

THE EFFECT OF THE CHEMICAL SHIFT OF THE X-RAY  $K_{\alpha}$  LINES IN HEAVY ATOMS.  
 SYSTEMATIZATION OF THE EXPERIMENTAL DATA AND COMPARISON WITH  
 THEORY

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Submitted June 3, 1969

Zh. Eksp. Teor. Fiz. 57, 1716–1727 (November, 1969)

The general systematics of the experimental data of<sup>[1-9]</sup> (Table I) on the changes in the  $K_{\alpha}$ x-ray line energies ( $\Delta E$ ) of heavy ( $32 \leq Z \leq 74$ ) elements (metals) occurring during the formation of chemical compounds (containing oxygen or elements of its group) are considered. It is found that in the summary plot of the experimental data  $\Delta E/i = f(m)$  [Fig. 1, where  $i$  the Pauling ionicity (1) and  $m$  the oxide valence] a definite trajectory (straight line) corresponds to each horizontal row of the periodic table. All rare-earth metals, the effects for which are presented in the insert in Fig. 1, fall (with the exception of Eu and Yb) onto the same point with  $m = 3$  on the Ba–W trajectory. All of the trajectories (straight lines) which contain altogether more than 40 experimental points can approximately be described by two parameters  $C_{sp} = 80 \pm 10$  meV and  $C_d = -115 \pm 10$  meV which are their slopes. The role of the  $f$  electrons (for example, the Eu and Yb points in the insert) is defined by the parameter  $C_f = -570 \pm 30$  meV. The effect can be described by relation (7) which is an additive expansion in occupation numbers  $m_l$  of the valence electrons of energy sublevels with orbital quantum numbers  $l$ , i.e., it is determined by the valence configurations. The experimental constants  $C_l$  defined as the change in the energy of the  $K_{\alpha_1}$  line due to the complete removal of a valence electron of the  $l$  type are compared with theoretical "vacuum" values obtained by self-consistent (Hartree-Fock type) calculations for isolated atoms.<sup>[10-13]</sup> Satisfactory agreement between the theory and the experiments is observed in this case. The cause of such a "simplicity" of the effect (sensitivity mainly to the configurations, the constancy of the  $C_l$ ) is analyzed. It is found that it appears only in the case of transitions between sufficiently inner levels in sufficiently heavy atoms ( $Z \gtrsim 30$  for K and L levels).

## INTRODUCTION

RATHER extensive factual material has been accumulated in a series of preceding papers<sup>[1-9]</sup> devoted to the experimental observation and investigation of the effect of the chemical shift of x-ray  $K_{\alpha_1}$  lines in comparatively heavy atoms ( $32 \leq Z \leq 74$ ). The features of a simple systematization of the phenomenon, whose presentation for the complete aggregate of the data is indeed the primary purpose of this paper, have gradually become apparent.

There also appears at present the possibility of a comparison of experimental data with the results of theoretical self-consistent calculations (of the Hartree-Fock type),<sup>[10-13]</sup> of a quantitative justification of the proposed mechanism of the phenomenon (the screening mechanism) and of the initially semi-empirical relations describing the effect. It appears to be possible to explain (understand) the basic features of the effect characteristic for transitions between sufficiently internal levels in sufficiently heavy atoms. It is in particular possible to explain the practically important dependence of the effect on the so-called valence configurations, i.e. on the distribution of the super-core (valence) electrons over the  $l$  sublevels ( $l$  is the orbital quantum number) making it possible to utilize the effect under investigation as an experimental method of determining the valence configurations of crystallochemical bonds.

## SYSTEMATIZATION OF THE EXPERIMENTAL DATA

In Table I we present a general summary of the experimental data<sup>[1-9]</sup> on the energy differences of x-ray  $K_{\alpha_1}$  lines in metals and oxides (or compounds with elements of the hydrogen group) for relatively heavy atoms ( $Z \geq 32$ ). The errors  $\sigma(\Delta E)$  are mean-square errors essentially determined by the scatter of the individual experimental series. In addition to the values of  $\Delta E = E_{\text{oxide}} - E_{\text{metal}}$ , we also present the degree of ionicity of the bond  $i$  in the compounds and the coordination numbers of the crystal lattices required for calculating the ionicities. In all cases we have employed the same ionicity scale of Pauling<sup>[14]</sup> with a correction for the crystallographic coordination:

$$i = 1 - (m/N) \times \exp(-0.25\Delta X^2) \quad (1)$$

where  $m$  is the valence,  $N$  is the coordination number, and  $\Delta X$  is the difference in the electronegativities of the partners in the compound. The values of  $\Delta X$  were in all cases taken from a summary table of Batsanov.<sup>[15]</sup> The ionicities of the metals were always taken to be zero.

