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CHEMICAL SHIFTS OF THE K_{α_1} X-RAY LINE IN COMPOUNDS OF TIN AND GROUP VI ELEMENTS

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This work was undertaken to elucidate further the chemical-shift mechanism of inner levels in heavy elements,[4,5] and to demonstrate the significance of the effect for chemical investigations. For this purpose the energy changes of the K_{α_1} x-ray line (relative to white and gray tin) was investigated in divalent and tetravalent compounds containing elements of the oxygen group (SnO, SnS, SnSe, SnTe, SnO_2, SnS_2, and $SnSe_2$). The shift of the tellurium K_{α_1} line in SnTe and the shift of the selenium K_{α_1} line in SnSe and SnS_2 were also measured. The theoretically predicted proportionality between the magnitude of the shift and the ionicity of the bond is confirmed. It is shown that whereas the experimentally measured factor, which depends on the valency and on the wave functions of the valence electrons and carries information regarding the structure of the chemical bond, is practically constant for compounds of a given valency containing analogous elements, its sign and magnitude change in compounds containing valence electrons of a different type.

INTRODUCTION

THE x-ray shifts which depend on the chemical state of the emitting atoms (the so-called chemical shifts of x-ray lines) have been used in recent years as an additional method of studying the structure of the chemical bond.[1-3] The discovery of an analogous effect for the emission of x-ray lines representing transitions between inner (K and L) levels of relatively heavy ($34 \leq Z \leq 74$) atoms[4,5] and the development of an experimental technique for measuring this effect quite accurately[6] inspire the hope that this method may be extended to all or almost all elements and many compounds.[5] However, before this possibility can be firmly established more detailed information is needed regarding the mechanism of the shift in heavy atoms, along with direct experimental proof of the relation between the shift and the chemical-bond structure and chemical parameters.

The most likely mechanism accounting for the chemical shifts of inner levels in heavy atoms is the so-called internal screening.[1,5] Here a valence electron is, during a fraction P of the total time, closer to the nucleus than to the inner K or L electron; the valence electron compensates, or is said to screen, a portion of the nuclear charge that acts on inner electrons. If $\Delta E_{Z,Z-1}$ is the energy difference between the (K or L) levels of two elements having nuclear charges Z and Z-1 (which is obviously the energy shift when the nuclear charge is reduced by one unit), the energy reduction that results from screening a fraction P of a unit charge will be given by

$$\Delta E = P\Delta E_{Z,\,Z-1}, \tag{1}$$

where P can be expressed simply, for s electrons at least, in terms of the radial wave functions R_{ns} for the inner and $R_{n's}$ for the valence electron:[7]

$$P = \int_0^\infty R_{ns}{}^2(r_1)\left[\int_0^{r_1} R^2_{n's}(r)\,dr\right]dr_1.$$

Equation (1) obviously gives the inner-level shift when one valence electron is removed entirely. This is the case of a monovalent chemical compound with 100% ionicity of the bond compared with analogous compounds having purely covalent bonds. In a real compound of valence m, the same number m of electrons can participate in forming a bond of ionicity i. The level shift will then be given by

$$\Delta E = imP\Delta E_{Z,\,Z-1}, \tag{2}$$

and the shift of the emission line corresponding to a transition between L and K levels will be

$$\Delta E_{K_{\alpha_1}} = \Delta E_K - \Delta E_L = im\{P_K\Delta E_{K;\,Z,\,Z-1} - P_L\Delta E_{L;\,Z,\,Z-1}\}. \tag{3}$$

This last expression is, of course, a rather rough estimate.[5] We may assume that a realistic expression for the shift will have the form

$$\Delta E_{K_{\alpha_1}} = im\{C\}, \tag{4}$$

where the factor in curly brackets is analogous to the bracketed factor in (3) and thus depends on the wave functions of the valence electrons that are involved in forming the chemical bond.

The factors P and C, which are determined by overlapping of the wave functions for the valence and inner (K or L) electrons, will obviously depend strongly on the valence electron type (s, p, d, or f electron). In the general case $\{C\}$ of Eq. (4) may therefore be expressed by

$$\{C\} = \sum_l m_l C_l, \qquad \sum_l m_l = m, \tag{4'}$$

where m is the total number of electrons of the given atom that participate in forming a hybridized chemical bond (the valence of the atom); m_l is the number of electrons of the indicated symmetry that participate in bond formation; C_l corresponds to the factor inside the brackets of Eq. (3), and is therefore the change in K_{α_1} line energy when one valence electron having l symmetry is removed completely.

The realization of Eq. (4) would obviously permit very interesting chemical applications of the shift, since the summation in the right-hand member of (4′) essentially represents the structure of the chemical bond. However, it is not obvious that this equation applies to the considered shift of inner levels in relatively heavy atoms. Moreover, one could mention phenomena that would in principle also lead to a chemical shift and would therefore distort or obscure the internal screening effect. Among such phenomena are multiple ionization of an atom through photoabsorption[8] and the direct (not through valence electrons, as in the internal screening mechanism) interaction of inner-shell electrons in the atoms forming the chemical compound (the band effect). The present work was undertaken to test Eq. (4) experimentally.

