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CHEMICAL SHIFTS OF THE K_{α_1} *X-RAY LINES IN COMPOUNDS CONTAINING ELEMENTS OF THE* Ag–Sb *SERIES*

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Changes in the energies of the K_{α_1} X-ray lines, observed when elements of the Ag–Sb series formed compounds with oxygen, were measured. The experimental values of the shifts ΔE were in good agreement with those calculated using the formula[6,7] $\Delta E = imC_{sp}$, where i is the degree of ionicity of the bonds,[8] m is the valence, C_{sp} is a constant which takes into account the contribution of the sp electrons (its value was obtained by analysis of the experimental data for the Sr–Mo series[7]). Thus, more extensive experimental data confirmed once again the validity of this simple relation. The results obtained also showed that in all the investigated compounds of the Ag–Sb series, the chemical binding was mainly due to the sp electrons (participation of the d electrons in the bonds had not been observed).

INTRODUCTION

INVESTIGATIONS of the dependence of the chemical shift of the K_{α_1} lines of the heavy $(30 \leq Z \leq 74)$ elements[1,2] on the parameters representing the chemical binding have established the quantitative validity of a very simple relationship[3-7]

$$\Delta E = i \sum_l m_l C_l, \tag{1}$$

where $\Delta E \equiv \Delta E_{comp} - E_{elem}$ is the measured difference between the K_{α_1} line energies of the investigated compound (usually oxide) and the element (metal); $i = 1 - (m/n)\exp(-0.25\,\Delta x^2)$ is the degree of ionicity according to Pauling;[8] $m = \sum_l m_l$ is the valence; m_l is the number of the l valence electrons (of the s-, p-, or d-type); n is the coordination number; Δx is the difference between the electronegativities of the elements in the compound;[9] C_l ($\overline{C}_{sp}$ and C_d) are the experimentally determined constants which are independent of, or weakly dependent on, the principal quantum number and, consequently, on the atomic number of the element Z. Thus, it has been found that the K_{α_1} shifts of divalent and tetravalent compounds of tin satisfy, within the limits of the experimental error (~10–20%), a linear dependence on i and are approximately additive in respect of m; the constants C_{5s} and C_{5p}, corresponding to the shifts in the case of the complete removal of one 5s or 5p valence electron are approximately equal:[6]

$$C_{5s} \approx +95\,\text{meV}, \; C_{5p} \approx +80\,\text{meV},$$

or, using a simpler model:

$$C_{5s} \approx C_{5p} \equiv \overline{C}_{5sp} = +77 \pm 8\ \text{meV}. \tag{2}$$

An investigation of the K_{α_1} metal–highest oxide shifts for the transition elements in the fifth period (Sr–Mo series) has confirmed the linearity of the dependence on i and the additivity of m; the experimental values of ΔE have been found to fit very well (to within $\lesssim 10\%$) a straight line:[7] $\Delta E = i[\overline{C}_{5sp} + (m-1)C_{4d}]$. It it worth stressing that the experiments on transition metals have yielded the following value of the constant $\overline{C}_{5sp}$:

$$\overline{C}_{5sp}(\text{Sr}-\text{Mo}) = +80 \pm 12\ \text{meV}, \tag{3}$$

which is practically identical with the value found in earlier experiments on tin compounds [cf. Eq. (2)]; the following value has been obtained for C_{4d}:

$$C_{4d}(\text{Sr}-\text{Mo}) = -120 \pm 4\ \text{meV}. \tag{4}$$

Analysis of the experimental data on the K_{α_1} shifts for transition metals in the sixth period (Ba–W series) gives similar dependences on i and m. Moreover, the following values are found for the constants $\overline{C}_{6sp}$ and C_{5d}:[7]

$$\begin{aligned} \overline{C}_{6sp}(\mathrm{Ba}-\mathrm{W}) &= +71 \pm 12\ \mathrm{meV}, \\ C_{5d}(\mathrm{Ba}-\mathrm{W}) &= -108 \pm 13\ \mathrm{meV}, \end{aligned} \tag{5}$$

so that, within the limits of the experimental error, the following equalities are satisfied:

$$\begin{aligned} &\overline{C}_{5sp}(\mathrm{Sn}) \approx \overline{C}_{5sp}(\mathrm{Sr}-\mathrm{Mo}) \approx \overline{C}_{6sp}(\mathrm{Ba}-\mathrm{W}), \\ &C_{4d}(\mathrm{Sr} \div \mathrm{Mo}) \approx C_{5d}(\mathrm{Ba}-\mathrm{W}), \end{aligned} \tag{6}$$

which indicate that the constants C_l are universal, i.e., they depend little on the atomic number of the element Z or on the principal quantum number of the valence electrons.