All the experimental values from Table I for which the ionicities are indicated were plotted in  $\Delta E/i = f(m)$  coordinates on the summary graph of Fig. 1. The numbers near the points correspond to the serial numbers in the Table. The experimental errors [ $\sigma(\Delta E)$  from Table I divided by  $i$ ] are also indicated whenever room

Table I. Summary of the experimental data of the chemical shifts of the x-ray  $K_{\alpha_1}$  lines in the chalcogenides of heavy ( $Z \geq 32$ ) elements

No.	Z	Investigated pair		$\Delta E = E_B - E_A$ , meV	Coordination number N	Pauling ionicity i	Source
		A	B				
1	32	Ge	GeO <sub>2</sub>	+244 ± 20	6	0.62	[7]
2	32		GeS <sub>2</sub>	+123 ± 13	6	0.39	[7]
3	32		GeS	+110 ± 11	6	0.70	[7]
4	33	As	As <sub>2</sub> O <sub>3</sub>	+151 ± 6	3	0.43	[7]
5	33	Sr	SrO	-30 ± 4	6	0.93	[4]
6	39	Y	Y <sub>2</sub> O <sub>3</sub>	-146 ± 10	6	0.37	[4]
7	40	Zr	ZrO <sub>2</sub>	-229 ± 15	8	0.82	[4]
8	41	Nb	Nb <sub>2</sub> O <sub>3</sub>	-260 ± 5	6	0.63	[4]
9	42	Mo	MoO <sub>3</sub>	-199 ± 5	6	0.39	[4]
10	47	Ag	Ag <sub>2</sub> S	+51 ± 4	2	0.56	[6]
11	43	Cd	CdO	+115 ± 6	6	0.85	[6]
12	43		CdSe	+32 ± 13	4	0.56	[6]
13	49	In	In <sub>2</sub> O <sub>3</sub>	+112 ± 8	6	0.73	[6]
14	50	Sn <sub>α</sub>	Sn <sub>β</sub>	+37 ± 10	4	0	[3]
15	50		SnO*	+103 ± 12	6	0.85	[3]
16	50		SnO	+131 ± 10	6	0.85	[5]
17	50		SnS	+113 ± 14	6	0.72	[3]
18	50		SnSe	+79 ± 11	6	0.70	[3]
19	50		SnTe	+103 ± 12	6	0.63	[3]
20	50		SnO <sub>2</sub>	+229 ± 10	6	0.64	[1]
21	50		SnO <sub>2</sub>	+204 ± 11	6	0.64	[3]
22	50		SnO <sub>2</sub>	+210 ± 10	6	0.64	[5]
23	50		SnS <sub>2</sub>	+149 ± 12	6	0.40	[3]
24	50		SnSe <sub>2</sub>	+113 ± 13	6	0.37	[3]
25	51	Sb	Sb <sub>2</sub> O <sub>3</sub>	+121 ± 17	3	0.51	[6]
26	51		Sb <sub>2</sub> O <sub>4</sub>	+172 ± 10	6	0.59	[6]
27	51		Sb <sub>2</sub> O <sub>5</sub>	+200 ± 15	6	0.49	[6]
28	52	Te	TeO <sub>2</sub>	+176 ± 5	6	0.59	[6]
29	52		TeO <sub>3</sub>	+269 ± 5	?	?	[6]
30	56	Ba	BaO	+142 ± 20	6	0.94	[4]
31	57	La	La <sub>2</sub> O <sub>3</sub> (A)	-3 ± 10	6	0.39	[8]
32	53	Ce	CeO <sub>2</sub>	-457 ± 15	8	—	[8]
33	59	Pr	Pr <sub>2</sub> O <sub>3</sub> (A)	-20 ± 15	7	0.39	[9]
34	59		PrO <sub>3</sub> (A)	-263 ± 9	—	—	[9]
35	60	Nd	Nd <sub>2</sub> O <sub>3</sub> (A)	+14 ± 11	7	0.87	[8]
36	60		Nd <sub>2</sub> O <sub>3</sub> (C)	+50 ± 10	6	0.85	[8]
37	62	Sm	Sm <sub>2</sub> O <sub>3</sub> (B)	+32 ± 11	6	0.85	[8]
38	63	Eu	Eu <sub>2</sub> O <sub>3</sub> (C)	-64 ± 10	6	0.7	[8]
39	64	Gd	Gd <sub>2</sub> O <sub>3</sub> (C)	+36 ± 12	6	0.85	[8]
40	65	Tb	Tb <sub>2</sub> O <sub>3</sub> (C)	+19 ± 15	6	0.75	[9]
41	65		TbO <sub>1.86</sub>	-266 ± 13	—	—	[9]
42	65		TbO <sub>1.72</sub>	-394 ± 18	—	—	[9]
43	66	Dy	Dy <sub>2</sub> O <sub>3</sub> (C)	+10 ± 14	6	0.35	[8]
44	67	Ho	Ho <sub>2</sub> O <sub>3</sub> (C)	+1 ± 17	6	0.35	[9]
45	68	Er	Er <sub>2</sub> O <sub>3</sub> (C)	+18 ± 43	6	0.35	[8]
46	69	Tm	Tm <sub>2</sub> O <sub>3</sub> (C)	+46 ± 16	6	0.75	[8]
47	70	Yb	Yb <sub>2</sub> O <sub>3</sub> (C)	-532 ± 30	6	0.7	[8]
48	70		Yb <sub>2</sub> S <sub>3</sub>	-520 ± 25	6	0.69	[9]
49	71	Lu	Lu <sub>2</sub> O <sub>3</sub> (C)	+3 ± 20	6	0.85	[8]
50	72	Hf	HfO <sub>2</sub>	-6 ± 30	8	0.82	[4]
51	73	Ta	Ta <sub>2</sub> O <sub>5</sub>	-113 ± 30	6	0.63	[4]
52	74	W	WO <sub>3</sub>	-110 ± 33	6	0.39	[4]

