped with a bakable vertical Seya-Namioka monochromator. The spectral yield of this optical facility has proven suitable for photoemission experiments on core levels at least up to 60 eV. The photoelectrons were collected and analyzed with a PHI double-pass cylindrical mirror analyzer (CMA) at typical energy resolutions of 250–350 meV. The axis of the analyzer was at 45° with respect to the sample normal. The experimental system enabled us to change the direction of polarization of the photon beam with respect to the sample without modifying the photoelectron collection geometry.[17] In the present experiments we have employed linearly polarized radiation with electric field either parallel to the surface of the sample or at 45° from the sample normal without finding any remarkable photon polarization dependence of R. The samples have been prepared *in situ* under ultrahigh vacuum conditions, base pressure 5×10^{-10} Torr. The sample preparation technique was cleavage for InSe, PbI_2, SnS_2, BiI_3, Bi_2Te_3, and InSb and evaporation for In metal. The surface contamination of the samples as checked by Auger-electron spectroscopy was below the 0.01 monolayer limit in all our experiments.

Figures 1 and 2 show typical results for the In 4d doublet in InSe and for the Bi 5d doublet in BiI_3. In both cases the lower photon energy is close to the photoionization threshold. The deviation of R from its statistical value 1.5 is quite evident. For $\hbar\omega$ close to threshold R is much larger than 1.5—this appears to be a general feature of all the d-level branching ratios investigated here or reported in the literature.[1,5,7,9,10,12-14]

The branching ratio R has been estimated from the raw experimental data upon subtraction of a smooth background due to inelastically scattered secondary electrons[15] (see dashed lines in Figs. 1 and 2). The area of each peak has been esti-

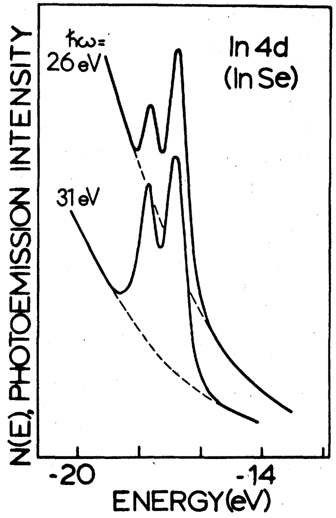

FIG. 1. Photoemission spectra exhibiting the In 4d doublet. The spectra have been taken on InSe at two different photon energies. There are evident deviations of the branching ratio from its statistical limit, 1.5. These deviations clearly depend on $\hbar\omega$.

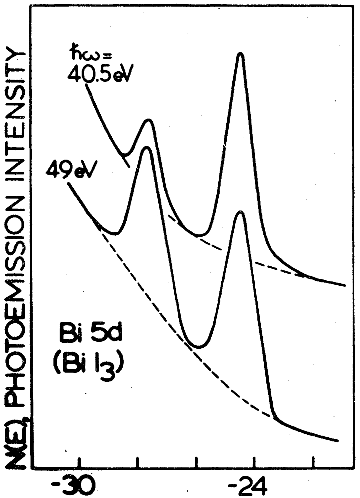

FIG. 2. Bi 5d doublet in BiI$_3$ photoemission spectra at two different photon energies. As in Fig. 1, close to threshold the branching ratio appears much larger than 1.5 and then it decreases.

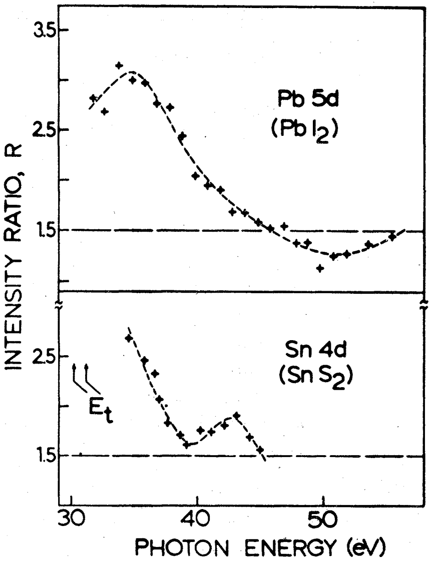

FIG. 4. R vs $\hbar\omega$ for Pb 5d in PbI$_2$ (top) and for Sn 4d in SnS$_2$ (bottom).

mated from its height and width. In some cases we have also estimated the area by a numerical integration technique.[15] The values of R given by the two techniques coincide within 5%. We emphasize that the experimental evaluation of R is approximately unaffected by systematic errors. The errors in estimating the background for the two spin-orbit components tend to cancel each other while calculating R. Therefore, correcting the data for the secondary-electron background is a reasonably accurate procedure even close to the photoionization threshold. That is a great advantage with respect to *absolute* cross-section measurements where the background correction is different close to threshold.