The validity of relationships of the Eq. (1) type is important because the sum on the right of this equation represents the distribution of the valence electrons over the available l sublevels, i.e., it effectively gives the valence configuration of the investigated chemical bond. The difference in the magnitude and sign of the constants C_{sp} and C_d is important because it makes it possible to distinguish easily sp and d electrons while applying a similar analysis to both. An example of the application of Eq. (1) in the determination of the valence configurations is given in[7]. Analysis of the experimental data on the K_{α_1} shifts, given in that paper, shows that the valence configurations of the transition metals (Sr—Mo and Ba—W series) are in good agreement with the theoretical predictions[10] although the theoretical results were not used in the analysis and the authors were not aware of the theory at the time.

However, the quantitative validity of relationships such as Eq. (1) [cf. Eqs. (1), (1′) and (1″) in[7]] is quite surprising. These relationships are based on the following assumptions: 1) the scale of the Pauling ionicities is assumed to be quantitatively valid (to within ± 10%) with corrections for the crystal structure; 2) the degree of ionicity of all electrons participating in the binding is taken to be constant irrespective of their l-type; 3) the additivity of m is assumed, i.e., it is postulated that the effect of the "pulling away" of n electrons of the given l-type is n times stronger than the "pulling away" of one such electron; 4) it is assumed that the shift depends solely on the valence configuration (i.e., on the distribution of electrons over the l sublevels) and is practically independent of the more detailed structure of the energy spectrum of the levels, which is determined, for example, by the characteristic features of the ligand field.

This list of assumptions can be easily extended, and it should be considered in conjunction with the constancy of the coefficients C_l, which has been referred to already.

Initially, our intention was to use relationships such as Eq. (1) only as the first rough approximation with a minimum number of parameters but we found that the experimental data fitted these relationships within a relatively very narrow range of experimental error. In principle, the reason for the great simplicity of these relationships may be the great depth of the investigated levels so that various secondary effects disappear or are weak, and the internal screening mechanism produces an effective compensation so that the K and L levels suffer changes in the valence shell[7] which are not only very coarse but also very important. Nevertheless, the suspicion remains whether all these results are perhaps accidental and, therefore, Eq. (1) should be checked using a much more extensive set of experimental data. This was the purpose of our investigation. We studied elements of the Ag—Sb series and their compounds (mainly oxides).

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental method was identical with that employed in our earlier investigations[2,6,7] and was based on the successive introduction of the samples being compared into the field of view of a Cauchois diffraction spectrometer with a compensated aperture aberration.[11]

The experimental results are presented in the table (column 5, rows 1—5). The differences between the K_{α_1} line energies of the compound and the metal ($E_{\mathrm{comp}} - E_{\mathrm{elem}}$) are given in the table. The lower part of the table (rows 8—17) contains the results for tin compounds taken from[6], as well as the recently published results of the American group led by Boehm,[12] who used our experimental method (these results are indicated by the superscript B in the third column). The shifts of the lines of the tin compounds were measured relative to metallic white tin and were then reduced to gray α-Sn using the experimentally determined difference $E_{\beta\mathrm{Sn}} - E_{\alpha\mathrm{Sn}}$[6] (cf. table). The experimental errors, indicated in the table, are the rms values of the random errors. However, the main source of error was obviously related to some indeterminacy of the structure modifications of the investigated samples, which were not checked, for example, by x-ray structure analysis but were simply prepared in accordance with the prescribed chemical methods. In all the cases, measures were taken to prepare a compound with a definite (one) crystal modification (which is given in the last column of the table) but sometimes the substances obtained using different methods gave appreciably different shifts. An example of such indeterminacy is the two results given in the table for Sb_2O_3; the same factor was evidently responsible for some discrepancy in the results for SnO.

The experimental values [divided by the degree of ionicity, cf. the table and Eq. (1)] are plotted in the figure as a function of the valence of the compound m. Apart from the results of the present investigation (represented by dots in the figure), we included also the experimental points for tin chalcogenides taken from our earlier investigation[6] (squares) and the results of Boehm's group[12] (triangles). The continuous line in the figure shows the dependence which follows from Eq. (1) when the condition (2) is satisfied and the following simple assumptions about the structure of the chemical bonds in the investigated compounds are obeyed: 1) metals and α-Sn are purely covalent, with bonds due to the sp electrons; 2) all changes in the electron structure during the formation of a compound reduce to the "pulling away" of m electrons of the sp-type to their electronegative partners, in accordance with the degree of ionicity of the bond i.