\*The experimental values for the tin compounds measured in the original work with respect to Sn<sub>β</sub> are recalculated to Sn<sub>α</sub> by the addition of  $E_{Sn\beta} - E_{Sn\alpha} = 37 \pm 10$  meV.

allows. The graph has a simple structure. The experimental points corresponding to the elements of the Cu—Se and Ag—Te rows fall on curves (straight lines) which pass through zero and have a positive slope. The elements of the sequences Rb—Mo and Ba—W fall on straight lines with a negative slope. The rare-earth elements (metal—trivalent oxide pairs), the effects for which are shown in  $\Delta E/i = f(Z)$  coordinates in the insert, group (with the exception of Eu and Yb) about a single point corresponding to the valence three and located on the straight line of the Ba—W series. The numbers of the corresponding periods of the periodic system of the elements (the values of the principal quantum numbers  $n$  of the outermost valence shells) are indicated at the ends of the straight lines.

Let us introduce quantitative characteristics. The equations of the straight lines for the series Cu—Se and Ag—Te can obviously be written in the form

$$\Delta E/i = C_{nsp}m, \quad (2)$$

where  $n = 4$  for Cu—Se and  $n = 5$  for Ag—Te (we ignore the fact that the course of the Cu—Se series is somewhat bent)<sup>1)</sup>. Substituting in (2) the experimental values from Table I, we obtain

$$C_{4sp} = +93 \pm 9 \text{ meV (Cu—Se)}, \quad (3)$$

$$C_{5sp} = +78 \pm 3 \text{ meV (Ag—Te)}. \quad (3')$$

If one writes the equations of the straight-line series Rb—Mo and Ba—W in the form

$$\Delta E/i = 1 \cdot C_{5sp} + (m-1)C_{4d} \quad (\text{Rb—Mo}), \quad (4)$$

$$\Delta E/i = 2 \cdot C_{6sp} + (m-2)C_{5d} \quad (\text{Ba—W}) \quad (4')$$

and substituting the experimental values from Table I

<sup>1)</sup> The significance of the subscripts of C will be explained below. So far they constitute merely a notation which enables one to differentiate between the coefficients.

**Table II.** Comparison of the theoretical and experimental valence configurations of transition metals belonging to the fifth and sixth periods

Metal	Theory [16]	Experiment [4], according to relation		Metal	Theory [16]	Experiment [4,8], according to relation	
		(1), (4'), (13)	(8)			(4), (4'), (13)	(8)
Sr	$s^1d^1$	$s^1d^1$	$(sp)^{1,05}d^{0,95}$	Ba	$s^1d^1$ or $s^1p^1$	$s^1p^1$	$(sp)^{1,97}d^{0,03}$
Y	$s^1d^2$	$s^1d^2$	$(sp)^{0,97}d^{2,03}$	La—Lu*	$s^1d^2$ or $s^1p^1d^1$	$s^1p^1d^1$	$(sp)^{1,84}d^{1,16}$
Zr	$s^1d^3$	$s^1d^3$	$(sp)^{1,02}d^{2,98}$	Hf	$s^1d^3$ or $s^1p^1d^2$	$s^1p^1d^2$	$(sp)^{2,23}d^{1,72}$
Nb	$s^1d^4$	$s^1d^4$	$(sp)^{0,94}d^{4,06}$	Ta	$s^1d^4$ or $s^1p^1d^3$	$s^1p^1d^3$	$(sp)^{1,92}d^{3,08}$
Mo	$s^1d^5$	$s^1d^5$	$(sp)^{1,06}d^{4,94}$	W	$s^1d^5$ or $s^1p^1d^4$	$s^1p^1d^4$	$(sp)^{1,95}d^{4,05}$

\* With the exception of Eu and Yb.

solves the resulting overdetermined system (4) and (4') by the least-squares method for  $C_{5sp}$  and  $C_{4d}$ , and for  $C_{6sp}$  and  $C_{5d}$  respectively, then one obtains<sup>2)</sup>

$$C_{5sp} = +80 \pm 12 \text{ meV}, C_{4d} = -120 \pm 4 \text{ meV}, (\text{Rb} - \text{Mo}), (5)$$

$$C_{6sp} = +77 \pm 14 \text{ meV}, C_{5d} = -107 \pm 11 \text{ meV}, (\text{Ba} - \text{W}). (5')$$

The following approximate equalities are fulfilled

$$C_{4sp}(\text{Cu} - \text{Se}) \approx C_{5sp}(\text{Ag} - \text{Te}) \approx C_{5sp}(\text{Rb} - \text{Mo}) \approx C_{6sp}(\text{Ba} - \text{W}) \\ \equiv C_{sp} = +80 \pm 10 \text{ meV}, (6)$$

$$C_{4d}(\text{Rb} - \text{Mo}) \approx C_{5d}(\text{Ba} - \text{W}) \equiv C_d = -115 \pm 10 \text{ meV}. (6')$$

The coefficients  $C_{sp}$  and  $C_d$  differ sharply from one another having different signs.

