CHEMICAL SHIFTS OF THE $K_{\alpha 1,2}$*,* $K_{\beta 1,3}$*, AND* $K_{\beta 2,4}$ *X-RAY LINES IN HEAVY ELEMENTS, DUE TO s, p, d, OR f VALENCE ELECTRONS*

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In the previous investigations of the chemical shift of x-ray lines in relatively heavy ($Z \geq 37$) atoms, principal attention was paid to the $K_{\alpha 1}$ line. Accordingly, the method used to study the structure of the crystal-chemical bonds on the basis of this effect was essentially a one-parameter method. In the present paper it is ascertained what study of other lines can contribute to an understanding of the physics of the effect. The shifts of the $K_{\alpha 1,2}$, $K_{\beta 1,3}$, and $K_{\beta 2,4}$ lines following removal of valence s(p), d, or f electrons are measured. They are also calculated theoretically on the basis of the Hartree-Fock-Slater method, with allowance for relativistic effects. Similarity of the theoretical and experimental shift vs. line type curves is noted, the curves for the s(p), d, or f electrons having different but characteristic shapes. The mechanism governing these dependences is discussed, as well as the causes (or consequences) of consistency of the theoretical and experimental curves, and also the possibility of using these dependences to investigate the structure of crystal-chemical bonds.

1. INTRODUCTION

IN our earlier investigations of the effect of the chemical shift of x-rays we measured the $K_{\alpha 1}$ shifts $\Delta E = E^{\text{comp}}_{K_{\alpha 1}} - E^{\text{met}}_{K_{\alpha 1}}$ for a large number of compounds (including oxides and chalcogenides), covering more than 30 elements of the periodic table in the region $32 \leq Z \leq 74$. The general systematics of these experimental data was considered in a review by one of the authors[1]. It was shown that the main mechanism of the effect is the screening mechanism and that the effect is sensitive in the main to the distribution of the valence electrons over the l sublevels (valence configurations) and can be described approximately by a very simple relation of the type

$$\Lambda E \approx i_{\text{cr}} \sum_{l} m_l C_l, \quad i_{\text{cr}} = 1 - (m/N)\exp(-0{,}25\Delta X^2), \tag{1}$$

where C_l is the change of the energy of the $K_{\alpha 1}$ line following complete removal of one valence electron of the l(s, p, d, f) type, $M = \Sigma m_l$ is the valence, m_l is the number of valence electrons with given quantum number l, i_{cr} is the degree of ionicity of the bond after Pauling[2], N is the coordination number, and ΔX is the difference between the electronegativities of the bond partners[3].

The results obtained to date pertain mainly to the $K_{\alpha 1}$ line only, and the method of investigating chemical bonds on the basis of this effect is accordingly of the single-parameter type. However, relation (1) contains several unknown parameters, and in the determination, say, of the valence configurations[4] it was necessary to use the calculated (after Pauling) values of the degree of ionicity of the bond. The hope of making the method multiparametric is based on the use of the remaining intense lines of the K series other than $K_{\alpha 1}$, namely $K_{\beta 1,3}$ (1s–3p transition) and $K_{\beta 2,4}$ (1s–4p). It is therefore important to ascertain the degree to which the notions concerning the mechanism of the effect and its properties, pertaining to the shift of the $K_{\alpha 1}$ lines, remain valid also for the harder lines of the K series, where, in principle, the superposition of several mechanisms is possible[5]. The most complete answer to this question concerning the main mechanism of the effect for all the K-series lines can be obtained by a quantitative comparison of the experimental dependences of the shift ΔE on the type of the line ($K_{\alpha 1,2}$(1s – 2p); $K_{\beta 1,3}$(1s – 3p); $K_{\beta 2,4}$(1s – 4p), i.e., on the initial level of the transition 2p, 3p, 4p) with theoretical calculations say, by the Hartree-Fock method. If the main mechanism of the effect is still screening, which is most correctly accounted for by self-consistent calculations, then the experimental and theoretical relations are expected to coincide.

The behavior of ΔE(np) as a result of the mutual screening mechanism can be qualitatively predicted, for example, by using the results of Mikhaĭlov and Khanonkind[6]. They considered, in the first orders of petrubation theory, the change of the line energy as a result of perturbation of the atom potential when a valence electron is removed. Figure 1 shows schematically the plot of the potential for a valence electron with density uniformly distributed over a sphere of radius r_0 (dashed) and for a case closer to the real distribution (continuous curve). It is important that the potential

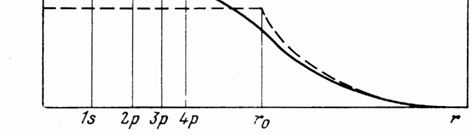

FIG. 1. Character of the behavior of the potential of the valence electron (used to explain the mechanism of the chemical shift of x-rays).