Plots of R vs $\hbar\omega$ are reported in Figs. 3, 4, and 5 for the In 4d, Sn 4d, Pb 5d, and Bi 5d core levels. We estimate the typical errors in the experimental points to be less than 5%–7% of the value of R. The smooth dashed curves drawn through the experimental points emphasize the R vs $\hbar\omega$ features detectable above the noise.

Table I reports the values of the binding energy and of the photoionization threshold for each one

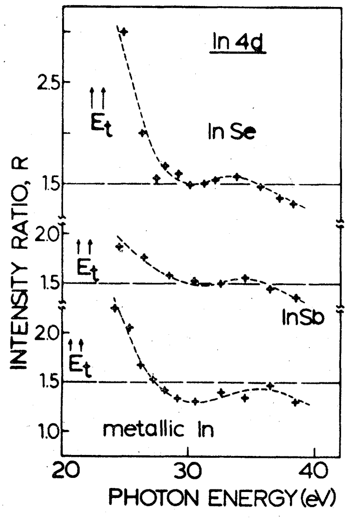

FIG. 3. Plots of R vs $\hbar\omega$ for In 4d in three different materials. E_t is the photoionization threshold for the d doublet.

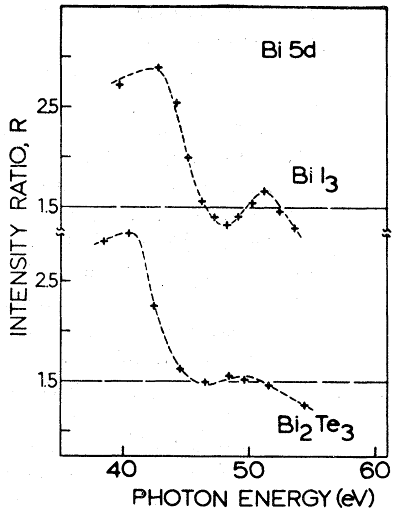

FIG. 5. R vs $\hbar\omega$ for Bi 4d in BiI$_3$ and Bi$_2$Te$_3$.

TABLE I. Binding-energy and photoionization-threshold values for *d* core levels.

Core level	Material	Binding energy[a] $j=\frac{5}{2}$	Binding energy[a] $j=\frac{3}{2}$	Photoionization threshold[b] $j=\frac{3}{2}$	Photoionization threshold[b] $j=\frac{5}{2}$
In 4*d*	InSe	16.9	17.7	23.2	22.3
	InSb	17.0	17.8	22.1	21.3
	In metal	16.35[c]	17.25[c]	21.6	20.7
Sn 4*d*	SnS_2	24.1	25.2	31.2	30.1
Pb 5*d*	PbI_2	18.3	20.8	29.15	26.65
Bi 5*d*	BiI_3	24.7	27.7	32.7	29.7
	Bi_2Te_3	24.6	27.7	31.8	28.6

[a] Binding energies in eV, measured from the top of the valence band (except for In metal). Uncertainty ± 0.1 eV.

[b] Threshold energies in eV. Uncertainty ±0.1 eV.

[c] Measured from the Fermi level.

of the *d* core levels investigated here. The binding energy has been defined in Table I as the kinetic energy distance measured in the photoelectric spectra between the core level and the Fermi edge for In metal or the top of the valence band for all other samples. The measured binding energy did not change while the photon energy was changed—this is a relevant result as far as the nature of the so-called core excitonic shifts is concerned (see discussion in Ref. 18).

III. RESULTS AND DISCUSSION

A. Atomic effects close to the photoionization threshold

A comparative inspection of the results shown in Figs. 3, 4, and 5 shows remarkable similarities between all the experimental R vs $\hbar\omega$ curves. In a region 6–8 eV wide right above threshold R is much larger than its statistical limit and generally decreasing. Beyond that region the behavior is more complicated and to some extent different for different core levels. In this section we will discuss the $\hbar\omega$-dependence of R close to threshold, while in Sec. III B the discussion will be extended to higher energies.