No.	Valence, m	Compound	i	ΔE exp, meV	ΔE exp/i, meV	ΔE^{***} calc/i, meV	C_{5sp} exp, meV	Δx [9]	n and cryst. modif.
1	1	Ag_2S—Ag	0.56	51±4	91±7	80±12	91±7	0.7	2*
2	2	CdO—Cd	0.85	115±6	135±7	160±24	68±4	1.8	6; *B*1 [15]
3		$SnCl_2$—α-Sn	0.86	158±12	183±14		92±7	1.4	8—9*
4	3	In_2O_3—In	0.78	112±8	144±10	240±36	—	1.8	6; D_{53} [14]
5		Sb_2O_3—Sb	0.51	138±6 104±5	271±22 204±10		90±4 68±3	1.7	3; rhomb. [13]
6	4 **	Sb_2O_4—Sb	0.59 **	172±10	292±17	320±48	73±4	1.7 and 1,4	6, type $SbTaO_4$ [13]
7	5	Sb_2O_5—Sb	0.49	200±15	408±31	400±60	82±6	1.4	6*, cubic
8	2	SnO—α Sn	0.85	108±12	127±14	160±24	63±7	1.8	6
9		SnO^B—α Sn	0.85	131±10	154±12		77±6		
10		SnS—α Sn	0.72	113±14	157±19		79±9	0.9	6
11		SnSe—α Sn	0.70	79±11	113±16		57∓8	0.7	6
12		SnTe—α Sn	0.68	103±12	151±18		76±9	0.4	6
13	4	SnO_2—α Sn	0.64	204±11	319±17	320±48	79±4	1.6	6
14		SnO_2^B—α Sn	0.64	210±10	323±15		81±4		
15		SnS_2—α Sn	0.40	149±12	372±30		93±7	0.7	6
16		$SnSe_2$—α Sn	0.37	113±13	305±35		76±9	0.5	6
17		β Sn—α Sn	—	37±10	—	—	—	—	—
							$\bar{C}_{5sp}^{1-7} = 81\pm4$		
							$\bar{C}_{5sp}^{8-16} = 76\pm4$		
							$\bar{\bar{C}}_{5sp}^{1-16} = 78\pm3$		

*Structures not known exactly. The values of the coordination numbers are somewhat arbitrary.

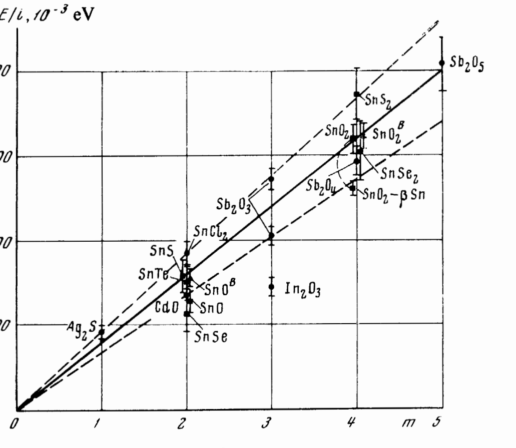
**The average valence and the effective ionicity are given here (see text).

***$\Delta E_{calc}/i = mC_{5\,sp}(Sr{-}Mo)$.

When these assumptions are made, Eq. (1) becomes

$$\Delta E = im\bar{C}_{sp}. \quad (7)$$

In plotting the continuous line in the figure, we used the value of $\bar{C}_{sp}$ obtained for the Sr–Mo series [cf. Eq. (3)]. The limits of the errors in the values of $\bar{C}_{sp}$ (Sr–Mo) are represented by the dashed lines in the figure. Thus, we compared not the relative values of $(\Delta E/i)_{exp}$ for various valences, i.e., not the deviations of the experimental points from some arbitrary straight line, but the absolute calculated and experimental values of the deviations of the experimental points from a calculated line. We found that the calculated and experimental results agreed very well (cf. also columns 6 and 7 in the table). The exception was the point representing In_2O_3—In; this discrepancy was probably due to the fact that metallic indium did not have the hypothetical purely covalent binding, i.e., the deviation was similar to the actually observed difference between metallic β-Sn and the covalent α-Sn (cf. the table and the figure where the points SnO_2—β-Sn and SnO_2—α-Sn are connected by a dashed arc).



Dependence, on the valence m, of the reduced (divided by the degree of ionicity i) values of the K_{α_1} shifts ($\Delta E = E_{comp} - E_{elem}$) for elements of Ag–Sb series. The continuous straight line is calculated from the relationship $\Delta E/i = mC_{sp}(Sr{-}Mo)$, where $C_{sp} = +80 \pm 12$ MeV is a constant found [7] by analysis of the shifts for the transition elements in the Sr–Mo series; the dashed lines represent the boundaries of the error in C_{sp}. The points represent experimental values: the dots are the results reported in the present paper; the squares are the results reported in our earlier paper [6]; and the triangles are the data of Gokhale, Chesler, and Boehm. [12]