EXPERIMENT AND RESULTS

The first investigated objects were tetravalent compounds of tin and analogous elements of the oxygen group—SnO_2, SnS_2, and $SnSe_2$, where the shift of the tin K_{α_1} line was measured relative to that line of gray tin regarded as a pure covalent tetravalent compound of tin. It was to be expected that the similarity of the analogous elements would prevent changes in the valence structure of the tin atom [$\Sigma m_l C_l$ in Eq. (4′)] in the compounds, and that only the ionicity of the bond would be altered.

The experimental apparatus and technique remained the same as in our earlier investigations; the samples to be compared were introduced alternately into the field of view of a two-meter Cauchois spectrometer with compensated aperture aberration.[5,6] A complication arose only in working with gray tin samples, which were transformed into white tin quite rapidly as a result of warming and irradiation during exposure. This transformation could be prevented only by cooling the samples in the vapor of boiling nitrogen during the measurements; the temperature was then maintained within the range (−5°)−(−3°)C. Because of the additional difficulties accompanying this procedure, all our measurements were taken relative to white tin. The results were corrected after the shift between white and grey tin was measured separately.

Table I gives the results obtained in separate series of shift measurements for βSn − $SnSe_2$. Four sources were compared at the same time—βSn, $SnSe_2$, βSn′, and $SnSe_2'$. The error indicated for the mean is the external rms error, calculated on the basis of the deviations from the mean of the results obtained in the separate series.

Table II gives the values finally obtained for the measured chemical shifts. In order to determine the influence of the valency change [the factor m in Eq. (4)], we obtained measurements for divalent compounds of tin and elements of the oxygen group—SnO, SnS, SnSe, and SnTe; the corresponding results are included in Table II.

Table I. Chemical shifts of the $K\alpha_1$ line of tin in $ShSe_2$ relative to βSn

No. of series	ΔE, 10^{-3} eV					
	$SnSe_2$ — β-Sn	$SnSe_2$ — β-Sn′	$SnSe_2'$ — β-Sn′	$SnSe_2'$ — β-Sn	β-Sn′ — β-Sn	$SnSe'_2$ — $SnSe_2$
	I	II	III	IV	V	VI
1	66±24	96±25	112±26	82±28	—30±16	15±25
2	81±30	66±25	56±24	70±25	14±20	—10±38
3	44±29	51±20	135±19	127±23	—8±20	81±28
4	63±29	53±30	41±32	50±28	10±20	—13±48
5	38±13	41±25	25±26	24±26	—1±22	—15±25
6	113±25	109±28	96±25	102±26	6±20	—12±27
7	104±20	76±16	32±19	62±18	30±16	—43±20
8	29±23	38±30	70±36	60±32	—9±24	30±28
9	82±30	31±33	91±27	143±32	52±20	61±36
10	107±25	84±25	118±32	142±31	24±15	34±38
Average	73±9	68±8	78±12	86±13	9±7	13±12

$$\overline{\Delta E}_{\text{I, III}} = 76\pm8;\quad \overline{\Delta E}_{\text{II, IV}} = 75\pm8;\quad \overline{\overline{\Delta E}} = 76\pm8$$

Table II.

Compound		$E_{K_{\alpha_1}}(2) - E_{K_{\alpha_1}}(1)$, 10^{-3} eV	Compound		$E_{K_{\alpha_1}}(2) - E_{K_{\alpha_1}}(1)$, 10^{-3} eV
1	2		1	2	
β-Sn	SnO_2	167±5	β-Sn	SnO	71±6
»	SnS_2	112±6	»	SnS	76±10
»	$SnSe_2$	76±8	»	SnSe	42±5
Se	$SnSe_2$	—39±4	»	SnTe	66±6
»	SnSe	—40±5	»	α-Sn	—37±10
Te	SnTe	—22±6			

We have already discussed, in connection with Eq. (4), the cases of the complete and partial loss of an electron (or of a few electrons) in the formation of a chemical bond, i.e., the line shift for the electropositive member of the compound. The same relationship should obviously hold equally well when electrons are added, i.e., for x-ray line shifts of the electronegative members (relative to their covalent compounds). In this case a minus sign will precede the right-hand member of Eq. (4), so that the sign of the shift will be reversed if the sign of {C} remains unchanged. This effect was tested by measuring the K_{α_1} shift of selenium in SnSe and $SnSe_2$ relative to metallic selenium and the K_{α_1} shift of tellurium in SnTe relative to metallic tellurium; the results are also given in Table II.