The solid straight lines in Fig. 1 correspond to Eqs. (2), (4), and (4') with averaged constants (6) and (6'). More than forty experimental points fall on them and can thus be fully satisfactorily described with the aid of two parameters. The points As (No. 4) and In (No. 13) with the largest "excursions" will be discussed below.

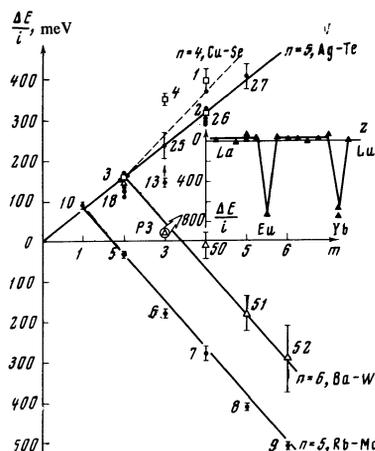


FIG. 1. Summary graph of the reduced (divided by the degree of ionicity  $i$ ) experimental energy differences of the  $K_{\alpha 1}$  lines of metal-oxide (chalcogenide) pairs for heavy ( $32 \leq Z \leq 74$ ) elements as a function of the valence  $m$ . The numbers at the points correspond to the serial numbers of Table I;  $\square$  — elements of the fourth period,  $\circ$  — of the fifth,  $\Delta$  — of the sixth period.

<sup>2)</sup> The coefficient  $C_{5sp}$  in (4) is considered as a new variable, i.e. the system (4) is solved independently of (2).

Equations (2), (4), and (4') can be written in the general form

$$\Delta E = i \sum_l m_l C_l, (7)$$

where  $C_l$  ( $C_{sp}$  and  $C_d$ ) are constants from relations (3), (5), and (6) and  $m_l$  are integer coefficients satisfying the normalization

$$\sum_l m_l = m, (7')$$

where  $m$  is the valence.

Equations (4) and (4') can be obtained by a somewhat different method useful for the following presentation. The equations of the straight lines for the series Rb—Mo and Ba—W can obviously always be written in the form

$$\Delta E / i = x C_{sp} + (m - x) C_{4(s)d}, (8)$$

where  $C_{sp}$  is in this case first taken from (3'),  $C_{4(s)d}$  are the slopes of the experimental straight lines Rb—Mo and Ba—W respectively, and  $x$  is an arbitrary quantity. Substituting  $\Delta E/i$  from Table I and solving Eq. (8) for  $x$ , one can find the value of  $x$  for each of the transition elements in the series under consideration. The obtained values of  $x$  in the form  $(sp)^x d^{m-x}$  are presented in columns 4 and 8 of Table II (see below). Our attention is drawn by the fact that they are close to being integers and group around unity for the series Rb—Mo and around two for the series Ba—W.

## DISCUSSION OF THE EXPERIMENTAL DATA. COMPARISON WITH THEORY

Let us assume that Eq. (7) is an additive expansion of the effect in the occupation numbers  $m_l$  of the sublevels  $l$  ( $s, p, d$ ) by valence electrons "pulled away" in the production of a crystallochemical bond ( $l$  is the orbital quantum number). In such a case the constants  $C_l$  obviously constitute the energy changes of the  $K_{\alpha 1}$  lines upon complete removal of one valence  $l$  ( $s, p, d$ ) electron. In a more general form the additive expansion of the effect in  $l$ -type electrons removed (as a result of transition to new  $l$  sublevels) or "pulled away" (on account of the ionicity of the bonding) can be written in the form

$$\Delta E \equiv E_B - E_A = \sum_l \Delta m_l C_l, (9)$$

where  $\Delta m_l = m_l^A - m_l^B$  is the difference between the occupation numbers of  $l$  levels in the investigated atom in compounds A and B.

In the special case when A is a purely covalent compound or a metal ( $i_A = 0$ ) and B is an ionic compound with a 100-percent ionic bond ( $i_B = 1$ ),  $m_l^B = 0$  (all the electrons are pulled away completely towards the ligand), and

$$\Delta E = \sum_l m_l^A C_l, \quad (10)$$

i.e., the measured effect is determined by the distribution of the electrons in the metal (a covalent compound) over the  $l$  sublevels or by the so-called valence configuration of the metal. With this

$$\sum_l m_l^A = m,$$

where  $m$  is the valence of the investigated element in the compound  $B^3$ . If  $i_B < 1$ , but only pulling away towards the electronegative partner occurs in the formation of the bond in accordance with the degree of ionicity  $i$  of the electrons (no transitions between  $l$  sublevels occur), i.e.  $\Delta m_l = i_l m_l^A$ , then Eq. (9) gives

$$\Delta E = \sum_l i_l m_l^A C_l, \quad \sum_l m_l^A = m, \quad (11)$$

where  $i_l$  are partial ionicities corresponding to the degree of pulling away of various  $l$ -type electrons towards the ligand.