produced by the real electron inside the atom is a function that increases monotonically with decreasing r. The first order of perturbation theory takes into account the interaction of the valence electron with internal electrons in the states 1s, 2p, 3p, ... without allowance for the change of the wave functions of the remaining electrons of the atom. Removal of the valence electron leads in this case to unequal increases in the binding energies of the internal electrons (the closer the internal electron to the nucleus, the larger the increase), i.e., to a positive shift of the x-ray lines due to the (1s—np) transitions (see Fig. 1)[1]. The second order of perturbation theory takes into account the compression of the wave functions of all the electrons remaining in the atom following removal of the valence electron, i.e., it leads to a situation opposite to that in first order, namely an increase of the electron density in the region of the levels 1s, 2p, ... and consequently to a negative shift of the x-ray lines.

For the s-p valence electrons penetrating into the region of the 1s, 2p levels of the atom and having consequently the steepest potential, the first order is decisive, and the shift is positive and increases in absolute magnitude on going from the K_{α_1} to the $K_{\beta_{2,4}}$ line (this corresponds in Fig. 1 to the transition from the segment a-b to a-d). The contribution of the second-order terms will be negligible, since the s-p valence electrons are located on the outermost shells of the atom and their removal leads to insignificant deformations of the wave functions of the remaining electrons. To the contrary, for the 4f electrons, the second order is decisive, since the electrons filling the 4f shell lie even deeper in a radial direction than the filled 5s and 5p shells, and therefore their removal leads to a strong deformation of the wave functions of many electrons. On the other hand, having a radial wave function with one maximum, the 4f electrons penetrate least into the internal 1s and 2p shells of the atom, and the first order will make a minimal contribution. Thus, when the 4f electron is removed, a negative shift of the $K_{\alpha_{1,2}}$ lines is expected. On going from the K_α(1s – 2p) line to the K_β(1s—3p, 4p) lines, the values of the second-order terms increase in analogy with the increase of the first order in this transition. For the $K_{\beta_{1,3}}$ lines, this should lead to an increase of the shift (of negative sign), since the first order, which gives a positive contribution, is still negligible.

However, on going to the $K_{\beta_{2,4}}$(1s—4p) line, a qualitative change sets in: the maximum of the distribution of the 4f electrons lies approximately at the same distance from the nucleus as the maximum of the 4p electrons; this causes a strong increase of the first-order terms, i.e., a decrease (in absolute magnitude) of the shift of the $K_{\beta_{2,4}}$ line. On the whole, the ΔE(np) dependence for the 4f electrons lies in the region of negative values of ΔE and has a V-shape. The d-type electrons constitute an intermediate case and it is therefore more difficult to predict the ΔE(np) dependence for them, although it can be stated that the role of the second-order terms in the shift will be smaller for them than for the f electrons. The course of the ΔE(np) dependence will begin with negative values for the K_{α_1} lines, with a possible transition into the positive region for the $K_{\beta_{2,4}}$ lines.

Thus, from physical considerations one can expect the shift to exhibit a characteristic dependence on the type of the investigated line. A comparison of the experimental and theoretical dependences can yield information on the nature of the effect and on the physical significance of the theoretical and experimental data.

2. CALCULATION OF THE CHEMICAL SHIFTS WITHIN THE FRAMEWORK OF THE RELATIVISTIC HARTREE-FOCK-SLATER APPROACH

A systematic study was made of the character of the shift of the $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, and $K_{\beta_{2,4}}$ lines for the elements with $37 \leq Z \leq 64$. The eigenvalues of the electron energy ϵ_{nlj} were obtained by using the procedure of the self-consistent fields of the ions and atoms in the relativistic Hartree-Fock-Slater (HFS) approximation. Here n is the principal quantum number, l the orbital number, and j the total angular momentum of the electron. The shifts ΔE on going from the neutral atom to the ion were calculated as the differences of the corresponding electron energies. For example, for the K_{α_1}-line shift we have

$$\Delta E = [\varepsilon(1s_{1/2}) - \varepsilon(2p_{3/2})]_{\text{ion}} - [\varepsilon(1s_{1/2}) - \varepsilon(2p_{3/2})]_{\text{atom}} \qquad (2)$$

Without presenting the details, we confine ourselves to a listing of the main premises. It is assumed that the charge of the nucleus is uniformly distributed over a sphere of radius $r_0 = 1.2\,A^{1/3}$ F (A is the mass number)[7]. The exchange part of the potential acting on the electron in the field of the atom was assumed, following Slater[8], to be proportional to the cube root of the

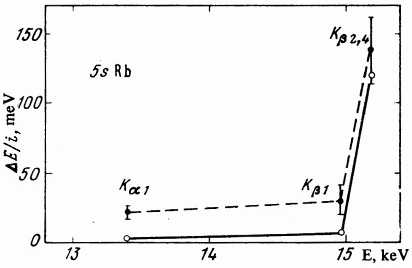

FIG. 2. Comparison of the experimental (dashed) and theoretical (solid) plots of the shift against the type of line for RbCl-Rb.

