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Crystal-field effects on the apparent spin-orbit splitting of core and valence levels observed by x-ray photoemission*

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Several anomalous relativistic effects in x-ray-photoemission spectra of metals and binary compounds are reviewed and explained in terms of combined spin-orbit and crystal-field interactions. The apparent spin-orbit splitting does not appear to be enhanced by renormalization effects, which would affect the expectation value of $\xi\vec{l}\cdot\vec{s}$ itself. The variation of $\xi\vec{l}\cdot\vec{s}$ with charge state is not large enough to be important in solids. Rather for both outer p and d shells, the splitting appears to be affected by "crystal-field" terms that carry the lattice symmetry. In III-V and II-VI compounds only the tellurium $4d$ shell may have a spin-orbit splitting different from that expected from free-atom data. Howerer the enhancement is small (3%) and consistent with a tetrahedral crystal field. The enhancement of d-shell spin-orbit splitting in Zn and Cd arises from the Y_2 terms in the crystal field because of the large c/a ratio in these lattices. There is no enhancement for Cd in a cubic lattice, while the enhancement in several lattices follows the quadropole coupling constant of ^{111}Cd, which presumably also arises from Y_2-symmetry terms. The d-band density of states in fcc Au and Ag is consistent with expectations based on a $\xi\vec{l}\cdot\vec{s}$ and Y_4 interaction, but band-structure effects so complicate these cases as to preclude such a simple interpretation. The absence of enhanced splitting in valence-shell p shells in Pb and Bi is explained in terms of the higher symmetry of the p wave functions as compared to that of the d electrons and the partial filling of p-derived valence bands in these metals.

I. INTRODUCTION

A feature readily observed in x-ray photoelectron spectroscopy (XPS) of heavier elements is a splitting of core levels, commonly referred to as spin-orbit (s-o) splitting. This splitting reflects the two possible couplings of the core-hole spin $\vec{s}$ with its angular momentum $\vec{l}$ forming total angular momentum eigenstates differing in energy by the difference in the expectation value $\langle\vec{l}\cdot\vec{s}\rangle$ multiplied by a factor ξ, the coupling strength.

Within the accuracy obtainable in earlier XPS work these splittings appeared to be equal in solids and gases, and they agree as well as could be expected with the s-o splitting obtained from optical data[1] and relativistic Hartree-Fock calculations.[2] Improvement in the resolution obtained in XPS and the availability of uv sources in an energy range that gave access to the least-bound core levels improved the accuracy with which these splittings could be measured to an extent that made it possible to measure small deviations of the spin-orbit splitting in solids from those measured in the gas phase. Furthermore even changes in the splitting of the outermost d levels in Zn and Cd have been observed in going from the metal to binary compounds containing one of these elements.[3,4]

In this paper we discuss some of the effects responsible for the observed splittings and their changes. In Sec. II we review the experimental data that will be discussed. In Sec. III we present the results of a simple model calculation that explains some of the puzzling experimental findings in terms of the influence of crystal fields of low symmetry on the energies of final states.

II. EXPERIMENTAL EVIDENCE FOR SPIN-ORBIT-LIKE SPLITTINGS IN ELEMENTS AND COMPOUNDS

We shall consider only electronic excitations extending to about 50 eV above the ground state. This allows us to compare data obtained from two or more of: optical spectroscopy, uv photoemission, and XPS. The resolution of photoemission spectroscopy then further restricts our study to levels split by at least ~ 0.4 eV; i.e., to the outermost d levels of the group II to VII elements and the p levels of some of the heavier elements in the sixth row of the periodic system. The available data on these levels are set out in Table I. The elements listed in Table I have d levels bound by at least 10 eV. These levels do not exhibit measurable band effects and are therefore referred to as corelike. In addition, the splitting of the outer d levels in Ag and Au and the p levels in Pb and Bi are listed in Table II. Although the atomic d levels are broadened into bands in these solids, the determination of an average splitting of the two broad peaks is still possible. The same observation holds for the p-like bands in lead and bismuth.

It is convenient to compare the splittings observed in solids to those for the free ions as a secure starting point for the discussion of various solid-state effects. To do this, we have extracted the free-ion spin-orbit splitting from the observed term values of the configuration $(d^9)^2D$ in the optical spectra of the ions.[1] While rendering the determination of the spin-orbit splitting straight-

TABLE I. Spin-orbit splittings in the free atoms and solids. Errors are given parenthetically. The roman numerals indicate the ionization state of the atoms (Zn II = Zn^+).