Let us use any ionicity scale, for example Pauling's scale of ionicities  $i$  [see relation (1)] representing some sort of average of the unknown values of  $i_l$  for the given compound. We rewrite (11) in the form

$$\Delta E = i \sum_l m_l C_l', \quad (12)$$

where  $C_l' = i_l C_l / i$  are the effective constants which differ from the true  $C_l$  by the factor  $i_l / i$ , i.e., by the ratio of the true and accepted ionicity.

We have gone back to the experimental relation (7), explaining the possible significance of the quantities entering into it. The straight lines of the series Cu—Se, Ag—Te, Rb—Mo, and Ba—W in Fig. 1 take on the meaning of the courses of the valence configurations of the investigated metals<sup>4</sup>. Equations (2), (4), and (4') respectively now signify that the electrons of the metals which on formation of the bond will participate in it, i.e., will be valence electrons, have the following configurations:

$$\begin{aligned} (sp)^m & \text{— for the series Cu—Se and Ag—Te,} \\ (sp)^1 d^{m-1} & \text{— for the series Rb—Mo,} \\ (sp)^2 d^{m-2} & \text{— for the series Ba—W.} \end{aligned} \quad (13)$$

The experimentally obtained configurations (13) for heavy transition metals are compared in Table II with the theoretically most preferred ones obtained in<sup>[16]</sup>. The observed agreement attests to the fact that the presented approach yields sensible results<sup>5</sup>. Of interest are columns 4 and 8 in which our attention is drawn to the practically integral nature of the experimental configurations.

In the insert in Fig. 1, in which the effects for the rare-earth metals (RE) and their (trivalent) sesquioxides are presented, the two points of Eu and Yb stand out with their anomalously large negative shifts. Unlike the other RE, in the metallic state Eu and Yb are divalent<sup>[17,18]</sup> with the configurations

$$(\dots 4f^n) 5d^1 6s^1 \text{ or } (\dots 4f^n) 6s^1 6p^1, \quad (14)$$

which realize the energetically convenient half ( $\eta = 7$ , Eu) or fully ( $\eta = 14$ , Yb) filled 4f shells. On the other hand, their sesquioxides, identical with those of the other RE,<sup>[19]</sup> are trivalent and probably have configurations corresponding to the general sequence of the Ba—W series established above (see Table II):

$$4f^{n-1} 5d^{1-i} 6s^{1-i} 6p^{1-i}.$$

It is important that the transition from the divalent to the trivalent state must be accompanied by a change (a decrease by one) of the number of 4f electrons. The expressions for the effects in the Eu—Eu<sub>2</sub>O<sub>3</sub> and Yb—Yb<sub>2</sub>O<sub>3</sub> pairs should in accordance with (9) be written in the form

$$\Delta E = E_{Me_2O_3} - E_{Me} = C_{4f} + i(C_{6sp} + C_{5d}) - (1-i)C_{6sp}, \quad (15)$$

if the first of structures (14) is realized, or

$$\Delta E = C_{4f} + 2iC_{6sp} - (1-i)C_{5d}, \quad (15')$$

if the second one is realized. A peculiarity of relations (15) and (15') is that the  $C_{4f}$  coefficient appears in them. It is natural to assume that the anomalies of the effects in Eu and Yb are due precisely to this coefficient.<sup>[18]</sup>

If the interpretation of the graph (Fig. 1) and of the effect presented above is correct, and the mechanism of the effect is due to electron interactions taken into account by present-day self-consistent calculations (for example, Hartree-Fock calculations), then one would expect in principle agreement of the experimental coefficients  $C_l$  with those theoretically calculated within some self-consistent model. However, in general there appears a difficulty connected with the difference between the true "vacuum" values of  $C_l$  calculated for isolated atoms and the experimental effective  $C_l'$  [see relation (12)] measured for atoms in a crystal lattice.

<sup>3</sup>) It is obvious that the effect furnishes information only about those electrons of the metal which in forming the compound participate in the bond and will be pulled away towards the ligand.

<sup>4</sup>) We note that we could have used any other ionicity scale proportional to that assumed. This would only change the absolute values of the experimentally determined constants  $C_l'$ , but their ratios, the structure of the summary graph (Fig. 1), and the obtained valence configurations would remain completely unchanged. On the other hand, it is not clear in how far the employed scale correctly reflects the transition from ligands of one type (oxygen and analogs) to ligands of another type (for instance, halogens). Therefore in plotting the summary graph we took only oxides or compounds with elements from the oxygen group (chalcogenides).

<sup>5</sup>) On a detailed plot of Ag—Te there are no kinks which would occur for a sufficiently marked difference between  $C_s$  and  $C_p$ . These coefficients have undoubtedly the same sign and are unfortunately indistinguishable within the framework of the approach employed (at any rate at the wavelength of the  $K\alpha_1$  line; possibly the use of  $K\beta_1$ , for for example, will make it possible to differentiate between them), since the experimental points can be satisfactorily described by a single averaged parameter  $C_{spp}$ (Ag—Te) (for details see [3]). The constants  $C_{spp}$  and  $C_{6sp}$  from the rows Rb—Mo and Ba—W which in fact correspond more than anything to  $C_{5s}$  and  $C_{6s}$  are also close to  $C_{spp}$ (Ag—Te). It is therefore possible in the experimentally determined structures (13) to separate only the groups of sp and d electrons.

