

Lawrence Berkeley National Laboratory

Recent Work

Title

THE ONSET OF RELATIVISTIC EFFECTS IN THE DENSITY OF STATES OF THE 6s6p ELEMENTS
Tl, Pb, AND Bi

Permalink

<https://escholarship.org/uc/item/9z72x4jv>

Authors

Ley, L.
Pollak, R.
Kowalczyk, S.
et al.

Publication Date

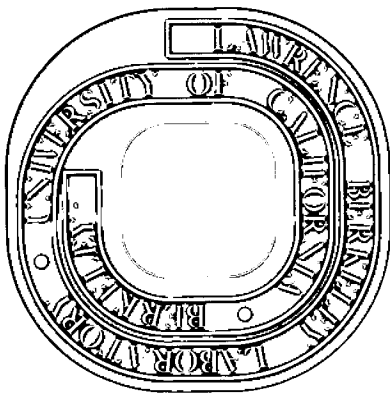
1972-07-01

THE ONSET OF RELATIVISTIC EFFECTS IN THE
DENSITY OF STATES OF THE $6s6p$
ELEMENTS Tl, Pb, AND Bi

L. Ley, R. Pollak, S. Kowalczyk, and D. A. Shirley

July 1972

AEC Contract No. W-7405-eng-48



For Reference

Not to be taken from this room

LBL-1203

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE ONSET OF RELATIVISTIC EFFECTS IN THE DENSITY OF STATES
OF THE 6s6p ELEMENTS Tl, Pb, AND Bi*

L. Ley, R. Pollak, S. Kowalczyk, and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1972

Spin-orbit splitting of the 6p band is manifest in the XPS spectra of Pb and Bi. Lowered energies of the 6s band indicate the presence of the mass-velocity and Darwin terms.

- - -

Relativistic effects, e.g. spin-orbit splitting, have to be taken into account in electronic level calculations for even the lightest atoms. For the valence and conduction electrons, however, crystal-field interactions are usually stronger by several orders of magnitude. Therefore spin-orbit splitting may well be treated as a small perturbation in band structure calculations.

This is certainly not the case for the elements Tl, Pb, and Bi, with atomic numbers 81, 82, and 83. Relativistic band structure calculations [1,2,3] show that spin orbit interactions result in band splittings that are comparable to crystal-field splittings. We report in this Letter experimental evidence that spin-orbit splitting in the valence p-electrons of Pb and Bi prevails in the presence of crystal-field splitting.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

Figure 1a shows the XPS-spectra of the valence region of Tl, Pb, and Bi obtained with monochromatic Al K_{α} x-rays in a Hewlett-Packard HP 5950A spectrometer. The samples were cleaned by argon-ion bombardment (1000 eV, 10 μ A) and were studied at 6×10^{-9} Torr. Other experimental details will be described elsewhere. The valence bands extend to 7 eV below E_F in Tl, to about 12 eV in Pb, and to 13.5 eV in Bi. Included in these spectra are the high intensity 5d peaks at energies which are listed in Table I.

The single broad peak at the bottom of the valence band represents electrons with mainly 6s-like character. The shift of this peak to higher binding energy as one goes from Tl to Bi can be explained by the increasing depth of the atomic potential with increasing atomic number. In Bi the 6s state is already very nearly a core level.

In Tl the p-like electrons are concentrated in one narrow peak near E_F . By contrast, Pb and Bi show two peaks at the top of the valence band which are split apart by 1.8 eV in Pb and 2.2 eV in Bi. The calculated spin-orbit splittings obtained at certain symmetry points in the Brillouin Zone are [4] 0.3 eV for Tl [1], 1.4 eV for Pb [2], and 2 eV for Bi [3]. The excellent agreement between these figures and the experimental values strongly supports our interpretation of these bands as being split by spin-orbit interactions rather than by the crystal field. In this connection it is of interest to note (Table I) that even free-atom HFS-calculations [5] reproduce the 6p-band splitting quite well.

In this discussion we have neglected the differences in crystal structure among these three elements. This is somewhat justified by the fact that the rhombohedral Bi lattice can be regarded as a slightly distorted cubic lattice, as compared with the cubic lattice of Pb. Of course the lattice symmetries were taken into account in the band-structure calculations [1-3].

Two other relativistic effects--the Darwin and mass-velocity terms-- should also be considered. These terms should have the effect of lowering the energies of the s bands. Comparison of the positions of the s-bands in Tl, Pb, and Bi with those of In, Sn, and Sb [6] shows a relative depression of the s-band energies in the heavier elements. We interpret this as a probable indication of these other relativistic effects. Loucks' relativistic APW calculation on Pb [2] located the 6s band lower relative to the 6p band than did an interpolated OPW calculation of Anderson and Gold [7]. Since the former used a relativistic Hamiltonian, it is probable that part of the difference is a consequence of the 6s bands being lowered somewhat by the Darwin and mass-velocity terms.

A more detailed interpretation awaits density-of-states calculations for these elements.

