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DISCLAIMER

THE EVOLUTION OF CORE STATES FROM ENERGY BANDS IN THE 4d5s5p
REGION FROM Pd TO Xe[*]

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Abstract:

    X-ray photoemission studies were carried out on high-
purity specimens of the 4d5s5p elements Pd through Te using
monochromatized Al (Kα) radiation. With increasing atomic
number the 4d structure evolves from d bands to spin-orbit
split atomic-like core levels. Band-structure broadening was
detectable in Cd, for which the 4d doublet is 11 eV below the
Fermi energy. Structure was observed in the 5s5p bands for the
first time by this method. The cohesive energy was attributed
to the 5p bands in In through Sb. The two-component 5p peak
in Te is interpreted as a bonding valence band at 4.0 eV and
a non-bonding band at 1.2 eV.

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Most discussions of band structure in metals are predicated on the

assumption that the tightly-bound electrons can be regarded as belonging to

separate ion cores, while those that are more loosely bound occupy valence

bands. In passing beyond the end of a transition series one would expect the

d bands to become narrower, fall below the Fermi energy E_F, and evolve into core levels. It is not always clear, however, just which atomic levels can be safely treated as core states and which ones must be explicitly included as part of the band structure. In this letter we report x-ray photoelectron spectroscopy (XPS)[1] experiments addressed to this question for the 4d5s5p elements Pd (Z=46) through I (Z=53). By following the $4d_{3/2}$ - $4d_{5/2}$ spin-orbit splitting from I down through Cd to Ag one can unambiguously trace the onset of band-structure broadening. We also report the first observation by XPS of structure in the sp bands. This structure exhibits systematic changes between Cd and Te.

The specimens studied were high-purity single crystals in each case except Sb and I, for which polycrystalline samples were used. All the specimens except I were studied in a Hewlett Packard 5950A spectrometer with a monochromatic Al($K\alpha$) x-ray source. The working pressure was always less than 5×10^{-9} Torr. Iodine was examined in the Berkeley iron-free spectrometer. Standard metallographic methods were used to produce clean surfaces. The typical procedure consisted of spark-cutting discs from single crystal rods, mechanically polishing, and finally electropolishing just prior to insertion into the vacuum chamber. Surface purity was monitored in situ and the sample was repeatedly argon etched until all impurity XPS lines were eliminated. This typically required 15 minutes of bombardment with a 10 μA beam of 900 V Ar^+ ions. Oxygen 1s and carbon 1s spectra taken after each valence-band measurement indicate that there was no oxygen build-up. A carbon layer corresponding to 1/10 the intensity of the carbon 1s line of graphite accumulated on the surface after 10 hrs.

Valence-band spectra are displayed in Fig. 1 and derived parameters are set out in Table 1. The position of the Fermi energy E_F in these spectra is

known to ± 0.09 eV relative to the Fermi edge of Au, which was measured together with each sample.

In the spectra of Pd, Ag, Cd, In, and Sn, E_F appears to fall at an energy where the density of states is rather large, and the maximum slope of the leading edge is consistent with the resolution of the instrument. For each of these cases the observed slope can be obtained by folding a Fermi distribution function with a Gaussian instrumental response function of 0.55 ± 0.02 eV FWHM. For Sb and Te there is no visible leading edge at E_F.

Doublet structure in the 4d shell is evident from Ag through I. The energy splitting ΔE between the two components of the doublet is plotted in Fig. 2a. Also plotted is a theoretical splitting which was estimated by normalizing orbital energy differences taken from free-atom relativistic Hartree-Fock-Slater calculations[2] to ΔE(Sb). That the free-atom values of spin-orbit splitting are appropriate in metals is confirmed by the good agreement of this normalized curve with the experimental splitting in gaseous xenon,[3] also shown in Fig. 2a. The free-atom values are lowered 0.1 eV by this normalization. The trend from Sn to I is in excellent agreement with the theoretical curve. The intensity ratio of the two components is in each case close to 1.3, in only fair agreement with the value 1.5 expected for a $d_{3/2}$, $d_{5/2}$ doublet on the basis of multiplicity alone. For the heavier elements Sn to I the 4d electrons can be assigned to the ion cores with confidence. The splitting in indium may be just slightly larger than the free-atom spin-orbit splitting. For Cd the experimental splitting ΔE = 0.99 eV greatly exceeds the predicted spin-orbit splitting of 0.73 eV, and is in fact even larger than the observed splitting in indium. We conclude that band structure affects the 4d shell in Cd, at