From this point of view the 4f electrons of the RE present unique possibilities, being inner electrons isolated from external interactions by the more outer 5s and 5d shells, not participating in the chemical bond, and not being pulled towards the ligands<sup>6)</sup>. One can, therefore, hope on the one hand that the  $C_{4f}$  coefficients determined in the experiment in a crystal lattice will coincide with those for an isolated atom (i.e., with the calculated values), and, on the other, that they enter in the expression for the effect [see, for example, (15)] without the poorly known multiplier—the ionicity  $i$ . Moreover, the “internal nature” of the 4f electrons leads to anomalously large values of the effects caused by them ( $C_{4f} \gg C_{5d} \approx C_{6sp}$ ); therefore, the quantity  $i$  for  $C_{5p}$  and  $C_d$  also turns out to be of little importance in this case. Indeed, substituting in (15)  $C_{5p}$  and  $C_d$  from (6) and (6') and  $\Delta E$  from Table I, we find

$$C_{4f}(\text{Eu}) = -564 - 45i = -603 \pm 15 \text{ meV},$$

$$C_{4f}(\text{Yb}) = -541 \pm 32 \text{ meV}, \quad (16)$$

if (15) is realized, and

$$C_{4f}(\text{Eu}) = -759 - 45i = -798 \pm 20 \text{ meV},$$

$$C_{4f}(\text{Yb}) = -736 \pm 35 \text{ meV}, \quad (16')$$

if (15') is realized.

Waber (see<sup>[10]</sup>) calculated the eigenenergies  $\epsilon$  of the  $1s_{1/2}$  and  $2p_{3/2}$  electrons for the configurations  $(\dots 4f^{\eta})6s^2$  and  $(\dots 4f^{\eta-1})6s^2 5d^1$  of rare-earth atoms within the framework of a self-consistent solution of the Dirac equation with account of the exchange interaction in accordance with one variant of Slater's approach<sup>7)</sup>. In our notation the differences in the energies of the  $K\alpha_1$  lines (represented as  $\epsilon_{1s_{1/2}} - \epsilon_{2p_{3/2}}$ ) in the compared configurations are, obviously, equal to the differences of the coefficients  $C_{4f}$  and  $C_{5d}$ . In Table III and Fig. 2 we compare the theoretical values of Waber with the first variant of the experimental values  $C_{4f}$  for Eu and Yb [relation (16)] subtracting the experimental value of  $C_d$  [see (6')]. Excellent agreement between the data is observed<sup>8)</sup>.

A similar comparison for the constants  $C_{4sp}$  of gallium, germanium, and arsenic, and  $C_{5sp}$ ,  $C_{4d}$ , and  $C_{4d} - C_{5sp}$  of molybdenum is made in Table IV. As theoretical values we took the results of averaging the data of the self-consistent calculation of Clementi<sup>[11]</sup> according to Hartree-Fock-Roothaan over the configurations  $sp^2$  for  $\text{Ga}_2\text{O}_3$ ,  $sp^3$  for  $\text{GeO}_2$ ,  $sp^3$  for  $\text{GeS}_2$ ,  $p^2$  for  $\text{GeS}$  and  $sp^2$  for  $\text{As}_2\text{O}_3$ :  $C_{4s}(\text{Zn}) = 90.3 \text{ meV}$ ,  $C_{4p}(\text{Ga}) = 38.9 \text{ meV}$ ,  $C_{4p}(\text{Ge}) = 65.6 \text{ meV}$ , and  $C_{4p}(\text{As}) = 79.5 \text{ meV}$ <sup>9)</sup>. For molybdenum we cite the theoretical

<sup>6)</sup> We are considering the “collapsed” [20,24] state of the 4f electrons normal for the rare earths.

<sup>7)</sup> The author is grateful to Professor J. Waber for kindly sending him the results of calculations for the rare earths.

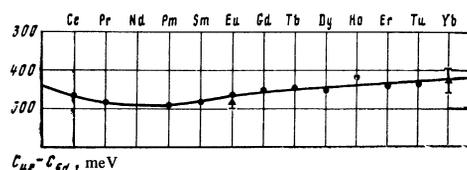
<sup>8)</sup> The experimental situation with the 4f electrons is described in more detail in [9]. In particular, an independent experimental determination of the valence configurations of Eu and Yb carried out showed that the first variant of (14) and correspondingly of (16) is realized.

<sup>9)</sup> In view of the lack of calculated values of  $C_{4s}$  for gallium, germanium, and arsenic we used the value for the neighboring zinc.

**Table III.** Comparison of the theoretical values of  $C_{4f} - C_{5d}$  obtained by means of self-consistent calculations for isolated atoms with the experimental values

Element	$C_{4f} - C_{5d}$ , meV		$\Delta$ , meV	$\delta$ , %
	Theory [10]	Experiment [8]		
Eu	-464	$-438 \pm 22$	24	5
Yb	-435	$-426 \pm 36$	-9	-2

\* Extrapolation from the neighboring Er (-438 meV) and Tu (-432 meV).