References

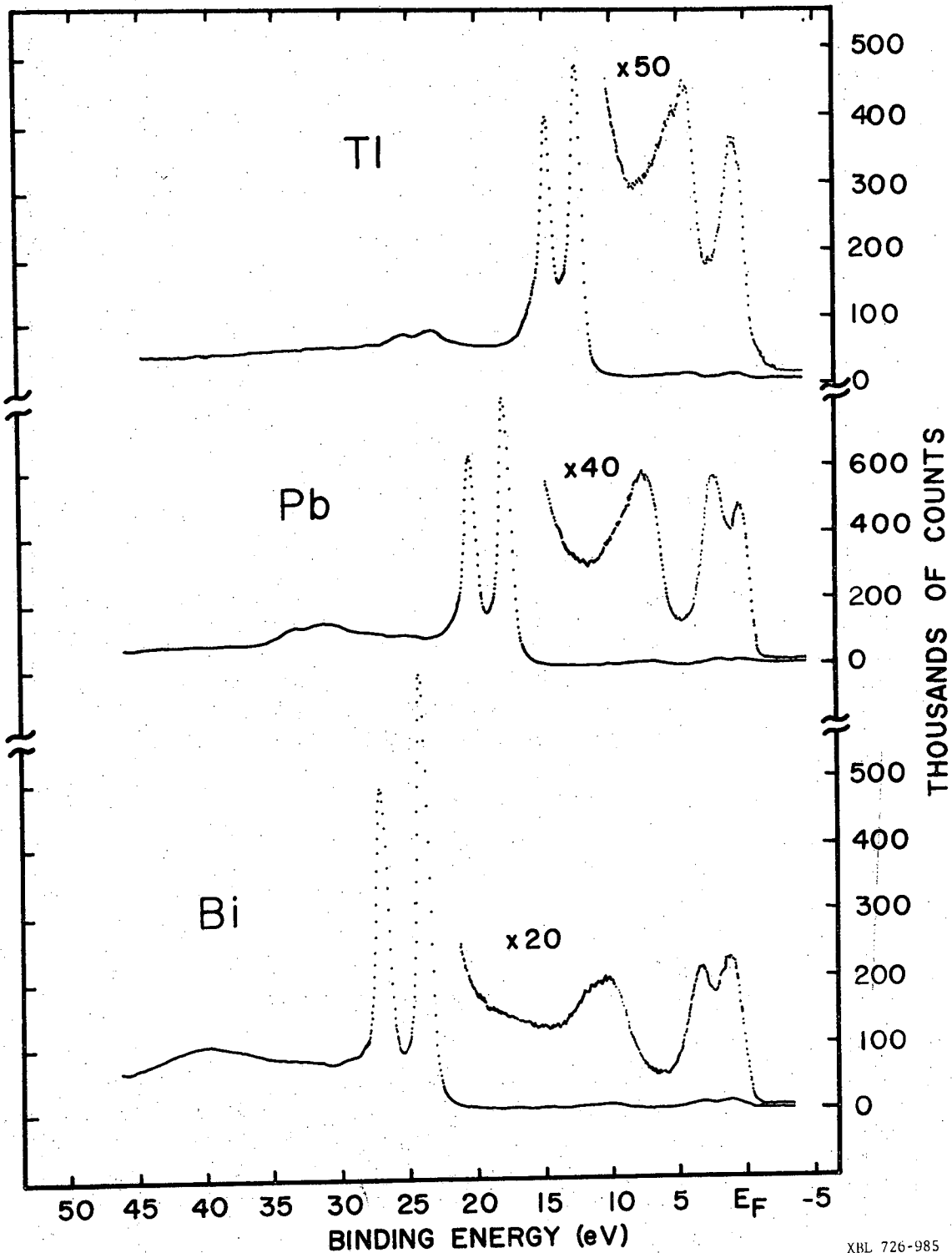
1. P. Soven, Phys. Rev. 6A (1972) 1706.
2. T. L. Loucks, Phys. Rev. Letters 14 (1965) 1072.
3. L. G. Ferriera, J. Phys. Chem. Sol. 28 (1967) 1891.
4. We deduced these splittings from published band-structure work. Theoretical densities of states are not yet available.
5. C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker, and C. W. Nestor, Jr., Atomic Data 3 (1971) 1.
6. R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Letters (to be published, July 31, 1972 issue).
7. J. R. Anderson and A. V. Gold, Phys. Rev. 139 (1965) A1459.

Table I. Valence-band binding energies

	Tl	Pb	Bi
Bind. Energ. $5d_{3/2}$	14.53(5) eV	20.32(5) eV	26.94(7) eV
Bind. Energ. $5d_{5/2}$	12.30(5)	17.70(5)	23.90(7)
d-splitting	2.23(2)	2.62(2)	3.04(2)
Free atom d-splitting (HFS theory, Ref. 5)	2.44	2.83	3.26
6s-band	4.90(25)	7.68(20)	9.95(18)
6p-band	0.80(12)	{ 2.33(8) 0.53(5)	{ 3.34(12) 1.18(12)
6p-splitting	--	1.80(5)	2.16(8)
Free atom 6p splitting (HFS theory) Ref. (5)	--	--	2.16

Figure Caption

Fig. 1. High-resolution XPS spectra of thallium, lead, and bismuth. The $5d_{3/2} - 5d_{5/2}$ doublet is the strongest feature in each spectrum. Characteristic energy-loss maxima appear to the left in each case, with the losses in thallium showing up as two well-resolved peaks. The broad peak to the right of the 5d doublet is the 6s band, and the narrower, spin-orbit split 6p bands fall near the Fermi energy.



XBL 726-985

Fig. 1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720