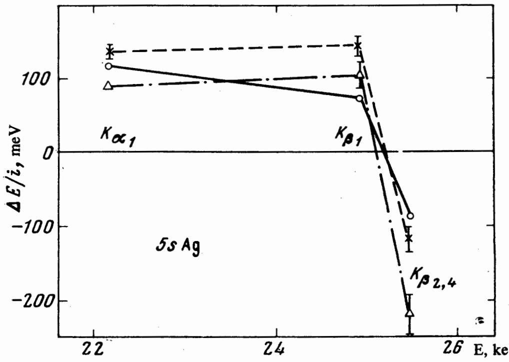

FIG. 3. The same for AgCl-Ag (dashed) and Ag_2S-Ag (dash-dot).

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[1] For a uniformly charged sphere, the shift of all the levels will be the same, and consequently will not lead to a change in the line energy.

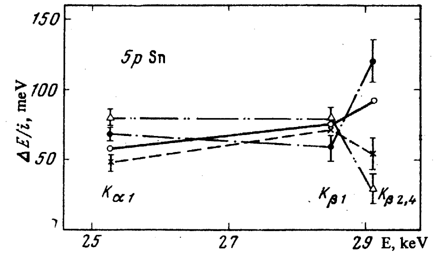

FIG. 4. The same for SnO-βSn (dashed), SnO_2-α Sn, $C_{5s\ exp}$ (dash-dot) and SnO_2–αSn, $C_{5s\ theor}$ (dash-double-dot).

charge density of all the electrons of the atom with a proportionality coefficient equal to unity. (A changeover to the coefficient 2/3, for which individual cases were also calculated, changes the shift little). The calculations were performed both for a potential with Latter's correction[9] (HFSL), and without this correction. The results differ strongly only in the case of ions with vacancies in the s and p valence shells of the atom. In all other cases HFS and HFSL calculations gave close values of the shifts.

Since lack of space does not permit a detailed analysis of the calculation results, we note that the calculated dependences of the shifts on the type of line, given in Figs. 5 and 6 for Zr and Mo, for vacancies in the 4d shells (continuous curves) are of the same character for all the elements of the fifth period. Similarly, Fig. 7 for Eu, for a vacancy in the 4f shell, is typical of all the rare-earth elements.

A somewhat more complicated picture is observed for vacancies in the s and p shells. The character of the shifts in this case can be traced in Figs. 8a and 8b. The solid and dashed curves represent shifts calculated for HFS and HFSL potentials, respectively. Attention is called to the following circumstance: in the HFS model the direction of the $K_{\beta 2}$-line shift depends significantly on whether the atom in the neutral state has one external s or p electron, or more than one. Figure 9 shows the shifts of the $K_{\beta 2}$ lines following removal of an s electron, as a function of Z. We see that the points calculated at the HFS potential lie on two curves—I and II. Curve I passes through elements that have one valence s electron in the neutral state. Curve II passes through elements having in the neutral state more than one electron of the sp group. For example, the point

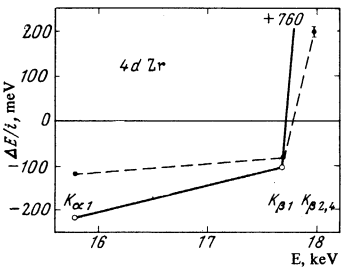

FIG. 5. The same for ZrO_2-Zr.

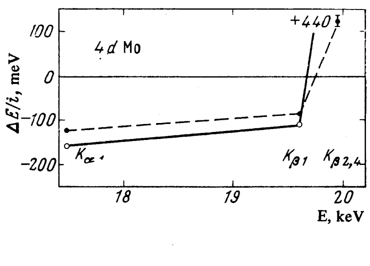

FIG. 6. The same for MoO_3-Mo.

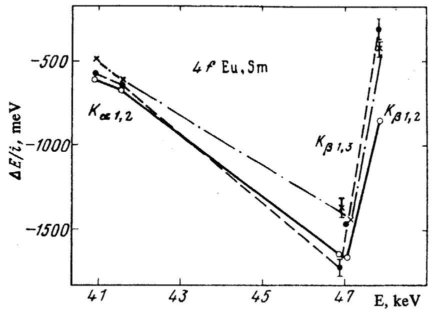

FIG. 7. The same for EuF_3-EuF_2 (dashed) and SmF_3-$SmCl_2$ (dash-dot) (the figure should read $K_{\beta 2,4}$ instead of $K_{\beta 1,2}$).

