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Electron Binding in Metals: Grey and White Tin*

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Core-electron binding-energy-shift data, obtained from photoelectron spectroscopy, are presented for β-Sn and α-Sn. These data and published results for the Mössbauer isomer shift and for internal conversion of ^{119}Sn in the β form have been analyzed in terms of free-atom valence-electron wave functions renormalized to the Wigner-Seitz radii characteristic of the two solids. The three sets of experimental data are readily accounted for in this analysis: β-Sn turns out to have 1.6 ± 0.3 $5s$ electrons; and the transition $\beta\text{-Sn} \rightarrow \alpha\text{-Sn}$ is associated with a surprisingly small change, $0.1e$ to $0.2e$, of valence-s to valence-p character. The concepts embodied in this analysis must be applied to the analysis of electron-binding-energy shifts observed in alloys and compounds, both insulating and metallic.

I. INTRODUCTION

Questions of differences in chemical binding among allotropic forms of an element are interesting; further, allotropy may be considered as a case of alloying in which there is no charge flow into or out of the atomic cell. The new experiments described in this paper were undertaken to see what could be determined about binding differences between grey (α) and white (β) tin from core-level shifts measured by photoelectron spectroscopy and from the combination of such results with Mössbauer isomer shifts and with results of subshell internal-conversion measurements made with ^{119}Sn.

These data have been analyzed in terms of a scheme incorporating screened valence-core Coulomb-interaction parameters obtained within the renormalized-atom approximation.[1] In order to make this analysis it is necessary to take into account the fact that level energies measured by photoelectron spectroscopy are determined in reference to the Fermi level. Experimental work functions[2] and the theory of Lang and Kohn[3] are used to derive the corrections required for comparison of the experimental results with energies calculated in reference to the zero of the potential in the crystal.

II. EXPERIMENT

A Varian IEE-15 photoelectron spectrometer with a Mg x-ray anode, $K\alpha_{1,2}$ energy 1253.6 eV, was used in these experiments. Samples were 99.9%-pure 0.005-in. tin foil wrapped around 1-cm diameter Al cylinders about 2-cm long. The spectrometer is furnished with a forechamber, isolable from the main vacuum volume, which was used for cleaning sample surfaces by glow-discharge ion sputtering in an atmosphere of 85% Ar–15% H_2 at about 2×10^{-2} Torr. A negative potential, 2000 V, was applied to the tin samples, and a silica-glass sleeve was used as a cover for other negative conductors to avoid contamination of the sample by material which would otherwise be sputtered from them. Condition of the tin surface was gauged by monitoring the O-1s and C-1s contaminant lines in addition to the Sn-$3d$ lines; the $3d$ lines from the samples after cleaning showed showed no evidence of oxide contaminant.

Conversion from β (tetragonal) tin to the α (diamond structure) form and vice versa were effected by control of the specimen temperature in the spectrometer. Measurements on the normal β form were done without sample cooling; under these conditions the sample foil temperature is about 40 °C. Below 13.2 °C the low-temperature allotrope is stable[4]; however, efforts to produce the α-tin in bulk by simple refrigeration of a rod of β-tin metal were not successful, apparently because of the large volume increase accompanying the transformation. When samples in the spectrometer were maintained at − 10 °C for several hours, a shift was observed in the position of the $3d$ lines. This shift was reproducible, was independent of cooling time beyond a minimum, and was independent as well of duration of the spectrum scan. Long scanning times did result in line shift towards the position for β-tin because of heating due to design limitations in the heat-transfer arrangement. A further characteristic of this line shift produced by cooling the tin is that it is completely reversible; the $3d$ lines were shifted back and forth between the "low"- and "high"-temperature positions at will. No such shift was observed when the same measurements were made with a gold-foil sample substituted for the tin. It was concluded that the temperature lowering produced a conversion on the foil surface from the β to the α form. That such a surface change can occur much more readily than a change in the bulk is reasonable in view of the large volume difference between the two crystalline modifications. Indeed, the transformation has been observed to propagate from nuclei at the