Element	Shell	Lattice	Splitting (eV)	Reference
Zn II	Zn 3*d*	free ion	0.337	1
Zn metal		hex	0.54(2)	a
Cd II	Cd 4*d*	free ion	0.669	1
Cd metal		hex	0.95(3)	a
Cd metal		hex	0.99(5)	3
CdTe		z.b.[f]	0.70(5)	b
CdTe		z.b.	0.83(20)	c
CdS		z.b.	0.76(12)	c
CdSe		z.b.	0.87(16)	c
AgCd alloy		cubic	0.70(8)	this work
In III	In 4*d*	free ion	0.849	1
In metal		tetragonal	0.90(1)	3
In metal		tetragonal	0.88(15)	b
In metal		tetragonal	0.86(3)	a
InSb		z.b.	0.83(3)	d
InSb		z.b.	0.85(5)	b
InSb		z.b.	0.84(8)	4
InP		z.b.	0.84(8)	4
Sb V	Sb 4*d*	free ion	1.239	1
Sb metal		rhombohedral	1.25(4)	3
GaSb		z.b.	1.21(4)	4
InSb		z.b.	1.22(4)	4
InSb		z.b.	1.15(10)	d
InSb		z.b.	1.25(5)	b
Te VII	Te 4*d*	free ion	1.409	1
Te metal		hex	1.51(1)	3
ZnTe		z.b.	1.47(2)	4
CdTe		z.b.	1.44(2)	4
HgTe		z.b.	1.44(2)	4
PbTe		NaCl	1.46(2)	4
PbTe		NaCl	1.35(10)	d
Hg I	Hg 5*d*	free atom	1.800	1
Liquid Hg		...	1.83(9)	4
HgTe		z.b.	1.77(2)	4
HgTe		z.b.	1.91(10)	c
HgSe		z.b.	1.81(10)	c
HgS		z.b.	1.79(10)	c
Pb IV	Pb 4*d*	free ion	2.643	1
Pb metal		fcc	2.62(2)	8
Pb metal		fcc	2.66(9)	a
PbS		NaCl	2.58(2)	e
PbSe		NaCl	2.61(2)	e
PbTe		NaCl	2.61(2)	e

[a] R.T. Poole, P.C. Kemeny, J. Liesegang, J.G. Jenkin, and R.C.G. Leckey, J. Phys. F 3, L46 (1973).

[b] D.E. Eastman, W.D. Grobman, and J. Freeouf (unpublished); D.E. Eastman, J. Freeouf, and M. Erbudak, Congres du Centenaire de la Société Francaise de Physique, Vittel, France, 1973 (unpublished).

[c] C.J. Veseley, R.L. Hengehold, and D.W. Langer, Phys. Rev. B 5, 2296 (1972).

[d] M. Cardona, C. Penchina, N. Shevchik, and J. Tejeda, Solid State Commun. 11, 1655 (1972).

[e] F.R. McFeely, S.P. Kowalczyk, L. Ley, R.A. Pollak, and D.A. Shirley, Phys. Rev. B 7, 5228 (1973).

[f] z.b. = zinc-blende structure.

forward and reliable, this method has the disadvantage that we have to deal in some cases with very highly ionized atoms. To assess the importance of this effect, we show in Table III the effect of the ionic charge on the spin-orbit splitting of the *d* electrons in Cu, Zn, Ag, and Cd. The values for the spin-orbit splitting are taken from Dunn's compilation.[5] This table makes two points clear: (i) for a given *d*-shell configuration, the spin-orbit splitting increases with increasing ionic charge by not more than 2% per unit charge; (ii) a change in the *d* configuration ($d^9 \rightarrow d^8$) affects the spin-orbit splitting considerably more than the corresponding increase in ionic charge.

These two points are consequences of the approximate form of the spin-orbit Hamiltonian operator:

$$H_{s\text{-}o} = \frac{\alpha^2}{2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{L}\cdot\vec{S},$$

neglecting exchange effects and the mutual spin-orbit and spin-spin interaction of electrons in unfilled shells.[6] Here α is the fine-structure constant and V is the shielded nuclear potential. The dependence of the expectation value $\langle H_{s\text{-}o}\rangle_\psi$ mainly on the inner part of the electronic wave function ψ has been pointed out by many authors. The variation in the operator $(1/r)\,(\partial V/\partial r)$ upon charge transfer in outer shells is very small in this region.

From these considerations it is clear that the atoms chosen in Table III are very unfavorable examples because the charge radii for *nd* and $(n+1)s$ electrons are not too different. Progressing in the periodic table would improve that difference, but the high degrees of ionization quoted in Table I for, e.g., Sb and Te makes the quoted free-atom values of the spin-orbit splitting upper limits by a margin of an estimated $(3\pm3)\%$.