11 eV below E_F, and is perhaps perceptible even for the 4d shell of In at

E_F - 17 eV.

The spin-orbit splitting energy ΔE is a uniquely reliable parameter

for detecting the onset of lattice effects because it is independent of

component linewidth, which can be affected by lifetime broadening. Nevertheless,

the total "4d bandwidth" can also be used to study broadening by the lattice.

In Fig. 2b the 4d bandwidth (FWHM) is plotted against Z. The bandwidth drops

monotonically with increasing Z across the 4d transition series from 6 eV in

Mo (not shown) to 3.4 eV in Ag, going through a minimum at In and increasing

thereafter because of spin-orbit splitting. The width in Cd is greater than in

In, showing again that band structure effects are present in Cd metal.

In the past, XPS studies of valence bands in transition-series metals have

yielded little information about s and p bands.[1,4,5,6] This was a consequence

of their small cross section for photoemission, the presence of $K\alpha_{1,2}$ lines, and

bremsstrahlung in the exciting radiation. With these unwanted components removed

by monochromatization it was possible to observe for the first time a considerable

amount of structure in the 5s5p bands of Cd, In, Sn, Sb, and Te. A detailed

analysis of the spectra must await more intensive measurements and further

density of states calculations, but the systematic variation of the 5s5p spectra

from Cd to Te (Fig. 1) suggests a preliminary interpretation in terms of a

transition from band structure to atomic core-level character for the 5s band

with a simultaneous filling of the 5p band. Three systematic effects occur

between Cd and Te. First, the s-p valence band which shows structure even in

Cd resolves into two peaks in Sn and Sb and three in Te. Second, the higher

binding-energy peak which we designate as 5s, falls monotonically below E_F as Z

increases. We designate the lower binding-energy bands in In, Sn, Sb, and Te as 5p. Finally, the experimental area ratio (5s/5p) in In to Te agrees well with the occupation number ratio (n/m) for the respective free-atom ground state configurations $5s^n 5p^m$ (Table 1).

We interpret this behavior in terms of the evolution of core-like 5s and 5p shells. Figure 2c illustrates the approach of the 5s and 5p bands toward the core s and p levels of Xe. The bars in Fig. 2c represent the widths (FWHM) of the 5s and 5p bands. In Cd through Te all bands are considerably broader than the corresponding levels in Xe. It should also be noted that the 5p splitting in Te is dominated by band structure effects, yielding a splitting much larger (2.9 eV) than the spin-orbit splitting in Xe (1.3 eV). Thus the systematic trend toward core-like levels aids assignment of the peaks, although solid-state interactions are clearly present in Cd to Te.

Further analysis of the 4d, 5s, and 5p peak positions permits us to attribute the cohesive energy to the 5p orbitals. Examination of the peak positions in Cd through Te shows that the 5s and 5p binding energies are nearer the 4d binding energies than are the corresponding free-atom orbital energies from Hartree-Fock-Slater estimates. We ascribe this discrepancy in part to the cohesive energy of the solid and in part to relaxation of the passive orbitals during photoemission. Valence-shell relaxation energies are usually much smaller than those of more tightly-bound levels.[7] Assuming this to be true for these elements, we may calculate the d-shell relaxation shift Δ according to

$$\Delta = [E_c + n(E_{5s} - \eta_{5s}) + m(E_{5p} - \eta_{5p})]/(n + m) \quad .$$