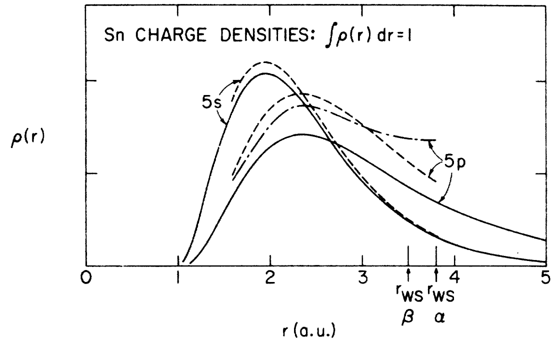

FIG. 1. Outer regions of the radial charge densities for the $5s^2\,5p^2$ configuration of Sn from a relativistic Hartree-Fock-Slater calculation; solid curves are for the free atom and the dashed curves represent renormalization to the Wigner-Seitz cell of α-Sn. The non-s conduction-electron component is expected to deviate from the renormalized $5p$ density, as indicated schematically by the dot-dash curve.

surface,[4] and since only a very small depth of a solid is sampled by x-ray photoelectron spectroscopy,[5] a very thin layer of α-tin on the surface would produce saturation of the α signal with essentially no β signal.

Except for the binding-energy shift, spectra from α- and β-tin are much the same. For both allotropes, the well-separated components of the $3d$ doublet are accompanied by plasmon-loss peaks, 14 eV lower in energy than the no-loss peak and about 1/6 as intense.[6] A similar plasmon peak was observed to accompany the unresolved $4d$ lines from white tin; this region was not studied in the case of grey tin. Between the two tin forms there does appear to be some difference, perhaps 15%, in the intensity of the plasmon peak relative to its parent.

Grey tin is a semiconductor[4] having a resistivity 5×10^{-4} Ω-cm at 0 °C. With such a material, shift of photoelectron line position due to electrostatic charging should be unobservably small; it was verified that the sample surfaces of both the α and β forms were indeed in good electrical contact with the support cyclinder. This was done by measurement of the spectra from both samples with and without application of a known bias voltage to the sample support cylinder.[7] Spectra from which the final results were obtained (Table I) were analyzed by computer fitting of Gaussian line shapes to the background-subtracted data; the background functions were obtained as least-squares fits of polynomials to regions between and on both sides of the peaks. Results from additional measurements, not included in the table, which were analyzed by hand from recorder plots, are in excellent agreement with the data in Table I.

III. WAVE–FUNCTION CHARACTER

The relative roles of s and of non-s character in the valence bands of α- and β-Sn will be of primary concern in the sections which follow. In "simple" metals it is frequently useful to describe the valence electrons either as plane waves of the form

$$\psi_k(r)=(1/V)^{1/2}e^{i\vec{k}\cdot\vec{r}}\ ,$$

where V is the volume of the Wigner-Seitz cell, or, alternatively, as such plane waves orthogonalized to the ion core. These descriptions do not appear to be useful here, as may be seen from the wave-function behavior shown in Fig. 1. Plotted in the figure are the $5s$ and $5p$ radial densities obtained from a free-atom relativistic Hartree-Fock-Slater calculation for Sn in the $5s^2\,5p^2$ configuration. Also indicated are the Wigner-Seitz radii, r_{WS}, appropriate to α- and β-tin. For α-Sn only 6% of the $5s$ charge lies outside r_{WS}; for β-Sn it is 9%. Approximately 31% and 38% of the $5p$ charge resides outside the W-S radii of α- and β-Sn, respectively; therefore, a total charge of 0.7–$0.9e$ is brought inside the atomic volume on formation of the solids from free atoms. Charge compression of this magnitude is characteristic of most metals: what is important in the case of Sn is that the $5s$ electrons are relatively unaffected by the condensation. The compressed charge introduces substantial screening at radii greater than that of the $5s$ maximum radial density. This implies that the $5s$ character in the solid is much like that in the free atom. It is appropriate, therefore, to use renormalized-atom wave functions[1] to describe the $5s$ functions in the solids:

$$\begin{aligned}\psi_{\mathrm{solid}}(r)&=N\psi_{\mathrm{free\ atom}}(r), & r&<r_{\mathrm{WS}}\\ &=0, & r&>r_{\mathrm{WS}}\ .\end{aligned}$$