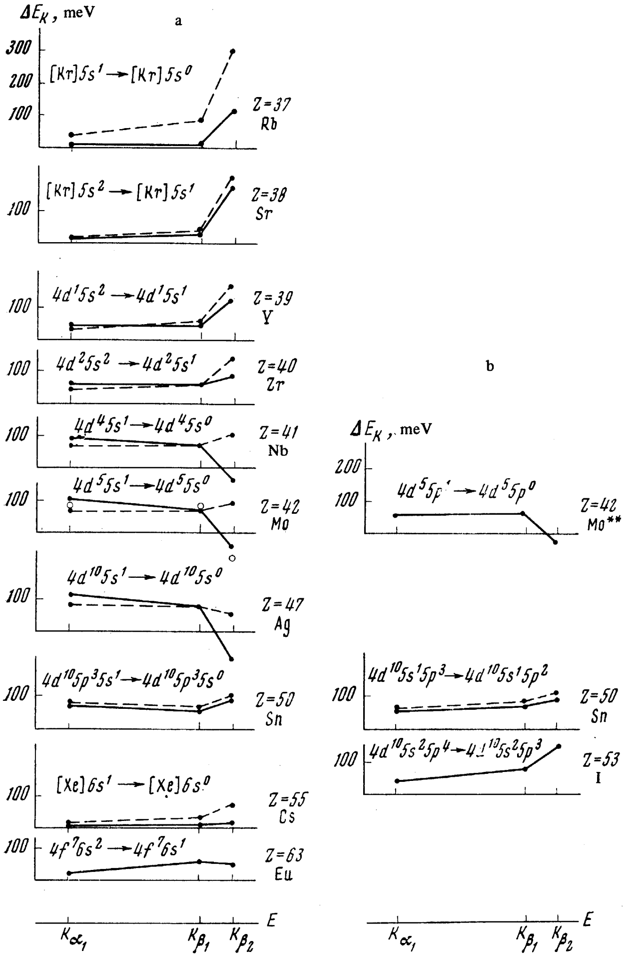

FIG. 8. Calculated energy shifts ΔE (meV) of lines $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2}$ on going from neutral atoms to ions with vacancies in the s or p shells: a—removal of 5s ($37 \leqslant z \leqslant 50$) and 6s (z = 55, 63) electrons; b—removal of 5p electron. The abscissa scale is chosen such as to make the distances from $E_{K_{\alpha_1}}$ to $E_{K_{\beta_1}}$ and from $E_{K_{\beta_1}}$ to $E_{K_{\beta_2}}$ respectively equal for all Z. The solid line pertains to HFS calculations, and the dashed one to HFSL calculations. The circles represent the points calculated by the Hartree-Fock method for Mo [10]. Figure 8b shows the data for the nonstrandard Mo** configuration $4d^4_{3/2}4d^1_{5/2}5p^1_{1/2}$.

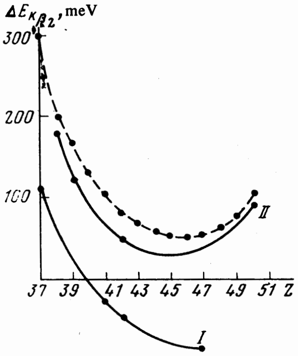

FIG. 9. Calculated shifts ΔE (meV) of the energies of the K_{β_2} lines following removal of a 5s electron for elements of the fifth period, as functions of Z. The dashed line pertains to HFSL calculations, and the solid lines to HFS calculations. Curve I passes through elements in which there is only one 5s electron in the neutral state (Rb, Nb, Mo, Ag). Curve II passes through elements having more than one electron of the sp group (Sr, Y, Mo*, Sn). For Mo*, the calculations were performed for the non-standard configuration $4d^4_{3/2}5s^2_{1/2}$.

with K = 50, pertaining to αSn with one valence 5s electron and three 5p electrons, lies on curve II. This shows that the character of the shift depends on the total number of the s and p valence electrons.

It can be concluded from Figs. 8 and 9 that the shifts in the HFS and HFSL models have the same character for atoms containing in the neutral state more than one electron of the sp group, and are different for atoms with one s electron. It is of interest to compare these results with Hartree-Fock calculations. The circles in Fig. 8a show the level shifts for Mo, calculated from the data of[10]. They have a character analogous to the shifts in the HFS model, i.e., latter's correction makes the result worse in this case.

Comparison of Figs. 8a and 8b shows that the character of the shifts following removal of valence s and p electrons is similar.