Returning to the data obtained from solids in Table I, we can make the following observations. The apparent $\Delta E_{s\text{-}o}$ of the 4*d* level in metallic Zn and Cd exceeds $\Delta E_{s\text{-}o}$ in the atoms by 59% and 45%, respectively. This increase is unique among the entries of Table I. The apparent $\Delta E_{s\text{-}o}$ of Cd in tetrahedrally coordinated binary compounds agrees within experimental error with the free-

TABLE II. Free-atom spin-orbit splitting and the apparent splitting of valence-band peaks in Ag, Au, Pb, and Bi.

Element	Shell	Lattice	Splitting (eV)	Reference
Ag I	4*d*	free atom	0.555	1
Ag metal		fcc	1.6(1)	3
Au I	5*d*	free atom	1.522	1
Au metal		fcc	3.8(2)	a
Pb I	6*p*	free atom	1.746	1
Pb metal		fcc	1.80(5)	8
Bi I	6*p*	free atom	2.163	b
Bi metal		rhombohedral	2.16(8)	8

[a] D.A. Shirley, Phys. Rev. B 5, 4709 (1972).

[b] C.C. Lu, T.A. Carlson, F.B. Malik, T.C. Tucker, and C.W. Nestor, Jr., Atomic Data 3, 1 (1971).

TABLE III. Spin-orbit splitting of d levels for various ionic charge states.

Element	Configuration	$\Delta E_{s\text{-}o}$(eV)	Reference
Cu I	$3d^9 4s^2$	0.253	1
Cu II	$3d^9 4s$	0.257	5
Cu III	$3d^9$	0.257	5
Cu II	$3d^8 4s^2$	0.268	5
Cu III	$3d^8 4s$	0.273	5
Cu IV	$3d^8$	0.271	5
Zn I	$3d^9 4s^2 p$	...	...
Zn II	$3d^9 4s^2$	0.337	5
Zn III	$3d^9 4s$	0.281	5
Zn IV	$3d^9$	0.341	5
Ag I	$4d^9 5s^2$	0.555	5
Ag II	$4d^9 5s$	0.567	5
Ag III	$4d^9$	0.570	5
Ag II	$4d^8 5s^2$	0.598	5
Ag III	$4d^8 5s$	0.580	5
Ag IV	$4d^8$	0.589	5

atom value. Combining the results of all three compounds, the apparent $\Delta E_{s\text{-}o}$ lies 0.08 eV above the free-atom $\Delta E_{s\text{-}o}$. The weighted mean value for the apparent $\Delta E_{s\text{-}o}$ in In metal lies at 0.89 eV, or 4.7% above the free-atom value of 0.85 eV. The values for In in tetrahedral coordination agree well with the free-atom $\Delta E_{s\text{-}o}$.

The Sb apparent $\Delta E_{s\text{-}o}$ values agree within the error limits with the free-ion value, for both compounds and the metal. The $4d$ splitting for InSb measured by Cardona *et al.*[7] seems to be low, as does their value for the Te $4d$ splitting in PbTe. With this one exception the Te $4d$ values are higher than the free-atom spin-orbit splitting by about 2.8% for the compounds and 7% for the metal.

The entries for Hg show no anomalous behavior, nor do those for Pb in various surroundings. The observed splittings in the valence d bands of Ag and Au (Table II) are considerably larger than the free-atom $\Delta E_{s\text{-}o}$. The p bands of Bi and Pb, however, do not exhibit such an increase, as has been observed earlier.[8] We can summarize this section as follows:

(i) Corelike d levels of elements in tetrahedral surroundings show no, or only a very small ($< 1\%$), increase in the apparent $\Delta E_{s\text{-}o}$ compared to free-atom values. The only exceptions are the Te compounds with an average increase of ~ 2.8%.

(ii) In, Te, Cd, and Zn metals have apparent $\Delta E_{s\text{-}o}$ in the outermost d levels which exceed the free-atom values by 4.7, 7, 45, 59%, respectively.

(iii) Pb and Sb show no such increase.

(iv) Valence d bands in Ag and Au are split by amounts far exceeding the free-atom $\Delta E_{s\text{-}o}$ value, in contrast to the valence p bands (Bi, Pb) which are split by energies close to $\Delta E_{s\text{-}o}$ for the free atoms.

In Sec. III, we will attempt to show that this behavior can be explained by the effects of crystal fields of different symmetries on atomic levels in the solid.

III. DISCUSSION

In this section we will discuss the influences on the apparent spin-orbit splitting of "corelike" d levels of an atom surrounded by other atoms in a solid. This applies to the case of Cd and other elements which do not show appreciable band-structure broadening of the d levels, in contrast to, e.g., Au, where the width of the two components is comparable to or even greater than the total splitting. We will refer to the latter as "bandlike" levels.

This distinction implies that in the former category energy dispersion with wave vector $\vec{k}$ may be neglected. That is, we treat those levels as if the energy ordering at $\vec{k} = \vec{0}$ is retained throughout the Brillouin zone. The justification for this approach is derived directly from experimental evidence (i.e., linewidths) rather than from assumptions about overlap integrals and potentials: it therefore possesses a high degree of validity.