The renormalization factors N deviate only slightly from unity; they are $\sqrt{1.06}$ and $\sqrt{1.09}$ for α- and β-Sn, respectively. The $5p$ functions used in this work are also truncated and renormalized; such renormalized functions are included in Fig. 1. In the $5p$ case the procedure is less appropriate than for $5s$, because the screening arising from compression causes a distortion of the average $5p$ behavior as illustrated schematically in the figure.

Internal-conversion and Mössbauer isomer-shift data, which involve the s density at the nucleus, will be treated in later sections. The nearly atomic character of the $5s$ shell allows a simple interpretation in terms of an s-like function whose contact density is only slightly greater, 6% or 9%, than that characteristic of the free atom.

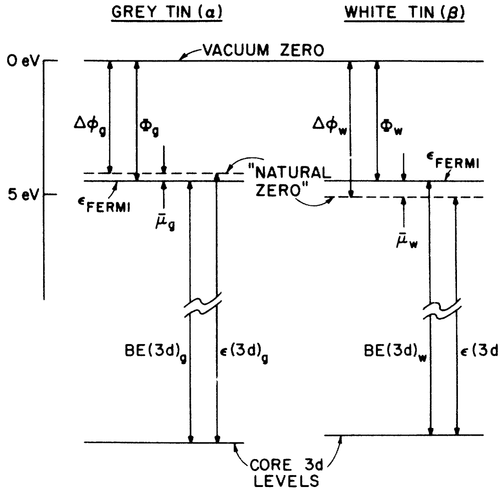

FIG. 2. Diagram of the energy levels in grey and white tin with respect to the vacuum zero. Level positions are indicated semiquantitatively; definitions are given in the text.

IV. INTERPRETATION

A. Internal Conversion

The relative intensities of internal-conversion electron lines associated with magnetic dipole nuclear transitions provide a direct measure of the relative electron-nuclear contact densities of the several s shells of the atom in question.[8] Internal-conversion experiments for β-Sn have been reported,[9] yielding $\rho_{5s}(0)/\rho_{4s}(0) = 0.108 \pm 0.004$. However, this ratio is obtained experimentally from the relative areas of two overlapping peaks, and recent experience[10] with such lines suggests that the ratio may more properly be

$$\rho_{5s}(0)/\rho_{4s}(0) \simeq 0.095 \ .$$

Relativistic calculations for Sn $5s^2 5p^2$ yield a free-atom ratio

$$|\psi_{5s}(0)|^2/|\psi_{4s}(0)|^2 = 0.110 \pm 0.015 \ .$$

This ratio is the average of results from two computational schemes[11] and the uncertainty ±0.015 represents the extremes. If the 5s function is renormalized to correspond to β-tin in the configuration $5s^2 5p^2$,

$$[\,|\psi_{5s}(0)|^2/|\psi_{4s}(0)|^2]_{\text{ren. atom}} = 0.12 \pm 0.02 \ .$$

Comparison of this ratio with experimental density ratio, 0.095, indicates that β-tin has a contact density equivalent to 1.6±0.3 renormalized 5s electrons in the valence bands. This value supports a choice of the approximate configuration $5s^2 5p^2$ for the atom in β-tin. Flinn[12] has assigned the configuration $5s^{1.4} 5p^{2.6}$ to β-Sn on the basis of isomer-shift data. The agreement between this and the internal-conversion result is somewhat fortuitous, as will be seen later in this paper.