The calculations have shown that the difference between the shifts, as a function of the total angular momentum of the electron, i.e., between $K_{\alpha 1}$ and $K_{\alpha 2}$ etc., does not exceed 20% for the heaviest element considered by us (Gd) and is less than 2% for Rb.

The dependences of the effects on the number of removed electrons, which characterize the degree of additivity, are shown in Table I.

The effects under consideration have a relative value $\Delta E/E \approx 10^{-5}-10^{-7}$. The calculation accuracy should exceed the indicated quantity by at least one order of magnitude. We performed calculations with the BESM-4 computer, which operates with nine-digit decimal numbers, and special measures were therefore taken to keep the relative error in the K-electron binding energy within 2×10^{-8}. The screening function $\varphi(r) = V(r)r/Z$ was calculated with an absolute error $\lesssim 10^{-7}$.

3. EXPERIMENTAL SHIFTS OF $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, AND $K_{\beta_{2,4}}$ LINES DUE TO s, p, d, OR f VALENCE ELECTRONS, AND THEIR COMPARISON WITH THE CALCULATIONS

We measured the chemical shifts (ΔE) of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta_{2,4}}$ lines for ionic-compound—metal pairs, using the usual procedure employed by us (see, for example[4]). The experimental results are listed in Table II. $\sigma(\Delta E)$ are the rms errors determined mainly by the scatter of the individual experimental runs. In addition to the values of ΔE, we give also the degrees of ionicity of the bond i_{cr} for the compounds under consideration, and the coordination numbers N of the crystal lattices, which are needed for the calculation of the ionicity (the same Pauling ionicity scale was used for all cases, see the Introduction); the ionicities of the metals were assumed to be equal to zero. From the experimental shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta_{2,4}}$ lines (for definite configurations and degrees of bond ionicities) we determined, using (1), the values of the coefficients $C_l^{\exp}$, which, as already mentioned in the Introduction, represent the change of the energy of the corresponding line following complete removal from the atom of one valence electron, and can be compared with the calculated ones by means of a relation of type (2).

The experimental and calculated values of C_{nl} for the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta_{2,4}}$ lines, i.e., the ΔE(np) dependences, are compared in Table III and in Figs. 2–7. The coordinates in the figures are the line shift ($\Delta E/i \equiv C_l$) and the line energy (E).

a) The ΔE(np) dependences for the 5s electrons were investigated using ionic compounds of Rb and Ag as examples. The choice of these elements was dictated by the fact that they have one valence 5s electron each (in excess of the filled shells [Kr] for Rb and [Xe] $4d^{10}$ for Ag). Rubidium, as is well known, is one of the most electropositive elements and forms classical ionic compounds with halogens[11]. It is therefore natural to assume that the formation of the chemical bond in RbCl is due to one 5s electron, and the valence configuration of this compound is [Kr] $5s^{1-1}$; for Ag_2S, the valence configuration [Kr] $4d^{10}5s^{1-1}$ was determined in one of our earlier papers[12]. The values of $C_{5s}^{\exp}$ obtained under

Table I. Calculated energy shifts ΔE_K(meV) of lines $K_{\alpha_{1,2}}$, $K_{\beta_{1,2}}$, $K_{\beta_{1,3}}$, and $K_{\beta_{2,4}}$ on going from the neutral atom to the ion, as a function of the number m of the removed electrons

Symbol	Removed electrons	m	$K_{\alpha 1}$	$K_{\alpha 2}$	$K_{\beta 1}$	$K_{\beta 3}$	$K_{\beta 2}$	$K_{\beta 4}$
^{42}Mo	$4d^1_{5/2}$	1	−156	−153	−99	−102	453	500
	$4d^1_{3/2}4d^1_{5/2}$	2	−363	−356	−140	−148	1430	1548
	$4d^2_{3/2}4d^1_{5/2}$	3	−614	−604	−101	−119	2961	3167
^{50}Sn	$5p^1_{3/2}$	1	60	58	78	77	104	107
	$5p^1_{1/2}5p^1_{3/2}$	2	163	157	218	216	311	321
	$5p^2_{1/2}5p^1_{3/2}$	3	307	295	430	425	662	683
^{58}Ce	$4f^1_{5/2}$	1	−752	−688	−1950	−1921	−846	−680
	$4f^2_{5/2}$	2	−1665	−1522	−4294	−4236	−1508	−1121

Table II. Experimental shifts ΔE (meV), $E_{comp} - E_{met}$ of the x-ray lines $K_{\alpha_{1,2}}$, $K_{\beta_{1,3}}$, and $K_{\beta_{2,4}}$ in ionic compounds