We note at the outset that we are dealing with *final-state* structure following photoemission from a closed shell. This is manifestly a one-electron (hole) problem. The appropriate d-hole-state Hamiltonian in the one-electron approximation has the form

$$H = h_0 + h_{\text{cryst}} + h_{s\text{-}o} \,. \tag{1}$$

Here h_0 contains the kinetic-energy operator and the spherical Coulomb potential of the nuclear charge screened by the inner electrons forming closed shells. The h_{cryst} term summarizes the potentials due to the neighboring atomic cores and the valence electrons including the valence electrons of the atom under consideration, and $h_{s\text{-}o}$ is the one-electron spin-orbit Hamiltonian.

We wish to show that the differences in the value for the d-level splittings, $\Delta E_{s\text{-}o}$, observed in different solid environments is a result of the influence of h_{cryst} rather than of a modification in $h_{s\text{-}o}$. To do so, let us first consider $h_{s\text{-}o}$ in more detail. The spin-orbit interaction is a first-order effect in the expansion of the relativistic energy expression for a spinning electron in an electric field U.[9] The reduction to a non-relativistic form[10] gives the result (in atomic units):

$$h_{s\text{-}o} = \xi \vec{l} \cdot \vec{s} = \frac{\alpha^2}{2} \left\langle \frac{1}{r} \frac{\partial U}{\partial r} \right\rangle_{nl} \vec{l} \cdot \vec{s} \,, \tag{2}$$

the expression already given in Sec. II. The brackets indicate the expectation value of $(1/r)$

$\times(\partial U/\partial r)$ evaluated in the state nl. We can rewrite the Landé factor ξ as

$$\xi_{nl} = \frac{\alpha^2}{2}\int_0^\infty \frac{(R_{nl})^2}{r}\frac{\partial U}{\partial r}\,dr\,, \qquad (3)$$

where $R_{nl}(r)$ is the normalized radial wave function of the electron in the state nl. A generalization of this result to a many-electron system is not straightforward; we refer the reader to the article by Blume and Watson[6] for a detailed discussion of this problem. Their result can be stated as follows: $h_{s\text{-}o}$ for electrons in an unfilled shell can be written

$$h_{s\text{-}o} = \frac{\alpha^2}{2}\left\langle\frac{1}{r}\frac{\partial U_{\mathrm{eff}}}{\partial r}\right\rangle\sum_i \vec{l}_i\cdot\vec{s}_i$$
$$+\ \text{(terms which include mutual spin-orbit interactions and spin-spin interactions in the unfilled shell).} \qquad (4)$$

The summation extends only over electrons in unfilled shells. Replacing U with U_{eff}, which is essentially a screened potential, including exchange, accounts for the mutual spin-orbit and spin-spin interaction between the open-shell and the closed-shell electrons. It has the effect of reducing the spin-orbit coupling constant.

With this operator in mind, let us now investigate the influence of different surroundings on $h_{s\text{-}o}$ and thereby on the intrinsic spin-orbit splitting of outer d electrons.

In Sec. II we already showed that the charge state of the ion has only a very small influence on $\langle h_{s\text{-}o}\rangle$, even for changes of several units in $|e|$. Charge transfers of a fraction of the elementary charge that are to be expected in partially ionic solids therefore have a quite negligible effect on $\langle h_{s\text{-}o}\rangle$.

So far we have dealt with the effects of charge transfer in the *valence* shell of the central atom on $\langle h_{s\text{-}o}\rangle$. We must also consider direct changes in the wave function of the d-electrons itself upon entering a solid or molecule. These changes can be considered in two parts:

(i) Renormalization of ψ_d due to the necessary orthogonalization of ψ_d with respect to wave functions on neighboring atoms. In the simplest case of orthogonalization to one other orbital, this leads to a renormalization factor of $(1-S^2)^{-1/2}$, where S is the overlap integral between the two orbitals. The extension to more than two orbitals has been given by Löwdin.[11] This leads to an increase in the coefficient of ψ_d and therefore in the Landé factor ξ_d. The components added to the wave function upon orthogonalization make only vanishing contributions for small r, the region which determines ξ_d.

(ii) A mixing of the d electrons with electrons of different symmetry located at the same atom. This mixing is always possible throughout the Brillouin zone but at $\vec{k}=0$ it is possible only for certain symmetry components of the potential. This effect leads to a decrease in the spin-orbit splitting, because the orbital that will mix most strongly to the nd wave function is $(n+1)p$, with a Landé factor smaller than that of the d orbital. We can therefore dispense with the second effect in explaining *increases* in the apparent $\Delta E_{s\text{-}o}$.