Here E_c is the cohesive energy as taken from Refs. 8 and 9, $\eta_{5s,5p} = \epsilon(5s,5p) - \epsilon(4d)$ is the difference between the s or p orbital energy and the 4d orbital energy in the free atom, $E_{5s,5p} = E_B(4d) - E_B(5s,5p)$ is the corresponding measured binding-energy difference in the solid, and n and m are the numbers of 5s and 5p electrons. Figure 3 shows the results of these simple calculations. The relaxation energies range from 1.1 eV to 2.0 eV for the elements In to Te. The values of Δ show very good agreement with expectations. A theoretical estimate of the magnitude of Δ for iodine may be obtained by comparing the orbital- and binding-energy estimates for the 4d, 5s, and 5p levels as given by Rosen and Lindgren[10] (their Methods "A" and "B"). The result, $\Delta(I) = 2.4$ eV, agrees quite well with our values.

An important result of this analysis is that the cohesive energy is almost entirely accounted for by the 5p electrons. In Te there are two 5p peaks of equal area at binding energies of 1.1 eV and 4.0 eV relative to E_F. The higher binding energy band alone accounts for most of the cohesive energy, and it is also wider than the 1.1 eV band. These observations strongly support the model for group-VI elements in two-fold coordination as discussed by Kastner.[11] In the chalcogens the valence band is formed by unshared-electron states in contrast to the tetrahedral semiconductors in which the bonding band forms the valence band and the antibonding band forms the conduction band. We assign the 4.0 eV peak in tellurium as the bonding band and the 1.1 eV peak as the unshared or lone-pair band.

FOOTNOTES AND REFERENCES

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Table I. Summary of experimental data.

	Ag	Cd	In	Sn	Sb	Te	I	Xe
Binding energy $4d_{3/2}$ (eV)	--	11.46(9)[a]	17.64(9)	24.76(9)	33.44(9)	41.80(9)	--	--
Binding energy $4d_{5/2}$ (eV)	--	10.47(9)	16.74(9)	23.68(9)	32.14(9)	40.31(9)	--	--
FWHM $4d_{3/2}$ = FWHM $4d_{5/2}$	--	0.81(18)	0.78(15)	0.83(8)	0.76(18)	0.94(2)	--	--
4d Splitting (eV)	1.6(1)	0.990(46)	0.899(10)	1.075(34)	1.254(42)	1.51(1)	1.76(16)	1.97[b]
HFS free atom 4d splittings normalized to Sb	0.59	0.73	0.88	1.06	1.25	1.48	1.72	1.98
Binding energy 5s (eV)	--	2.2(5)	4.1(4)	7.0(5)	9.1(2)	11.5(2)	--	--
FWHM 5s (eV)	--	5.0(7)	4.0(5)	5.8(5)	4.0(5)	5.3(5)	--	--
Binding energy 5p (eV)	--	--	0.75(13)	1.25(27)	2.35(25)	{ 4.0(2) / 1.13(5) }	--	--
FWHM 5p (eV)	--	--	2.0(2)	3.5(5)	3.9(2)	{ 2.3(2) / 2.1(2) }	--	--
4s/4p rel. areas	--	--	1.85	0.7	0.63	0.5	--	--
n/m	--	--	2.00	1	0.66	0.5	--	--