**FIG. 2.** Comparison of the theoretical [10] and experimental [8,9] values of the constants  $C_{4f} - C_{5d}$  of the shift of the  $K\alpha_1$  lines for rare-earth elements:  $\circ$  — theory,  $\Delta$  — experiment.

**Table IV.** Comparison of theoretical values of  $C_{4(5)sp}$  and  $C_{4d}$  obtained by means of self-consistent calculations for isolated atoms with the experimental values

Compounds	Constants compared, meV	Theory	Experiment	$\Delta$ , meV	$\delta$ , %
Ga — $\text{Ga}_2\text{O}_3$	$C_{4sp}$	+59 [11]	$+43 \pm 3^*$	+11	+23
Ge — $\text{GeO}_2$	$C_{4sp}$	+72	$+99 \pm 8$	-27	-27
Ge — $\text{GeS}_2$	$C_{4sp}$	+72	$+79 \pm 8$	-7	-9
Ge — GeS	$C_{4sp}$	+66	$+79 \pm 8$	-13	-17
As — $\text{As}_2\text{O}_3$	$C_{4sp}$	+83	$+117 \pm 5$	-34	-29
Mo	$C_{5s}$	+88 [12]	$+80 \pm 12^{**}$	+8	+10
Mo	$C_{4d}$	-197 [13]	$-120 \pm 4^{**}$	-77	+64
Mo	$C_{4d} - C_{5s}$	-165	$-200 \pm 13^{**}$	+35	-18

\* Experimental value for the Ga-In analog (see Fig. 1, No. 13).

\*\* Relation (5) averaged for the Rb-Mo series.

values of  $C_{5s}$  of Synek<sup>[12]</sup> and those of  $C_{4d}$ ,  $C_{4d} - C_{5s}$  of Froese<sup>[13]</sup> obtained as the differences of the self-consistent values of  $\epsilon_{1s}$  and  $\epsilon_{2p}$  for Mo and  $\text{Mo}^+$  with the configurations  $5s^1 4d^5$ ,  $5s^2 4d^4$ ,  $4d^5$ , and  $5s^2 4d^3$ . The agreement is not as exact as for  $C_{4f}$ , however it is sufficient to confirm the correctness, in its general outline, of the interpretation of the experimental data presented above. Possibly the agreement is even somewhat better indicating the practical nonrenormalizability of the constants  $C_{5p}$  and  $C_d$  on going from atoms in the crystal lattice to isolated atoms, or, more accurately, the satisfactory description of such a transition by means of the parameter  $i$  [relation (1)] containing a correction for the crystallographic coordination. The obtained results could also be interpreted as the ratio

<sup>10)</sup> The author is grateful to Professor C. Froese who kindly sent him the results of her calculations for molybdenum.

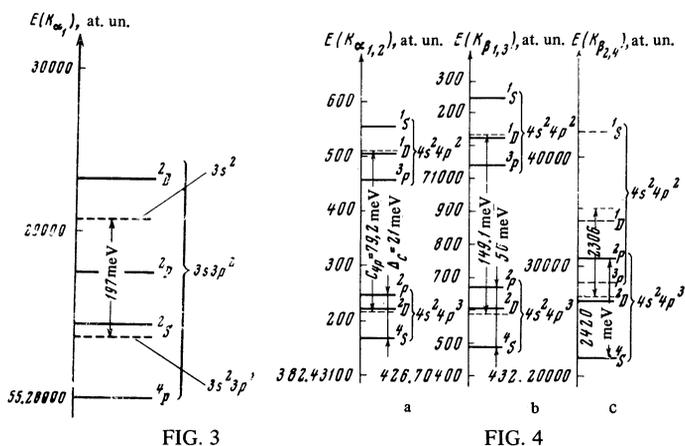


FIG. 3

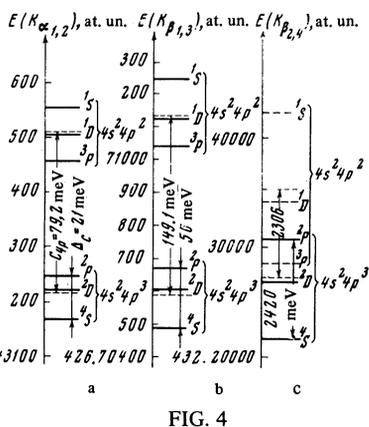
FIG. 3. Calculated values of the energy of the  $K\alpha_1$  line for several configurations and states of Al and  $Al^+$  [12].