The renormalization discussed under (i) *increases* $\langle h_{s\text{-}o}\rangle$, but the increase is overlap dependent. Overlap also determines the extent to which an atomic level is broadened into a band. This excludes renormalization as a decisive factor in the increase of $\langle h_{s\text{-}o}\rangle$ for corelike levels.

Renormalization might be thought to play a major role in the enhanced d-band splitting of silver and gold, to which these arguments do not apply, were it not for the absence of noticeable increases in the apparent $\Delta E_{s\text{-}o}$ in the p bands of Pb and Bi, which would fall into the same category.

In summary, direct changes in the expectation value of $h_{s\text{-}o}$ can not be responsible for the observed increases in the apparent $\Delta E_{s\text{-}o}$ over their free-atom values. The explanation must therefore be sought in the h_{cryst} term if we are to explain the enhancement within the framework of the Hamiltonian in Eq. (1).

The matrix element of h_{cryst} can be expanded into a series of spherical harmonics $Y_{LM}(\theta,\phi)$. The angular momentum $\vec{l}$ of the state under consideration limits this expansion to a sum over even orders in L. For d electrons the last nonvanishing term has $L_{\max}=4$, while for p electrons $L_{\max}=2$. The matrix element $\langle h_{\mathrm{cryst}}\rangle_i$ has the symmetry of the point group of the lattice and is in general given by

$$\langle h_{\mathrm{cryst}}\rangle_i = \sum_{L=0,2,4} A_L T_L(i)\,, \qquad (5)$$

where $T_L(i)$ is the linear combination of spherical harmonics of order L that transforms as the symmetrical irreducible representation of the point group of the lattice at the center of the Brillouin zone. A_L is the expansion coefficient, which contains the radial integral of the Coulomb and exchange interaction of the electron i with the valence electrons and the surrounding ion cores.[12]

Instead of calculating the A_L we shall treat them as free parameters. It should, however, be noted that for a normal expansion of the type in Eq. (5) A_L decreases with increasing L. We shall ignore the term with $L=0$ which corresponds to a generalized Madelung energy and cannot contribute to a splitting in the atomic levels. In solids which crystallize in lattices of cubic symmetry the A_2T_2 term in expression (5) vanishes. This applies to the face-centered-cubic (fcc) lattices of Ag, Au, and Pb and to the tetrahedrally coordinated binary compounds. All other symmetries encountered in this investigation require the retention of the $L = 2$ term.

It is evident from the data in Table I that all cases which exhibit an increase in $\Delta E_{s\text{-}o}$ for the core d levels fall into this latter group with the possible exception of the tellurium salts. The nonvanishing A_2T_2 term in expansion (5) seems therefore a necessary condition for an increase in $\Delta E_{s\text{-}o}$.

Let us explore this possibility in more detail using Zn and Cd as examples. Zn and Cd crystallize in a hexagonal lattice. In this case it is convenient to divide the $L = 2$ term into three factors

$$\langle h_{\text{cryst}}\rangle_i = f(c/a) A_2^{\text{hex}} T_2^{\text{hex}} + A_4^{\text{hex}} T_4^{\text{hex}} . \qquad (6)$$

The geometrical factor $f(c/a)$ depends on the ratio of the crystalline axes c and a. For $c/a = 1.63$, the ideal hexagonal lattice, $f(c/a)$ is zero and the A_2T_2 term vanishes for geometrical reasons. In Zn and Cd, however, c/a is equal to 1.86 and the $L = 2$ term enters with a considerable geometrical advantage [$f(c/a) > 1$ in the point-ion model]. We have diagonalized the two operators $h_{s\text{-}o} + h_{\text{cryst}}$ in the subspace of the d electrons. The method employed for this calculation uses standard angular momentum algebra as outlined by Edmonds.[13] The d^9 configuration is treated in the usual way as a d^1 configuration accompanied by a sign change in the coefficients A_L and the spin-orbit coupling constant ξ.

Figure 1(a) shows the level scheme for a d^9 configuration in the ideal hexagonal field [$f(c/a) - 0$] as a function of A_4. All degeneracies are lifted, yet the increase in the apparent spin-orbit splitting is negligible for values of A_4 which preserve the observed pattern of two d peaks, that is for $|A_4| < 0.4|\xi|$. Beyond this point the energy separation between individual levels becomes comparable to the experimental line width of each component line (~ 0.7 eV) and a spectrum would lose the character of a doublet.

Lifting the restriction of $c/a = 1.63$ introduces the A_2T_2 term, which changes the level pattern appreciably [Fig. 1(b)]. As mentioned above, A_2 is expected to be greater than A_4, and we have therefore plotted the level scheme under the assumption that $A_4 = 0$. For negative values of A_2 the spin-orbit split doublet evolves into a pattern of two nondegenerate doublets and a single level, which would result in a three-peak spectrum with relative intensities 1 : 2 : 2. For $A_2 > 0$ a drastic increase in apparent $\Delta E_{s\text{-}o}$ is possible without destroying the general appearance of a spin-orbit split d doublet with the correct intensity ratio of 2 : 3. The value of A_2 which gives the observed spin-orbit splitting in Zn and Cd is about $1.4\,|\frac{5}{2}\xi|$.