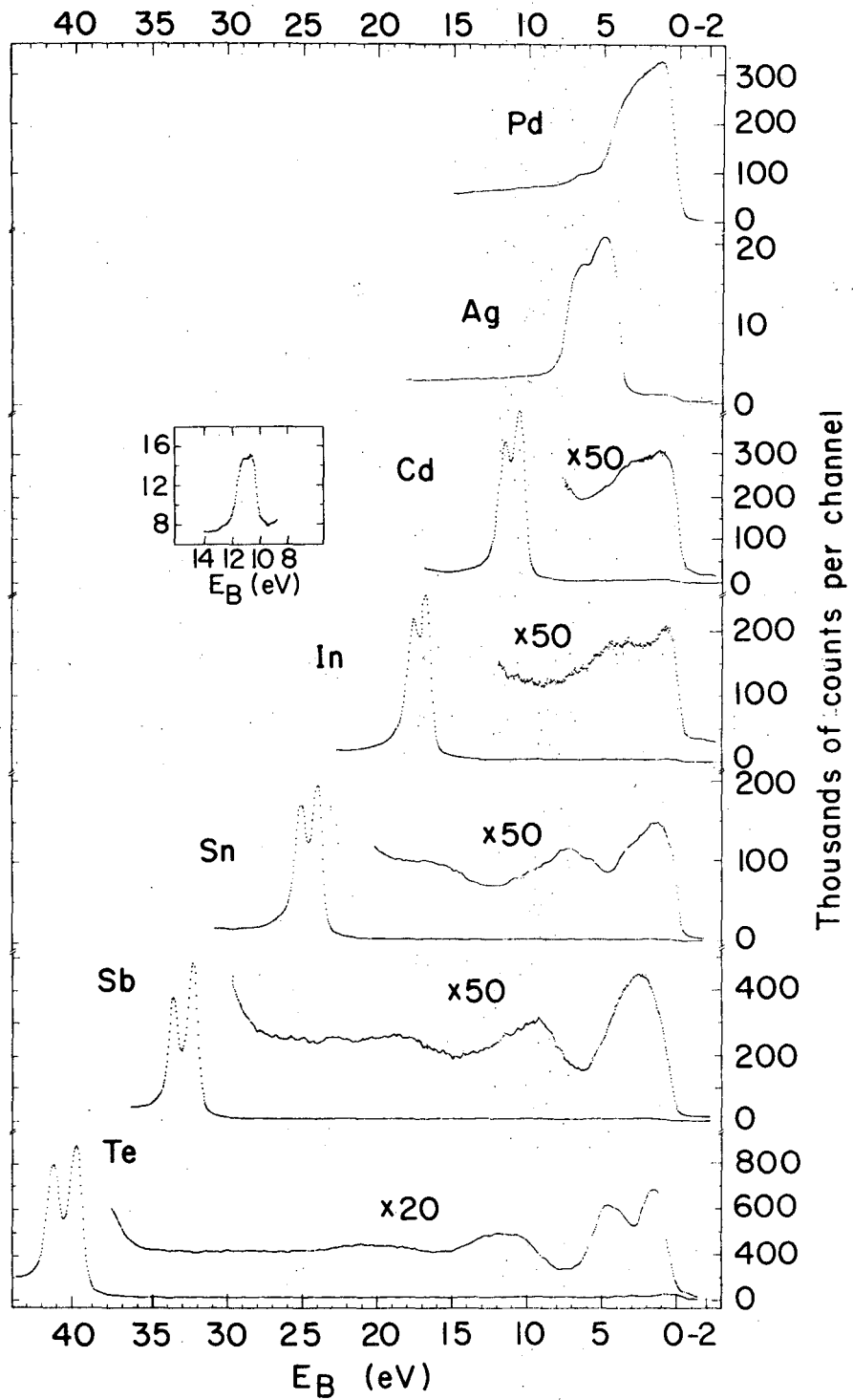[a]Errors in last place given in parenthesis.

[b]Ref. 3.