Column 8 in the table gives individual experimental values of the constant $C_{5sp} = \Delta E_{exp}/mi$ and the following averages: for the compounds investigated in the present work (rows 1–7 in the table),

$$\bar{C}_{5sp}^{1-7} = +81 \pm 14\,\mathrm{meV} \quad (8)$$

for the compounds of tin with elements in the oxygen group taken from[6] and supplemented by the results of Boehm's group[12] (rows 8–16),

$$\bar{C}_{5sp}^{8-16} = +76 \pm 4\,\mathrm{meV}$$

[cf. Eq. (2)], and, finally, the average value of the constant $\bar{C}_{5sp}$, obtained using all the data on the shifts of the elements in the Ag–Sb series:

$$\bar{\bar{C}}_{5sp}(Ag - Sb) = +78 \pm 3\,\mathrm{meV} \quad (9)$$

The errors indicated for these constants are the rms values of the deviations of individual experimental values of the constants from the average values. Thus, they include the errors due to the possible indeterminacy of the structure modification. The value obtained for the constant given by Eq. (8) is in excellent agreement with the value obtained in[7] by a similar analysis of the experimental shifts for transition metals in the fifth [cf. Eq. (3)] and sixth [Eq. (5)] periods.

Thus, the new results confirm the validity of Eqs. (1) and (7) and give the same value of the constant.

An important consequence of these results is the confirmation of the earlier assumption that the bonds in all the compounds considered are formed mainly by the sp electrons.[1)] This conclusion seems somewhat unexpected in the case of Sb_2O_4 and Sb_2O_5. It is therefore worth considering these compounds in more detail.

The structure of Sb_2O_4 consists of equal numbers of Sb^{III} and Sb^{V} atoms in octahedral positions.[13] The value of the shift of the K_{α_1} line can, therefore, be written in the form

$$\Delta E = \frac{\Delta E^{III} + \Delta E^{V}}{2} = \frac{3C_{sp}i^{III} + 5C_{sp}i^{V}}{2}, \tag{10}$$

or, introducing an average valence and reducing the relationship to its usual form,

$$\Delta E = 4\left(\frac{3i^{III} + 5i^{V}}{8}\right)C_{sp}; \tag{10'}$$

the quantity in parentheses is the effective ionicity, which is given for Sb_2O_4 in the table. Then,

$$\Delta E_{\text{calc}} = 4 \cdot 0.59 \cdot (80 \pm 12) = +189 \pm 31 \text{ meV};$$

$$E_{\text{exp}} = +172 \pm 10 \text{ meV}.$$

The calculated shift for the pentavalent compound Sb_2O_5 is $\Delta E_{\text{calc}} = 5iC_{sp} = 5 \times 0.49 \times (80 \pm 12) = +196 \pm 29$ meV, while the experimental value is

$$\Delta E_{\text{exp}} = +200 \pm 15 \text{ meV}.$$

In both cases, the calculated and experimental values agree if the bonds of pentavalent antimony are assumed to be due to five sp electrons (the $5s^1 5p^3 6s^1$ structure).

CONCLUSIONS

The reported investigation of the K_{α_1} metal–oxide shifts for elements of the Ag–Sb series has once again confirmed quantitatively the validity (within the limits of 10–20%) of the very simple expression given by Eq. (1), which relates the measured shift ΔE to the Pauling ionicity i and the factor $\Sigma m_l C_l$, which describes the distribution of the valence electrons over the l sublevels, i.e., the valence configuration of the chemical bonds.

The experimental material on the basis of which the validity of this relationship has been established for relatively heavy elements ($38 \lesssim Z \lesssim 74$) is now fairly extensive (~ 25 pairs of compounds) but the quantitative validity of the very rough relationship (1) is still surprising and further experimental checks, as well as theoretical analysis, are required. It would be very interesting to study the transition region (the Cu–Se series) between the heavy elements which we have investigated[1,2,6,7] and the light elements investigated earlier (cf., for example,[5]), for which the Hartree–Fock electron functions are better known and which, therefore, can be theoretically analyzed more easily.

So far, the investigations of the K_{α_1} shifts have been limited to elements and compounds with the s-, p-, and d-type valence electrons and it has been found that it is practically impossible to use the shift method to distinguish the s and p electrons ($C_s \approx C_p$[14,6,7]), while the difference between the sp group and the d electrons is considerable (the constants C_{sp} and C_d differ not only in their absolute values but also in their signs[7]). It would be very interesting to extend these investigations to elements with the f electrons, and to determine experimentally the sign and magnitude of the constant C_f in order to check the relationship given by Eq. (1) and to obtain data which would be of practical use.

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[1)] The constant C_d [cf. Eq. (4)] differs from C_{sp} not only in magnitude but also in sign. Therefore, even a small uncompensated admixture of the d electrons would be noticeable.