The *d*-doublet R values right above threshold have been found to be larger than statistical and decreasing with increasing $\hbar\omega$ in all our present experiments and also in all previous gas-phase experiments on Xe 4*d*,[10,13] Cd 4*d*,[7,14] Hg 5*d*,[6,7,11,14] and solid-state experiments on Pb 5*d*.[4] In this region the partial photoelectric cross section is a rapidly changing function of $\hbar\omega$. Therefore, the R vs $\hbar\omega$ behavior should be mainly due[1,2] to the slightly different kinetic energies of the final states in Eq. (2). An R value larger than its statistical limit must correspond to a rising partial cross section at these photon energies.[1,2] Since the value of R is decreasing we also expect the rate of variation of the cross section to decrease, i.e., the cross section approaches a maximum. These predictions are confirmed by the experimental data for the gas-phase experimental cross section of Xe 4*d* (Ref. 10) and of Cd 4*d* (Ref. 7) and by the data of Lindau *et al.*[19] on In 4*d* and Sb 4*d*. The theoretical calculations, too, indicate that for *d* levels σ increases but $|d\sigma/d\hbar\omega|$ decreases in this region.[1,2,7] The increase of σ eventually comes to an end and σ reaches a maximum corresponding to $R \approx 1.5$ in the data of Figs. 3, 4, and 5.

The above qualitative discussion is corroborated by the calculated R vs $\hbar\omega$ behavior for Hg 5*d*,[1,2] Cd 4*d*,[2] and Xe 4*d*,[13] with relativistic Dirac-Slater models. References 1, 2, and 13 all predict that R is larger than 1.5 and decreasing in this energy region. Besides being affected by the different final-state energies, however, the exact value of R is also affected by the radial wave functions of the initial states in the photoionization process. Reference 13 also predicts for R an extremely sharp increase in a very narrow photon energy region right at the threshold. This region might be too close to the threshold to see the increase of R in the experimental data. Indeed, the sharp increase is not even present in the *experimental* data presented by the same Ref. 13 for Xe 4*d*. We observe, however, that our data for Bi 5*d* do show some evidence for an increasing R at the threshold (see Fig. 5).

In summary, the dependence of R on $\hbar\omega$ at photon energies closer than 6–8 eV to the photoionization threshold appears to be a purely atomic effect. The behavior of R is mostly related to the dependence on $\hbar\omega$ of the partial *d*-level photoionization cross section σ. This leads to R values above the statistical limit 1.5 in all this energy region.

B. R versus $\hbar\omega$ behavior beyond the region close to threshold

The overall shape of $R(\hbar\omega)$ is still somewhat similar for In 4*d*, Sn 4*d*, and Bi 5*d* even at photon energies more than 6–8 eV above the photoionization threshold. In the range $\hbar\omega \geqslant 10$ eV the Pb 5d branching ratio exhibits instead a somewhat smoother behavior than the In 4d, Sn 4d, and Bi 5d branching ratios. For In 4d, Sn 4d, and Bi 5d the decrease of R ends with a minimum 7–12 eV above threshold. Then R increases for 3–5 eV, reaches a maximum, and afterwards decreases again. A similar behavior has been found by Shannon *et al.*[10] for gas-phase Xe 4d (the corresponding results on Xe 4d by Wuillemier *et al.*[13] do not present enough experimental points in this energy region to confirm or contradict the results of Ref. 10). The R vs $\hbar\omega$ behavior reported by Bancroft *et al.*[4] for Pb 5d is similar to ours, and a similarly smooth behavior has also been found for gas-phase Hg 5d.[11,14] Simple cross-section arguments do not help much in explaining the above data. Since σ is close to a maximum, the dependence of σ on $\hbar\omega$ is not as dramatic as it is close to threshold. At larger photon energies σ is expected to decrease (and eventually reach a Cooper minimum[20]), and consequently R should be below 1.5 as found in the high-energy end of our experimental R-$\hbar\omega$ curves.