FIGURE CAPTIONS

Fig. 1. X-ray photoelectron spectra of the valence band region for Pd through Te.
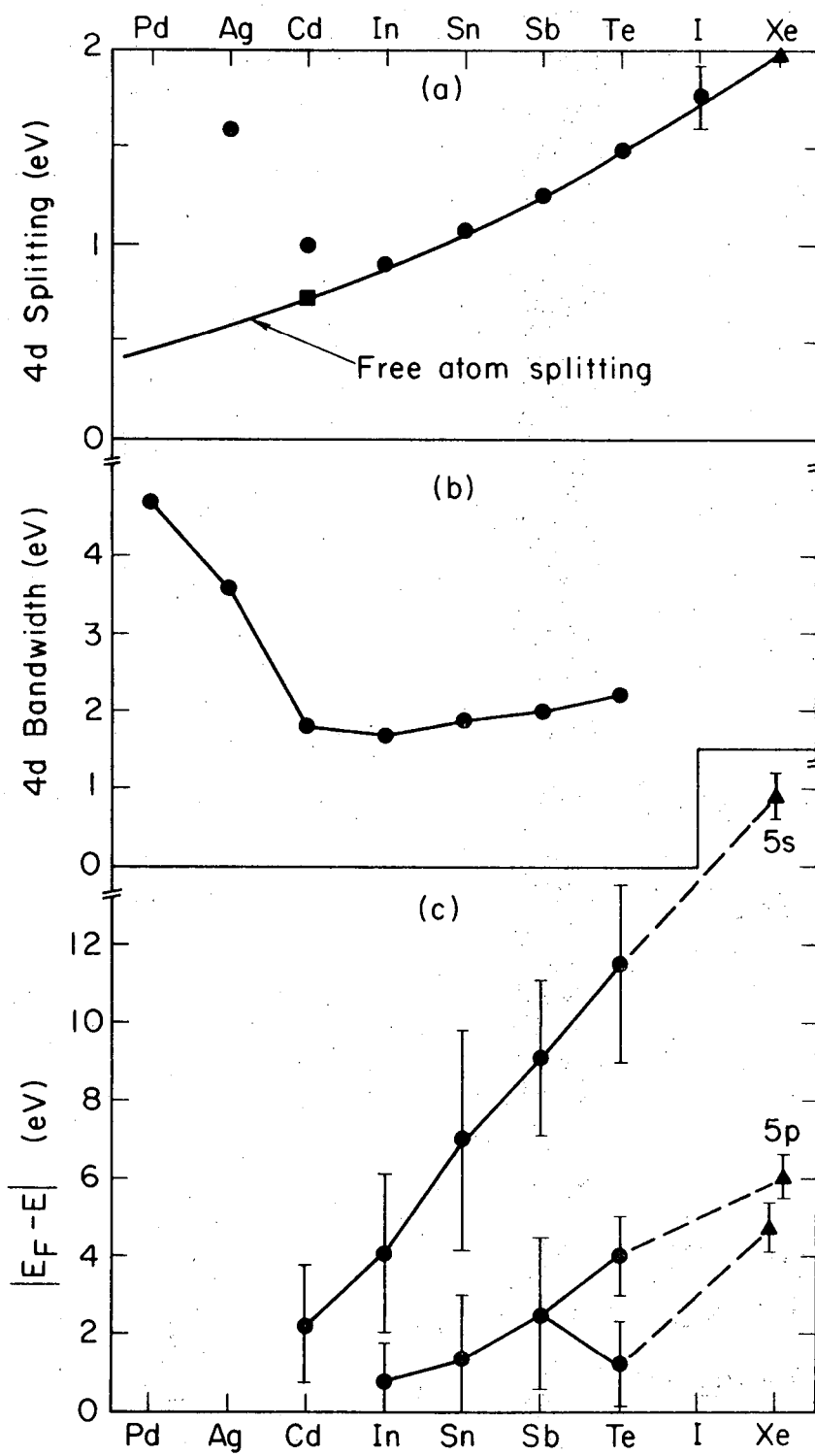
Fig. 2. a) Comparison of the experimental 4d level splitting with free atom HFS calculations[2]; the Cd-point ■ refers to the experimental value for Cd atoms sputtered onto a Au (111) surface. b) The experimental 4d-bandwidths. c) Positions of the 5s- and 5p-bands relative to the Fermi level; the vertical bars represent the bandwidths at half maximum. The Xe-values in a) and c) are taken from Ref. 3.