B. Photoelectron Spectroscopy

The data presented in Sec. II are values of the binding energy (BE) of a 3d core level with respect to the Fermi level ϵ_F. This is the case because the Fermi level of a conducting sample is brought to the Fermi level of the measuring apparatus. In Fig. 2 the level schemes of isolated α- and β-Sn samples are indicated schematically. Each Fermi level lies at a distance equal to the work function, Φ, below the vacuum zero and the core level lies at the experimentally determined distance, BE, further below. Φ is made up of two components[3]: $\bar{\mu}$ is the position of ϵ_F with respect to the zero of the potential within the crystal; and $\Delta\phi$ is the distance between the zero within the crystal and the vacuum. This latter quantity, a "barrier potential," is due to the induced polarization at the surface of the crystal. The position of the 3d core, as influenced by its Coulomb interaction with the valence-electron environment, is normally calculated with respect to a "natural zero," i.e., ϵ_F as well as the core undergoes chemical shift. Thus, the Coulomb shift sampled by the core is not simply the change in BE but instead

$$\Delta\epsilon(3d) = \Delta(\text{BE}) + \Delta\Phi - \Delta(\Delta\phi) = \Delta(\text{BE}) + \Delta\bar{\mu} \ . \quad (1)$$

Estimates of $\Delta\bar{\mu}$ in addition to the BE values observed in photoemission are therefore required for a precise assessment of the core chemical shift.

Up to this point we have not discussed in detail the meaning of a *measured* core-level binding energy BE. In calculations of the position of a core level or shift it is convenient to deal with the Hartree-Fock one-electron energy. In general, however, the photoemission peak position does not furnish a direct measure of this quantity; Meldner and Perez[13] and others have shown that, due to relaxation effects, it is the center of gravity of the line and its satellites which corresponds to the one-electron energy. This correspondence is exact providing that the initial state is describable as a single-determinant function. Inasmuch as there are no appreciable differences in the shapes of the 3d spectra of the two tin forms, it is presumed that a *shift* in peak position is an accurate measure of the *shift* in center of gravity. Therefore, the observed BE values are appropriate for Eq. (1).

One might employ *a priori* calculations to estimate the $\bar{\mu}$ of Eq. (1). Here, instead, experimental Φ and the calculated $\Delta\phi$ values of Lang and Kohn[3] will be used. Numerical uncertainties resulting from either approach are substantial on the scale of accuracy desirable. Fomenko and

Samsanov[2] tabulate essentially identical experimental photoemission Φ values of 4.51 and 4.50 eV for α- and β-Sn, respectively. (The value for α-Sn is the only one available in the literature and must be viewed as somewhat questionable.) Lang and Kohn[3] have tabulated computed $\Delta\phi$ values as a function of conduction-electron density. For the change in atomic volume on going from α- to β-Sn, their tabulation yields $\Delta(\Delta\phi) \equiv \Delta\phi\alpha - \Delta\phi\beta = -0.95$ eV. This difference should be more reliable than the absolute $\Delta\phi$ values, which have been employed in Fig. 2. From Eq. (1) and the foregoing $\Delta(\Delta\phi)$ and Δ(BE) values, one obtains

$$\Delta\epsilon(3d) = 1.25 \text{ eV} ,$$

the core level in α-Sn being the more tightly bound. As is often the case, $\Delta\bar{\mu}$, 0.95 eV, is larger than Δ(BE).

Although the Wigner-Seitz cell surrounding a Sn atom is electrically neutral, the spherical Coulomb interactions of the $3d$ shell with the valence electrons are different in α- and β-tin due to the difference in cell volume and in valence wave-function character inside the cell. One may write

$$\Delta\epsilon(3d) = \int \rho_{3d}(\vec{r}_1)\, \Delta\left(\int^{\text{W-S cell}} \rho_{\text{val}}(\vec{r}_2) \frac{1}{r_>}\, d\tau_2\right) d\tau_1 , \tag{2}$$

where ρ_{3d} and ρ_{val} are the densities of a $3d$ electron and of all the valence electrons, respectively. If the valence electrons are of s and p character, this may be rewritten

$$\Delta\epsilon(3d) = \Delta[n_s F^0(3d, s) + n_p F^0(3d, p)] , \tag{3}$$

where n_s and n_p are the respective valence-electron counts and the F^0 is a Slater integral:

$$F^0(3d, \text{val}) \equiv \int r_1^2\, dr_1 P_{3d}^2(r_1) \int r_2^2\, dr_2 \frac{1}{r_>} P_{\text{val}}^2(r_2) . \tag{4}$$

Here P_{3d} is the radial core function and P_{val} is the average radial function appropriate to the s or the p character. Atomic P_l, truncated at the Wigner-Seitz radius, r_{WS}, and renormalized inside were used in evaluating F^0 integrals. Equation (3) accounts for change in s or p count ($\Delta n_s = -\Delta n_p$ since the site remains uncharged) and for any change in valence wave-function character associated with the changing atomic volume. A part of this induced change in valence wave-function character results from screening associated with changing s,p count. Errors of as much as a factor of 2 can accrue if such screening effects are not considered.