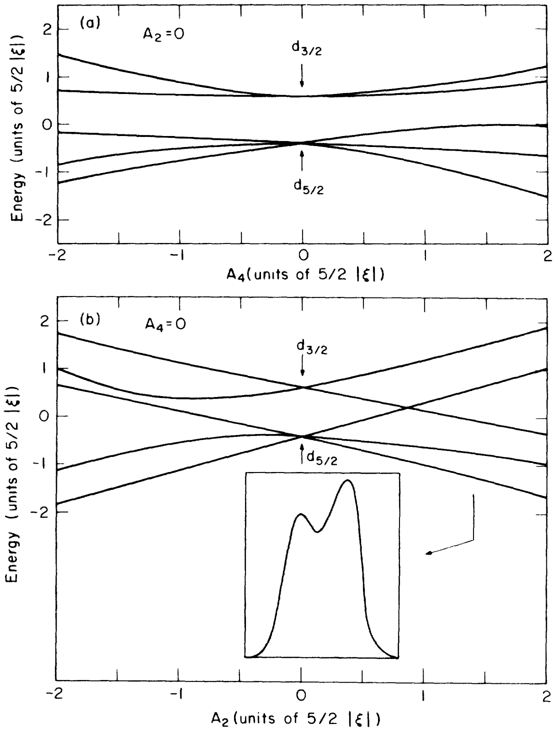

FIG. 1. Energies of a d^9 configuration as a function of the generalized crystal-field parameter A_L. (a) Ideal hexagonal field: $c/a = 1.63$, $A_2 = 0$; (b) general hexagonal field: A_4 is assumed to be zero. The insert shows a spectrum for $A_2 = 1.4\ |\frac{5}{2}\xi|$. The linewidth of each component is equal to ξ.

A spectrum generated from the level scheme at this point does-indeed resemble the observed Cd spectrum closely. The linewidth was set to be $\frac{5}{2}\xi = 0.7$ eV, and the increase in spin-orbit splitting as measured from the spectrum appears to be 58%. The ratio of the *amplitudes* of the two components is reduced to 1.21 from the expected value 1.5 when equal linewidths are assumed. This is in good agreement with the value 1.3 quoted in Ref. 3 for the Cd 4d spectrum in Cd metal and lends further support to our interpretation.

The influence of a nonvanishing A_4 on the level scheme of Fig. 1(b) has been tested, and is found to be compatible with the above discussion as long as A_4 is negative and does not exceed ~ 30% of the absolute value of A_2.

This direct evidence that the increase in apparent $\Delta E_{s\ o}$ in Cd and Zn is symmetry induced is supported by three pieces of additional experimental data.

(i) Figure 2 shows the Cd 4d doublet for a AgCd alloy (10-at.% Cd). The substitutional introduction of the Cd atom into the cubic surrounding of the Ag lattice reduces $\Delta E_{s\text{-}o}$ to the free-atom value.

(ii) The photoemission spectrum of Cd deposited

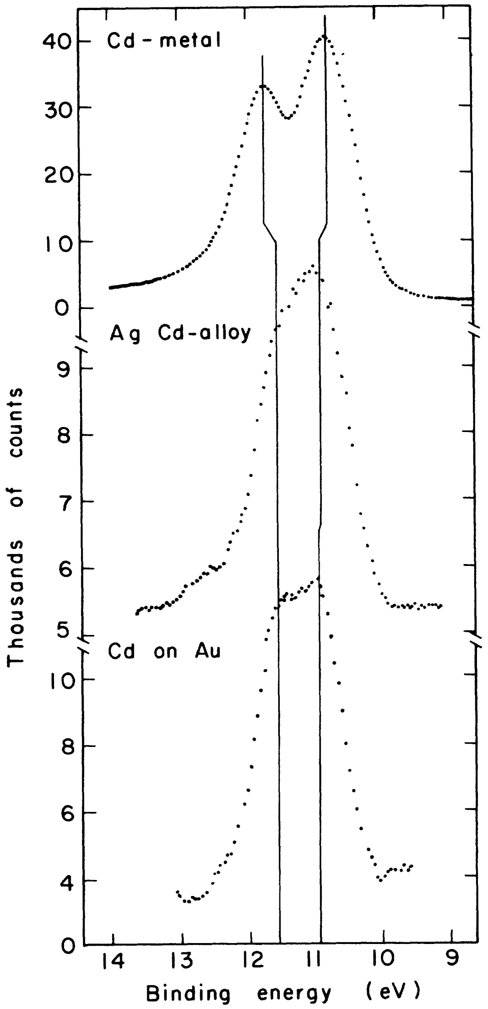

FIG. 2. Cd $4d$ spectrum of (a) Cd metal, (b) an AgCd alloy (10-at. % Cd), and (c) surface isolated Cd atoms.