Fig. 3. The 5s- and 5p-band contributions to the cohesive energy E_c of the metals In through Te. a) Experimental values. b) Experimental values shifted by the 4d relaxation energy Δ given by equation (1). c) Free atom HFS values (Ref. 2).
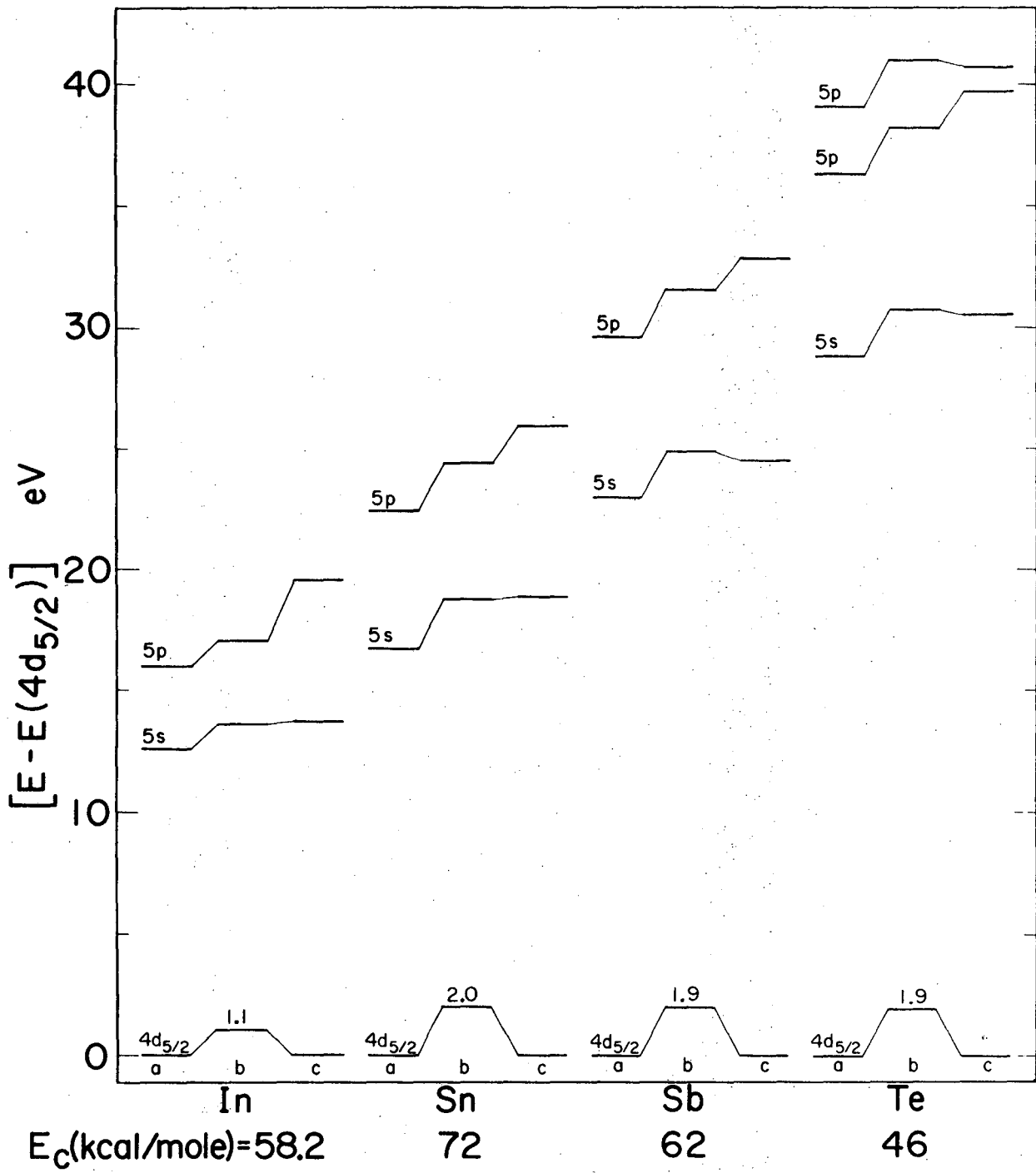
Fig. 1

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Fig. 2

Fig. 3