Compound	$K_{\alpha 1}$ (1s—2p)		$K_{\beta 1}$ (1s—3p)		$K_{\beta 2,4}$(1s—4p)	i_{cr}	Coordination number N
RbCl—Rb	+21±4		+28±10		+131±22	0.95	6
Ag_2S—Ag	+51±4		+59±10		—125±15	0.56	2
AgCl—Ag	+122±5		+129±9		—104±16	0.88	6
SnO_2—αSn	+204±11		+193±16		+101±30 +142±24	0.64	6
SnO—βSn	+81±5		+122±11		+89±21	0.85	6
ZrO_2—Zr	—229±5		—149±8		+480±15	0.82	8
MoO_3—Mo	—199±5		—137±5		+224±15	0.39	6
	$K_{\alpha 2}$	$K_{\alpha 1}$	$K_{\beta 3}$	$K_{\beta 1}$			
EuF_3—EuF_2	—644±11	—582±15	—1450±40	—1730±50	—300±65	0.96; 0.95	8; 9
SmF_3—$SmCl_2$	—606±14	—488±19	—1455±40	—1360±50	—415±50	0.90; 0.94	9; 9

these assumptions are given in Table III and in Figs. 2 and 3 (dashed and dash-dot lines), together with the values C_{5s}^{theor} calculated for the same valence configurations as used to determine C_{5s}^{exp} (continuous lines in Figs. 2 and 3). It should be noted that the coefficient C_{5s} for Rb is much smaller than the average values obtained by us earlier (see, for example,[1]). This is probably due to the weak bond between the valence 5s electron of Rb and the atomic core [Kr], as is evidenced also by the minimum value of the ionization potential. It is also important that the ΔE(np) curves of the $K_{\beta 2,4}$ lines of Rb and Ag (for 5s electrons in both cases) go in opposite directions (the effects have opposite signs).

b) The ΔE(np) dependence for 5p electrons was obtained from the experimental shifts for the pairs SnO_2-αSn and SnO-βSn. As is well known, αSn is a classical example of a covalent compound with a valence configuration $5s^1 5p^3$; the valence configuration $5s^{1-i} 5p^{3(1-i)}$ of SnO_2 was determined earlier (see, for example,[1]). The magnitude of the effect ΔE(SnO_2-αSn) will thus consist of contributions made by one 5s and three 5p electrons. In calculating the shift due to one 5p electron (C_{5p}^{exp}) it is therefore necessary to take into account also the relatively small contribution (≈ 1/4 of the effect) of the 5s electron. This can be done by using either the value C_{5s}^{theor} (see Table IV) calculated for removal of one 5s electron from a tin atom with configuration $5s^1 5p^3$, or the experimental value of C_{5s}^{exp} for an element having a relatively close value of Z, say Ag. This gives rise, accordingly, to two variants of experimental values of ΔE(np). Both are given in Table II and in Fig. 4 (dash-dot lines). It is also possible to determine the ΔE(np) dependence for the 5p electron from the experimental data for SnO-βSn. In this case, the employed valence configurations $5s^2 5p^{2(1-i)}$ and $5s^2 5p^2$ are less reliably established, but there is no need to introduce a correction for C_{5s}. The values C_{5p}^{exp} obtained from these experimental data are also given in Table III and in Fig. 4 (dashed).

c) The ΔE(np) dependences for the 4d electrons were determined from the measured values of ΔE in ZrO_2 and MoO_3 relative to the metallic Zr and Mo. The val-

Table III. Comparison of experimental and calculated values of chemical shifts C_l (meV) of the x-ray lines due to removal of one valence electron