TABLE I. Experimental binding energies and widths of the $3d$ lines of grey (α) and white (β) tin.

Allotrope		Binding energy[a] (eV)		Width (eV)	
		$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$
α		493.32 (1)[b,c]	484.88 (1)	1.39 (2)	1.48 (1)
		493.29 (1)	484.87 (1)	1.38 (2)	1.48 (1)
	Av[d]	493.31 (1)	484.88 (1)	1.38 (2)	1.48 (1)
β		492.99 (1)	484.56 (1)	1.41 (2)	1.51 (1)
		493.00 (1)	484.57 (1)	1.38 (2)	1.51 (1)
	Av	492.99 (1)	484.56 (1)	1.39 (2)	1.51 (1)
Measurements with bias of 7.816 V					
α		501.11 (1)	492.69 (1)	1.38 (2)	1.48 (1)
	Bias shift[d] (eV)	7.81 (1)	7.82 (1)		
β		500.81 (1)	492.38 (1)	1.39 (1)	1.51 (1)
	Bias shift	7.82 (1)	7.82 (1)		

[a] On this binding energy scale the Au $4f$ lines are located at 87.37 (1) and 83.69 (1) eV relative to the Fermi level.

[b] The figure in parentheses is the standard deviation in the last digit of the computed value. It was obtained from the variance-covariance matrix of the least-squares fit to the Gaussian line shape to the experimental data.

[c] Each row of figures represents data from a single experiment.

[d] Averages and bias shifts were computed from the data before roundoff.

TABLE II. Comparison of chemical level-energy shifts calculated from theory with the value inferred from experiment.

Configuration			
α-Sn	β-Sn	$\Delta\epsilon_{\text{theo}}$ (eV)	$\Delta\epsilon_{\text{expt}}$ (eV)
s^2p^2	s^2p^2	1.1	1.25
sp^3	sp^3	1.2	
sp^3	s^2p^2	2.8_5	
$s^{1.9}p^{2.1}$	s^2p^2	1.2_5[a]	

[a] Interpolated value.

It has been shown that β-Sn is approximately described by a $5s^2\,5p^2$ configuration. Grey (α)-Sn has a 27% larger Wigner-Seitz cell and is often thought to have a larger p count, tending toward the sp^3 tetrahedral bonding configuration. Equation (3) may be evaluated, given the respective s and p counts and the r_{WS} values. A set of these calculations is given in Table II. Because the valence electrons are more diffuse in the larger lattice of α-Sn than they are in β-Sn, the core electrons are more tightly bound. The removal of s and addition of p charge affects the spatial behavior of remaining valence electrons, modifying their Coulomb interaction with the core. This screening is included in the 2.85-eV value quoted in the table. Comparison of these $\Delta\epsilon(3d)$ values with the experimentally based value of 1.25 eV suggests immediately that there is little change in s count; and the interpolation between the values 1.1 and 2.85 gives the result

$$\Delta n_s(\beta \rightarrow \alpha) = -\Delta n_p \simeq -0.1 ,$$

a quantity much smaller than that which has been inferred from chemical arguments. Uncertainties in the various quantities and assumptions required to arrive at this Δn_s estimate combine to produce a considerable uncertainty in it. Nevertheless, as will be seen in the following sections, the estimate agrees with the Δn_s value deduced from the Mössbauer isomer-shift data.