FIG. 4

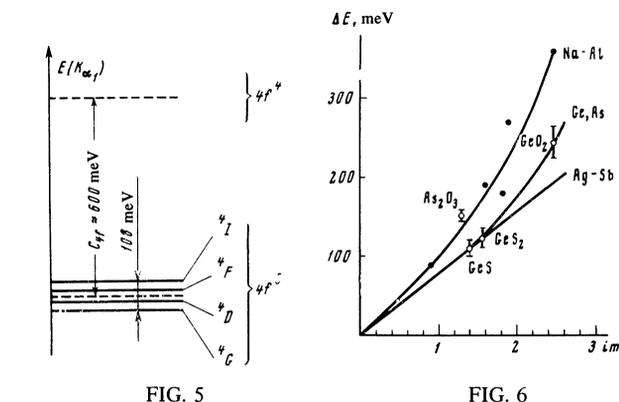
FIG. 4. Calculated values of the energies of the x-ray K lines for configurations and states of As and  $As^+$  [11]: a -  $K\alpha(1s-2p)$ , b -  $K\beta_1(1s-3p)$ , c -  $K\beta_{2,4}(1s-4p)$ .

FIG. 5

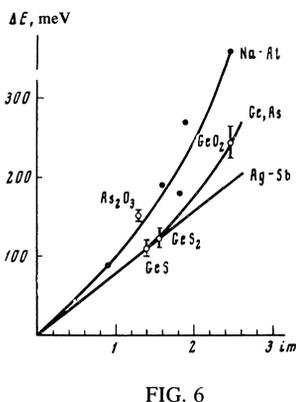
FIG. 5. Comparison of the effect of states and configurations on the energy of the  $K\alpha_1$  line of Nd (states of the configuration  $4f^3$  from calculations of [23], distances between the configurations from [8,10]).

FIG. 6

FIG. 6. The dependences of the shift of the  $K\alpha$  line on the transferred charge  $q = im$  for the Na-Al, Cu-As, and Ag-Te series illustrating the appearance of additivity for heavier elements.

$i_l/i$  in the relation  $C_l' = (i_l/i)C_l$  [see (12)] being close to unity.

## CONCLUSION

Possibly a natural reaction to the above systematization of the experimental data on the  $K\alpha$  shifts is surprise at the unusual simplicity of the phenomenon emphasized by references to the complexity of the usually observed structure of the energy levels (bands) in molecules and crystals and a corresponding conclusion regarding the primitive nature of the proposed description. More specifically, doubts are raised by the statement that the effect is mainly sensitive to the configurations (i.e., to the distribution of valence electrons over the  $l$  sublevels) and can appropriately be described by relations of the type (7) and (9) which are expansions in

the configurations, whereas a much more complicated pattern of states is decisive both in optical and even directly in the x-ray spectra of light atoms (see, for example, [21]).

In Figs. 3, 4a, and 5 we present the energies of the  $K\alpha$  lines as a function of the configuration and of the states of the valence electrons of isolated atoms in accordance with data from self-consistent calculations. (As the energies of the  $K\alpha$  lines we used the differences of the values of the eigenenergies of the corresponding levels in the self-consistent potential.) In the light aluminum the energy differences of the  $K\alpha$  lines for different states are indeed greater than for different configurations (Fig. 3). However, even for arsenic (Fig. 4a) the distance on the  $K\alpha$  scale of the  $(1s-2p)$  energies between configurations is appreciably larger than between states, i.e., the configuration becomes the decisive factor upon which the energy depends.

This situation is even more clearly expressed in neodymium (Fig. 5). It is interesting that the influence of the configurations in sufficiently heavy atoms is dominating only for lines due to transitions between the innermost levels. Thus, even in arsenic at the wavelength of the  $K\beta_{2,4}$  line ( $1s-4p$ , Fig. 4c) the states belonging to different configurations are mixed up. An intermediate situation occurs for the  $K\beta_1$  line ( $1s-3p$ , Fig. 4b). Correspondingly the approximate constancy of the coefficients  $C_l$  is apparently also the clearer, the heavier the compared atoms and the deeper the levels between which the transitions are observed. The case illustrated in Fig. 2 (theoretical curve) is one of the best examples of such constancy. On the other hand, gallium (indium) and arsenic (Fig. 1, points No. 4 and 13 in Table IV) provide examples of appreciable oscillations of  $C_l$ .

A part of the general graph of Fig. 1 in somewhat changed coordinates is repeated in Fig. 6. The purpose of this Figure is to illustrate the change of the situation with the additivity of the effect (the constancy of  $C_l$  as a function of the removed charge  $q = im$ ) as one goes over from light to heavy atoms. The Figure is supplemented with a curve for the elements of the third period plotted on the basis of data from the literature on the shifts of the  $K\alpha$  lines [21] recalculated for the standard ionicity scale (1). As one proceeds towards heavier elements the additivity [the linearity of  $\Delta E = f(im)$ ] improves, so that for the Ag-Te series the effect is approximately additive up to values  $q = im \lesssim 2.5$ .

Thus the simplicity of the effect apparently follows from the physics itself and should cause no surprise. The situation simplifies specifically for sufficiently inner levels and sufficiently heavy atoms. Thus for the  $K\alpha_1$  line the situation becomes simple starting from the Cu-Se series, for the  $K\beta_1$  line, possibly starting with Rb, etc. In short, the conditions for its simplicity apparently coincide approximately with those which were accepted up to the publication of [1-9] as the conditions for the certain absence of the effect of the chemical shift. [22]

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Translated by Z. Barnea  
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