Type of electron	Compound	Configuration	$K_{\alpha 1}$ (1s — 2p)		$K_{\beta 1}$ (1s — 3p)		$K_{\beta 2,4}$(1s — 4p)	Notes
5s	RbCl—Rb	$[Kr]\,5s^1 \rightarrow \cdots 5s^{(1-i)}$	+22±5		+30±11		+138±23	
	Calculation	$[Kr]\,5s^1 \rightarrow \cdots 5s^0$	+3		+6		+120	
	Ag_2S—Ag	$[Kr]\,4d^{10}5s^1 \rightarrow \cdots 5s^{(1-i)}$	+91±7		+105±18		—224±28	
	AgCl—Ag	$[Kr]\,4d^{10}5s^1 \rightarrow \cdots 5s^{(1-i)}$	+139±6		+146±10		—118±18	
	Calculation	$[Kr]\,4d^{10}5s^1 \rightarrow \cdots 5s^0$	+117		+74		—87	
5p	SnO_2—αSn	$[Kr]\,4d^{10}5s^1 5p^3 \rightarrow \cdots 5s^{(1-i)}\,5p^{3(1-i)}$	+68±8		+59±10		+120±15	$C_{5s\,exp}$ from Ag
	SnO_2—αSn	$[Kr]\,4d^{10}5s^1 5p^3 \rightarrow \cdots 5s^{(1-i)}\,5p^{3(1-i)}$	+80±6		+79±8		+30±10	$C_{5s\,calc}$ for Sn
	Calculation	$[Kr]\,4d^{10}5s^1 5p^3 \rightarrow \cdots 5s^1 5p^2$	+60		+78		+106	
	SnO—βSn	$[Kr]\,4d^{10}5s^2 5p^2 \rightarrow \cdots 5s^2 5p^{2(1-i)}$	+48±3		+72±7		+53±13	
	Calculation	$[Kr]4d^{10}5s^2 5p^2 \rightarrow \cdots 5s^2 5p^1$	+58		+76		+93	
4d	ZrO_2—Zr	$[Kr]\,4d^3 5s^1 \rightarrow \cdots 4d^{3(1-i)}\,5s^{(1-i)}$	—119±2		—82±3		+199±6	$C_{5s\,calc}$ for Zr
	Calculation	$[Kr]\,4d^2 5s^2 \rightarrow \cdots 4d^1 5s^2$	—220		—103		+760	
	MoO_3—Mo	$[Kr]\,4d^5 5s^1 \rightarrow \cdots 4d^{5(1-i)}\,5s^{(1-i)}$	—122±3		—85±3		+124±8	
	Calculation	$[Kr]\,4d^5 5s^1 \rightarrow \cdots 4d^4 5s^1$	—157		—109		+440	$C_{5s\,calc}$ for Mo
			$K_{\alpha 2}$	$K_{\alpha 1}$	$K_{\beta 3}$	$K_{\beta 1}$		
4f	SmF_3—$SmCl_2$	$[Xe]\,4f^6 \rightarrow \cdots 4f^5$	—488±19	—606±14	—1360±50	—1455±40	—415±50	
	EuF_3—EuF_2	$[Xe]\,4f^7 \rightarrow \cdots 4f^6$	—582±15	—644±11	—1730±50	—1450±40	—300±65	
	Calculation	$[Xe]\,4f^7 6s^2 \rightarrow \cdots 4f^6 6s^2$	—605	—671	—1648	—1682	—852	

Table IV. Calculated values of the x-ray line shifts ΔE (meV) due to removal of one valence 5s electron from the atom, used to determine the experimental $\Delta E(np)$ dependences

Element	Configuration	$K_{\alpha 1}$ $(1s-2p)$	$K_{\beta 1}$ $(1s-3p)$	$K_{\beta 2,4}$ $(1s-4p)$
Zr	$[Kr]\,4d^3 5s^1 \rightarrow \cdots 4d^3 5s^0$	78.0	64.0	−12.0
Mo	$[Kr]\,4d^5 5s^1 \rightarrow \cdots 4d^5 5s^0$	100.0	72.6	−46.0
Sn	$[Kr]\,4d^{10} 5s^1 5p^3 \rightarrow \cdots 4d^{10} 5p^3 5s^0$	78.1	66.2	99.0

ence configurations of the metals and of the limiting oxides ZrO_2 and MoO_3 were determined earlier[4], namely $5s^1 4d^3$ for $Zr(ZrO_2)$ and $5s^1 4d^5$ for $Mo(MoO_3)$. In the calculation of the values of C_{4d}^{exp}, a correction was introduced for the contribution made to the effect by one 5s electron; this correction obtained theoretically as the shift of the corresponding lines between the configurations $5s^1 4d^3 \rightarrow 5s^0 4d^3$ for Zr and $5s^1 4d^5 \rightarrow 5s^0 4d^5$ for Mo (see Table IV). The obtained values of C_{4d}^{exp} are given in Table III and in Figs. 5 and 6 (dashed), where they are compared with the calculated values (continuous line).

d) The $\Delta E(np)$ dependences for 4f electrons were obtained from the experimental shifts of the lines $K_{\alpha 2}$, $K_{\alpha 1}$, $K_{\beta 3}$, $K_{\beta 1}$, and $K_{\beta 2,4}$ between the compounds EuF_3-EuF_2 and SmF_3-$SmCl_2$. In these compounds, with a bond ionicity close to 100%, the valence electrons have been almost completely removed from the Eu and Sm atoms. This makes it possible to regard Eu and Sm as doubly- and triply-charged ions, respectively, with configurations $4f^6 \rightarrow 4f^7$ and $4f^5 \rightarrow 4f^6$ (see[13]). The line shift is thus completely governed by the unity change in the number of 4f electrons, i.e., it is possible here to compare the values of the experimental and theoretical quantities directly, with practically no corrections for the degree of ionicity of the bond. It should also be noted that the 4f electrons, being internal and isolated from the external actions by the filled 5s and 5p shells, are least subject to the influence of the crystal lattice. Consequently, the experimental shifts produced when the number of 4f electrons is changed should coincide in best fashion with those calculated for isolated atoms. The experimental values for Eu and Sm are given in Table III and in Fig. 7 (dashed and dash-dot lines, respectively), where they are compared with the calculated values (continuous line) for Eu using the configurations $[Xe]4f^7 6s^2 \rightarrow [Xe]4f^6 6s^2$.