C. Mössbauer Isomer Shifts

For Sn in chemically different forms, the isomer shift I_S of the ^{119}Sn Mössbauer spectrum, expressed in terms of the change in contact density, is

$$I_S(\text{mm/sec}) = 0.096\ \Delta\rho(0)\,(\text{a.u.}^{-3})\ , \qquad (5)$$

where the constant includes the nuclear parameter values.[9,14,15] Among these nuclear parameters, the value $(1.8\pm0.4)\times10^{-4}$ chosen for $\delta R/R$, the fractional change in nuclear radius on excitation, is from two separate experimental determinations which gave essentially identical results: one based on a comparison of internal-conversion and isomer-shift data[9] and a second on comparison of isomer-shift and Knight-shift data.[15] These schemes avoid ambiguities, to be discussed later, which can result from the use of assumptions about the electron configurations of tin compounds to obtain the Mössbauer calibration constant. The measured isomer shift on going from α- to β-tin[16] is 0.62–0.65 mm/sec, with α-Sn exhibiting the smaller contact density, $\rho(0)$, as might be expected on the bases both of its larger atomic volume and of its presumably somewhat smaller valence s count.

In order to separate the volume effect from s count change one requires a measure of the isomer shift corresponding to a unit change in the valence s electron count, all else remaining fixed. Mann's Fock-Dirac free-atom calculation for $5s^25p^2$ Sn yields[17,18] $\rho(0)=33$ a.u.$^{-3}$ for a single $5s$ electron. In terms of such a wave function, the observed α-Sn → β-Sn isomer shift is equivalent to an increase of 0.2 in the $5s$ electron count.

Volume effects may be described in terms of renormalized free-atom $5s$ functions. With the neglect of effects of volume-induced changes in $5p$ screening, such $5s$ functions yield a ρ_{5s} value for α-Sn only 2% less than that for β-Sn, because of the strongly atomic character of the $5s$ shell as shown in Fig. 1. Furthermore, the calculations used to obtain the Table II results indicate that the screening changes accompanying s-p interconversion have little effect on $5s$ contact densities. This fact, together with the small influence of volume change on $\rho_{5s}(0)$, leads to the conclusion that the observed isomer shift β-Sn → α-Sn must be associated with a decrease in renormalized $5s$ electron count

$$\Delta n_s(\beta\rightarrow\alpha)\simeq -0.2\ ,$$

or perhaps a little smaller in absolute magnitude. This result is to be directly compared with the value based on binding energy shift, $\Delta n_s = -0.1$. In view of the uncertainties in both estimates, the agreement is striking.

In an alternative approach, volume effects have been described in terms of plane-wave valence-band states of the type discussed in Sec. III, for which the contact density is inversely proportional to the atomic volume in the solid. This approach is somewhat improved if the plane waves are orthogonalized to the ion cores, in effect excluding a small core volume ν to give the relation

$$\rho^{\alpha}_{\text{val}}(0)/\rho^{\beta}_{\text{val}}(0) = (V_\beta-\nu)/(V_\alpha-\nu)\ , \qquad (6)$$

where ν is of the order of 10% of V, the atomic volume. The 27% increase in volume in the transition from β-Sn to α-Sn would then produce a 23% decrease in valence-electron contact density. Given the effective valence s count for β-Sn inferred from the internal-conversion results, 1.6 ± 0.3, this density decrease by itself would correspond to an isomer shift of about 1.2 mm/sec, or twice that observed. Inglesfield[19] has used the volume-normalized plane-wave approach with pseudopotential-band-structure terms, which reduce the simple orthogonalized-plane-wave (OPW) $\rho(0)$ difference by roughly two-thirds; the result is a value somewhat smaller than but in approximate agreement with the β-Sn → α-Sn isomer-shift experiment. If Inglesfield's $\rho(0)$ difference is interpreted, in the sense of Fig. 1, as a change in localized $5s$ electron count attendant to the volume and chemical changes in the β-Sn → α-Sn transition, it corresponds to $\Delta n_s \sim -0.1$, consistent with the photoemission and isomer-shift Δn_s values inferred here and with the widely held view[20] that α-Sn has a smaller $5s$ count than β-Sn.