in submonolayer coverage onto a Au single crystal shows no increase in spin-orbit splitting of the $4d$ level (compare Fig. 2). We interpret that as the observation of single Cd atoms which are subjected to no crystal field. The existence of single Cd atoms in the presence of surface diffusion is favored by the exceptionally low dissociation energy of a Cd cluster.[14] When the Cd coverage is increased to the extent that the formation of Cd clusters becomes possible, the d-level splitting increases to the value in Cd metal.

(iii) Another physical property that is known to be proportional to the $L = 2$ term in an expansion similar to that of expression (5) is the electric field gradient at the nucleus. This field gradient can be measured by observing the interaction of the nuclear quadrupole moment Q with the field gradient q. Values of the coupling constant eqQ/h for ^{111}Cd in host lattices of Pb, In, Zn, and Cd[15] are plotted against the increase in apparent $\Delta E_{s\text{-}o}$ for these metals in Fig. 3. The plot shows a quite convincing correlation between the excess splitting and the quadrupole interaction for the few points available.

The only noncubic metal that does not clearly exhibit the expected increase in $\Delta E_{s\text{-}o}$ is Sb. The group-V semimetals As, Sb, and Bi crystallize in the same rhombohedral structure which can be thought of as being composed of two interpenetrating trigonally distorted fcc lattices.[16] The trigonal distortion decreases in this series with increasing atomic number. It appears that the distortion in Sb is already too small to result in a measurable increase in the splitting of the $4d$ levels. This conclusion is corroborated by the results of the quadrupole interaction of ^{204}Pb in the series of As, Sb, and Bi host lattices.[15] The interaction strength eqQ/h decreases by factors of 2 from one lattice to the next. The $\Delta E_{s\text{-}o}$ enhancement in In represents about the smallest value measurable by photoemission; therefore in Sb, where eqQ/h is reduced by a factor of 0.8 from its value in In, the enhancement should not be detectable.

We have used the analogy between the electric field gradient and the enhanced spin-orbit splitting as a diagnostic tool in the last few paragraphs. It should, however, be stressed that this analogy extends only to the similarity in the geometrical conditions which make both effects possible. We cannot expect that the actual matrix elements involved in the description of these quite different phenomena are equal. The nuclear quadrupole interaction deals with the field gradient at the nucleus of a neutral impurity atom. The increase in $\Delta E_{s\text{-}o}$ comes about through the interaction of d electrons in an ionized lattice atom with the surroundings.

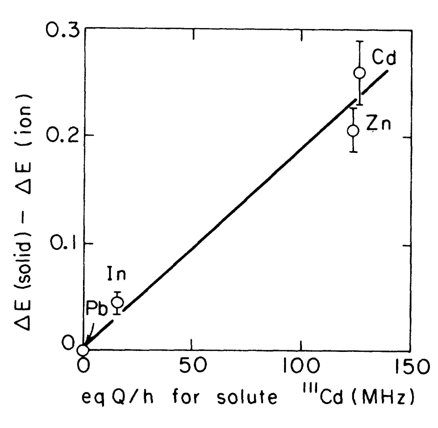

FIG. 3. Excess in apparent spin-orbit splitting $\Delta E_{s\text{-}o}$ versus the electrical quadrupole interaction strength eqQ/h of ^{111}Cd for a number of metals.

Before we turn to the valence bands, let us consider the case of the tellurium salts. The level scheme for a d^9 configuration in a tetrahedral environment is shown in Fig. 4 as a function of A_4^{tet}. The degeneracy of the $d_{5/2}$ state is partially lifted into a singly degenerate state Γ_8 (excluding spin degeneracy). The degeneracy of $d_{3/2}$ (Γ_8) is preserved.

For $A_4 < 0$ the apparent splitting between the upper Γ_8 level and the lower $\Gamma_7 - \Gamma_8$ doublet could increase significantly over $\frac{5}{2} | \xi |$ without altering the overall appearance of the spectrum greatly, provided that the natural width of the component lines is fairly large, as would be the case for the semiconductors discussed here.

For $A_4 > 0$ no such increase in the apparent spin-orbit splitting would be observed for small A_4 ($A_4 < 1$) but rather the evolution of three separate lines which finally ($A_4 > 1.5$) resolve into two lines with a reversed intensity ratio of 3: 2, in contrast to experimental observation.