The direct theoretical calculations of R vs $\hbar\omega$ for Hg 5d (Refs. 1 and 2) and for Xe 4d (Ref. 13) show some structure qualitatively similar to what we find in this energy region for In 4d, Sn 4d, and Bi 5d. Wuillemier *et al.*[13] have demonstrated that the exact energy position and prominence of the calculated structure critically depend on the choice of the exchange parameter in the Dirac-Slater model. This prevents one from carrying out a quantitative comparison between theory and experiment at the present time and leaves the question unanswered whether the experimental structure in this region is purely atomic effect or, rather, contain also some residual solid-state effects. We believe the variation of R with $\hbar\omega$ is primarily an atomic effect, as we shall discuss in the following.

There is experimental evidence at these photon energies that band-structure effects in the final states are quite weak.[17,21] Photoemission curves taken in the constant-initial-state mode show, indeed, that even in materials with some molecular character in the conduction band such as SnS_2, solid-state effects are diminished at energies higher than ~5 eV above the vacuum level.[17,21] The atomic final states in Eq. (2) could, however, still be affected by the solid-state environment. Its wave functions can be backscattered by the neighboring atoms, as suggested by Lee[22] —and give rise to extended-x-ray-absorption-fine-structure-like oscillations in the σ vs $\hbar\omega$ behavior. The quantity $[R-(l+1)/l]$ is somewhat similar to $d\sigma/d\hbar\omega$ when σ is a rapidly changing function of $\hbar\omega$, and this quantity should oscillate too. This mechanism has been proposed by Bancroft *et al.*[4] to explain structure found by these authors in the R vs $\hbar\omega$ curves for Pb 5d. However, it would imply a simple relationship between the period of the oscillations, the distance in photon energy from the threshold, and the interatomic distances.[22] Any attempt to fit this relationship to our R vs $\hbar\omega$ structures for In 4d, Sn 4d, and Bi 5d leads to unreasonable values for the interatomic distances even if scattering phase shifts are taken into account. Therefore, our experimental structure in this region cannot be explained with any currently known solid-state effect.

Several facts suggest instead that this structure in R vs $\hbar\omega$ has an atomic origin at least for In 4d. First the overall shape of $R(\hbar\omega)$ for In 4d is quite similar in different indium compounds (see Fig. 3) and is unaffected by a change of photon polarization. A similar conclusion is actually valid for Bi 5d in Bi_2Te_3 and in BiI_3 (see Fig. 5) and for Pb 5d in different lead compounds (see Fig. 4 and Ref. 4). Second similar structure has been observed in free-atom Xe 4d.[10] Third structure of this kind is not excluded but actually predicted by the current atomic theories for R although at somewhat higher photon energies.[1,2,13] It has been shown that refinements in the theoretical calculations of $\sigma(\hbar\omega)$ can reveal extremely sharp structure at low energies,[23] which would be reflected by $R(\hbar\omega)$. In summary, even at these photon energies a predominantly atomic character of our experimental $R(\hbar\omega)$ curves appears reasonable at present, although some solid-state effects cannot be excluded as suggested by Smith *et al.*[3] for Cs thin films.

IV. CONCLUSIONS

In summary, our experimental results on the R vs $\hbar\omega$ behavior for In 4d, Sn 4d, Pb 5d, and Bi 5d in different crystals bear resemblance to gas-phase results on 4d and 5d levels in free atoms. In a spectral region extending from the photoionization threshold to 25–30 eV above it, the R vs $\hbar\omega$ behavior is mostly determined by atomic effects. In the lower quarter of this energy range the behavior is primarily related to the dependence on $\hbar\omega$ of the partial d-level cross section. In the upper three quarters of that region the results still have prevailing atomic character, but they cannot be fully explained by the current atomic calculations for R.

Our experiments do not rule out solid-state effects in the branching ratio, although they do not provide evidence for them. An answer to this question should be given by angle-resolved measurements of R for both molecules and solids. The asymmetry parameter β is a slowly varying function of $\hbar\omega$ in the absence of strong final-state resonances and the angular atomic effects should be predicted for molecules and atoms with current theoretical models.[2,6] Therefore, the possible angular solid-state effects should be easily deconvolvable from atomic angular effects by condensing the gas-phase atom or molecule and measuring R for the corresponding solid.

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*Present address: Physics Dept., Univ. of Wisc.-Madison, Madison, Wisc. 53706.

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