V. CONCLUSION

X-ray photoemission results have been obtained and these, taken with internal-conversion and isomer-shift data, have been used to compare the electronic structures of α- and β-tin. The difference between the members of this pair is of interest per se, but, in addition, the difference is a prototype for an isolated part of the "chemical" effect which must be accounted for in the more complicated cases of alloying and compound formation.

A simple experimentally consistent picture of α- and β-Sn comes from the analysis. White (β) Sn, on the basis of the internal-conversion results, is found, in agreement with expectation,[21] to be approximated by a $5s^{1.6\pm0.3}5p^{2.4\mp0.3}$ description, in which the $5s$ charge is defined in terms of a free-atom $5s$ distribution renormalized to the Wigner-Seitz cell volume. The very nearly atomic character of such a $5s$ function makes this definition plausible and useful. A renormalized $5p$ function has been taken for the non-s component of the conduction electrons. This choice, although not accurate as suggested in Fig. 1, only slightly influences the results. Independently, the isomer-shift and the photoemission results indicate an s electron count decrease of no more than 0.1–0.2 in the transition from β-Sn (white) to α-Sn (grey). This decrease is much smaller than that which would obtain if tetrahedral grey tin were in the $5s\,5p^3$ configuration.

There exists, of course, a large body of experimental and theoretical research on α- and β-Sn.[22] Attention has centered on Fermi surfaces and on the valence bands and their derivatives $(\delta\epsilon/\delta k)$ at high-symmetry points. Wave-function symmetry and the associated spin-orbit coupling at these points is important, but overall s and p counts, which involve the total wave-function character in the occupied bands, have not as yet been considered. With the exception of Inglesfield's work,[19] these studies, therefore, neither support nor disagree with the present results, which indicate a small value for Δn_s and an α-Sn configuration measurably different from sp^3. Inglesfield's pseudopotential estimates of $\rho(0)$ can be translated into a count of renormalized $5s$ electrons given an appropriate atomic $5s$ function. Inglesfield calibrated his results in terms of nonrelativistic Hartree-Fock-Slater free-atom functions; with these functions, his $\rho(0)$ values correspond to n_s values of 1.2 and 1.3 for α- and β-Sn, respectively. Although these $5s$ counts are slightly smaller than those obtained here, the two sets of values are in reasonable accord in view of the uncertainties. It is satisfying that Inglesfield's $\rho(0)$ estimates and the analysis of the experiments reported here agree in providing n_s values for the two tin forms which differ by 0.1–0.2 electrons with β-tin having the larger count. Contact can be made also with the earlier isomer-shift analyses.[16] Lacking an experimental estimate of $\delta R/R$, a factor in the constant of Eq. (5), the earlier investigators estimated $\delta R/R$ in effect by assuming specific $5s^n 5p^m$ assignments for several Sn species; one assignment invariably used was α-Sn with the configuration $5s\,5p^3$. This was a sensible and plausible choice at the time, but it led to an apparently incorrect constant, almost a factor of 2 smaller than that of Eq. (5). Flinn[12] used this constant and the α-Sn assignment to obtain his $5s^{1.4}5p^{2.6}$ description of β-Sn, which happens to fall close to our count.

The newer value for $\delta R/R$ has implications in general for conclusions based on the isomer shift about the chemistry of other Sn compounds. Lees and Flinn[16] assumed the pure Sn^{4+} $5s^0 5p^0$ configuration for Sn in K_2SnF_6. However, from Eq. (5), the s electron count here inferred for β-Sn and the observed β-Sn–K_2SnF_6 isomer shift[16] one concludes that Sn in K_2SnF_6 has a contact density equivalent to approximately one-half a $5s$ electron.[23] By hindsight, nonzero valence s character is not surprising, even in this compound.

The phenomena described here clearly occur in alloying and compound formation, which are further complicated by charge flow into or out of the atomic sites. Fermi-level shifts, $\Delta\overline{\mu}$ of Eq. (1), can be of magnitude similar to binding energy shifts, both for metals and insulators, and must be reckoned with. Finally, valence-electron screening effects must be taken into account in any accurate estimate of Coulomb shifts.

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