The 3% increase in apparent $\Delta E_{s\text{-}o}$ for the tellurides is therefore compatible with a negative A_4 of the order of $\sim 0.5 | \xi |$, or ~ 0.75 eV. This is a magnitude entirely consistent with expectations for a Te ion surrounded tetrahedrally by four group-II ions in the II-VI compounds or by six Pb ions in the NaCl structure of PbTe. The sign of A_4 is compatible only with primarily electronic contributions to the crystal-field Hamiltonian, however.

Because of the absence of any enhancement of $\Delta E_{s\text{-}o}$ for the cations of these lattices and for the d levels of all other binary compounds in Table I ($|A_4| < 0.2 |\xi|$) we are reluctant to draw conclusions about possible enhancement of the apparent $\Delta E_{s\text{-}o}$ in the tellurides.

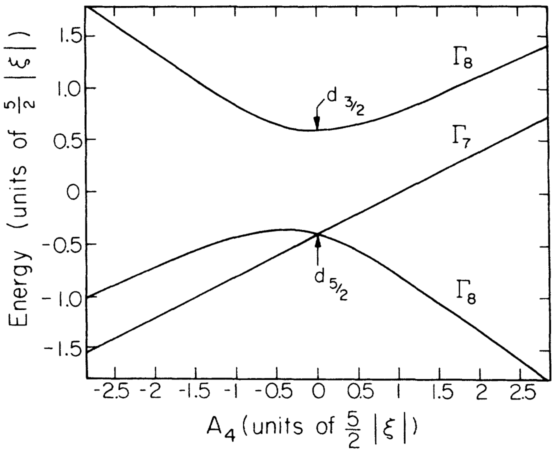

FIG. 4. Energies of a d^9 configuration in a crystal field of octahedral symmetry.

Let us return now to the splittings observed in the valence d shells of Ag and Au and the p shells in Pb and Bi. The interplay of spin-orbit and band effects in these metals is of course well known in band-structure theory.[17–19] It seems interesting, however, to seek an analogy between core- and valence-level cases. In doing so we must remember that valence levels can only be treated rigorously by taking into account their band character. Thus, level ordering at the Γ point ($\vec{k} = 0$) is not necessarily representative of the density of states $\rho(E)$ observed in the XPS spectrum, because the larger $\vec{k}$-space valence associated with the outer parts of the Brillouin zone (BZ) makes them dominant in determining $\rho(E)$.

The elements Ag, Au, and Pb crystallize in the fcc structure, while the Bi structure is slightly distorted from fcc. Thus the symmetries throughout the Brillouin zone are nearly the same for all four elements. The striking differences observed in the apparent $\Delta E_{s\text{-}o}$ between d bands (increase) and p bands (no increase) can be understood in terms of the symmetry-induced splitting at representative points of the BZ.[17–19] The d orbitals of Ag and Au are already split into two groups of bands, at Γ. Toward the outer parts of the BZ, these bands split further, accompanied by a rearrangement of levels according to the various irreducible representations at symmetry points of lower than cubic symmetry. The maximum splitting occurs at X, the center of the square face of the BZ. The pattern set by Γ and X may be regarded as roughly representative of the two-peaked structure in the density of states of Ag and Au, although the band structure is complicated by contributions from the rest of the BZ. The spin-orbit interaction enhances this splitting further without being the dominant factor.

The lower angular symmetry of the p valence electrons in Pb and Bi preserves their orbital degeneracy at Γ. Along the symmetry directions on the surface of the BZ this degeneracy is partially lifted, forming a singlet and a doublet level at each symmetry point except K. The energy dispersion of these bands along the surface of the BZ is in general smaller than their splitting, giving rise to a two-peaked density of states. In the presence of spin-orbit interaction the twofold-degenerate level at W splits. Inspection of the relativistic band structure of Pb by Loucks[17] reveals that this splitting is preserved over much of the surface of the BZ, giving rise to the observed doublet in the occupied part of $\rho(E)$. In the tight-binding approximation and in the absence of s-p hybridization the splitting at W equals the atomic splitting, in good agreement with experiment.

The similarity between the d band $\rho(E)$ in Cu, Ag, and Au and spin-orbit split core-level d-shell spectra makes a simplistic interpretation of the former in simple crystal-field terms. This would be unrealistic, however, as a simple example shows. The *d* bands of Au fall in the order Γ_8, Γ_7, Γ_8 at the center of the BZ. In terms of Fig. 4 this would suggest $A_4 > 0$. At X, however, there is a lower group of two bands (X_6 and X_7), and an upper group of three (X_7, X_6, X_7). Presumably this would require $A_4 < 0$ in Fig. 4. Another reversal occurs at W. These energy-level orderings can be rationalized, but a direct comparison with core-level spectra is not very useful.

ACKNOWLEDGMENT

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