4. DISCUSSION OF RESULTS

A comparison of the experimental and theoretical $\Delta E(np)$ dependences for different types of valence electrons reveals a sufficiently good agreement between the experimental and theoretical quantities, not only in the characteristic shape of the $\Delta E(np)$ curve, which is different for each type of valence electron, but also in the absolute values. The general picture of good agreement between the experimental and theoretical quantities allows us to conclude that for sufficiently heavy atoms $(Z \geq 37)$, for all the intense K-series lines, the main mechanism of the chemical x-ray line shift is mutual screening, taken into account within the framework of self-consistent calculations. The greatest discrepancy between the numerical theoretical and experimental quantities is observed for the lines $K_{\beta 2,4}$. This may be due to the fact that the $K_{\beta 2,4}(1s-4p)$ transitions are connected with the 4p level close to the valence shells, where a strong influence of other mechanisms and of the nature of the ligands is possible. In addition, different modifications of the theoretical-calculation scheme (i.e., modifications of the allowance for the screening mechanism itself) sometimes give noticeably different results just for the $K_{\beta 2,4}$ lines. For example, such a relatively small change in the calculation scheme as the replacement of the HFS model by the HFSL model (see Fig. 8a) makes the curves of Mo, Nb, and Ag assume the characteristic shape of the Rb curve, and exerts practically no influence on the shifts of the $K_{\alpha 1}$ and $K_{\beta 1}$ lines.

The self-consistent calculations can be made numerically accurate to within 10^{-8}. The question arises, however, whether the last digits in the values of ϵ are physically significant. The accuracy of the values of ϵ themselves, treated as binding energies, apparently do not exceed 10^{-2}; however, since the investigated quantities ΔE constitute second differences of ϵ, one can hope to obtain them by means of relations of the type (2) with the same relative accuracy, i.e., 10^{-1}–10^{-2}. The observed agreement between the theoretical and experimental values of ΔE confirms this assumption.

While noting the agreement between experiment and theory, it should be recognized that the theoretical values were obtained for free atoms (ions) while the experimental ones were obtained for a solid, where the wave functions of the outer electrons experience considerable deformations. As shown by the calculations of Griffin et al.[14], the transition from the free atom to the actually existing dimensions of the Wigner-Seitz sphere can lead to effects on the order of 100 meV. However, since one measures differences of line energies in two solid compounds, the shift will include only a certain fraction of the total compression effect; this fraction is proportional to the difference between the metallic (ionic) radii of the compared compounds[2]. It should also be noted that, with the exception of the case of the 4f electrons, the quantities C_l^{exp} include also the somewhat indeterminate bond-ionicity parameter. The observed agreement between the absolute values of the shifts means apparently that the Pauling scale of the crystal ionicities (at least for the compounds investigated by us) gives values close to the true ones[3].

5. CONCLUSIONS

1. We have shown that the effect of the chemical shift of the fundamental x-ray lines of the K series $(K_{\alpha 1,2}, K_{\beta 1,3}, K_{\beta 2,4})$ in relatively heavy atoms $(Z \geq 37)$ is determined mainly by the mutual screening mechanism and can be calculated within the framework of the self-consistent models of the Hartree-Fock type. A

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[2] The influence of the crystal field (interaction of the Madelung type) does not lead to a change in the energy of the K-series x-ray lines, since it causes an identical shift for all the internal levels (see Introduction, Fig. 1, dashed curve).

[3] One cannot exclude, however, the possibility that the errors due to compression and ionicity cancel each other in some way.

comparison of the experimental and theoretical values shows, in general, that they are in good agreement.

2. The dependences of the values of the shift on the type of line (on the initial level of the transition) are different for different valence electrons (s(p), d, or f electrons), are unique "facsimile" representations of the corresponding electrons, and can be used to identify events connected with the change in the number or distribution of these electrons[4)].

The use of intense K-series lines other than K_{α_1} makes it possible to make the method multiparametric. For example, if one compares the shapes of the curves and not the absolute values of the shifts, knowledge of the degree of ionicity of the bond is no longer necessary.

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[4)] Exceptions are probably the s and p electrons, whose "facsimiles" are similar or differ only for the $K_{\beta 2,4}$ line, where the experimental and theoretical situations are least clear.

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