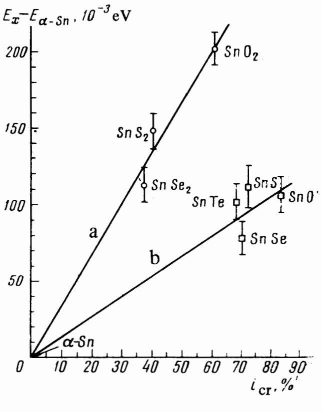

FIG. 1. K_{α_1} line shifts (relative to gray tin) in (a) tetravalent and (b) divalent compounds of tin and elements of the oxygen group versus ionicity (i). a – $m\{\overline{C}\} = 340 \pm 20$, $\{\overline{C}\} = 85 \pm 5$ MeV; (b) – $m\{\overline{C}\} = 138 \pm 10$, $\{\overline{C}\} = 69 \pm 5$ meV. [See Eqs. (3), (4), and (4′)].

DISCUSSION OF RESULTS AND CONCLUSIONS

Figure 1 shows the experimental K_{α_1} shifts (relative to gray tin) for the tetravalent and divalent compounds as a function of the ionicity of the bond, which is calculated from the Pauling formula[9]

$$i_{\text{mol}} = 1 - e^{-0,2(\Delta x)^2} \qquad (5)$$

(5)

(where Δx is the difference between the electronegativities of the members [10]) with a correction for crystalline structure that is also derived from the Pauling type of relation

$$(1 - i_{\text{cr.}}) = (1 - i_{\text{mol}}) m / n, \qquad (6)$$

where m is the valence, and n is the number of nearest neighbors in the crystal (the coordination number). We assumed n = 6 for all the studied tin compounds.1) Straight lines plotted through the experimental points and the zero point representing covalent αSn illustrate the fact that (4) is completely satisfied.

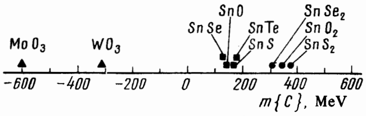

FIG. 2. Experimental values of $m\{C\}$ for divalent and tetravalent compounds of tin and elements of the oxygen group, and also for MoO$_3$ and W-WO$_3$.

The variation of the factor $\{C\}$ can account for the points that do not lie on one of the straight lines. Separate experimental values of $m\{C\} = \Delta E/i_{cr}$ are shown along the axis in Fig. 2. The measure of the scale used here becomes clear, i.e., we understand whether the close-lying experimental points are actually not far apart, when we consider how $m\{C\}$ varies when we go to elements and compounds that differ greatly from those studied here. For this purpose Eq. (4) was used to calculate the factors $m\{C\}$ from our earlier experimental data [5] on K_{α_1} shifts for Mo-MoO$_3$, W-WO$_3$, and the values of i_{cr} (m = 6, n = 6) calculated from (5) and (6);2) the resulting values of $m\{C\}$ were plotted in Fig. 2, where they are seen to differ greatly both in magnitude and sign from those in our present work.3)

The values of $m\{C\}$ for divalent tin compounds (m = 2, n = 6) are as closely grouped in Fig. 2 as those for tetravelent compounds. It is interesting that the values of $\{C\}$ are approximately constants for the two groups, with $\{\bar{C}\}_4/\{\bar{C}\}_2 = 1.2$. Tin atoms have s and p valence electrons; therefore the experimental values of $\{C\}$ are averages of C_s and C_p given by (4′): $\{\bar{C}\}_4 \approx \{\bar{C}\}_2 = \bar{C}_{sp} = +77 \pm 8$ MeV.4)

With regard to their valence electrons selenium and tellurium belong, like tin, to the (s, p) class of elements. We would therefore hardly expect any difference of sign for $\{C\}$ among these elements. On the other hand, selenium or tellurium has the role of the electronegative element when forming a compound with tin. We must therefore expect (from the foregoing discussion) a different sign of the K_{α_1} shift for selenium and tellurium (Se - SnSe$_2$, Se - SnSe, and Te - SnTe) than that of the K_{α_1} shift for tin in these same compounds; Table II shows that this actually occurs.

Summing up, we conclude that the chemical shifts of inner (K and L) levels in heavy elements are described entirely satisfactorily by the internal screening mechanism (4); other effects interfere very little. The given effect is directly related to the parameters characterizing the chemical bond. We can expect the shifts to provide a useful method of investigating the structure of the chemical bond.

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1) αSn, with n = 4, is an exception. The ionicity i_{cr} for αSn. calculated from (6), coincides with the expected (covalent) zero value.

2) For metallic molybdenum and tungsten i_{cr} was taken to be zero.

3) The sign of $\{C\}$ is reversed for Mo-MoO$_3$ and W-Wo$_3$ probably because d electrons participate in forming the bond.[1] The problem of the magnitudes and signs of contributions to the K_{α_1} shift coming from different valence electrons [C_s, C_p, C_d, and C_f in (4′)] merits detailed experimental investigation, which we hope to perform at some later date.

4) When we assume a definite model for the valence structure of the considered compounds, such as the model in which the valence structure of αSn is an s^1p^3 hybridized bond, that of tin in the tetravalent compounds is $s^{(1-i)}p^{3(1-i)}$, and that of the divalent compounds is $s^2p^{2(1-i)}$, then the experimental values of ΔE and Eqs. (4) and (4′) yield C_s and C_p separately. These are found to have the same sign and to have fairly close values: $C_s = +97$ Mev and $C_p = +81$ MeV.

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