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THE ROLE OF *f* ELECTRONS IN THE CHEMICAL SHIFT OF THE Kα_1 LINES

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The energy shifts of the Kα_1 lines appearing on removal of the 4f electrons from the atom (the C_{4f} coefficients) are measured for the rare-earth elements Ce, Pr, Tb, Sm, Eu, and Yb. The experimental results are compared with the theoretical calculations based on the self-consistent Dirac-Slater model.[13] Good quantitative agreement between the experimental and theoretical C_{4f} coefficients is observed.

INTRODUCTION

WE have shown in our previous papers[1-5] that the experimentally measured energy differences of the x-ray Kα_1 lines of a given element in compounds A and B satisfy in the region $32 \lesssim Z \lesssim 74$ the simple relation

$$\Delta E_{AB} = E_A - E_B = \sum_l \Delta m_l C_l, \tag{1}$$

where l is the orbital quantum number of the valence electron, Δm_l is the difference in the numbers of valence electrons of the l-th type in the investigated element in the compounds considered and C_l is a quantity equal to the shift of the Kα_1 line when one valence electron of the l-th type is completely removed.

The coefficients C_l entering in formula (1) can be determined experimentally from measurements of the chemical Kα_1 shifts or one can attempt to calculate them theoretically. The values of C_l for s, p, and d electrons have been determined experimentally in[3-5]. They turned out to depend weakly on the atomic number of the element Z and on the principal quantum number of the valence electron and their average numerical values for the range of Z investigated by us were as follows:

$$C_s \approx C_p \equiv C_{sp} = +80 \pm 10\,\text{meV} \quad C_d = -115 \pm 10\,\text{meV} \tag{2}$$

The fact that the Kα_1 shifts when the s and p electrons are removed differ sharply from the corresponding shifts when the d electrons are removed makes it possible to differentiate readily the participation of the sp and d groups in the chemical bonding and thus utilize the effect of the chemical shift of the Kα_1 lines as a method for determining the valence configuration of the investigated compounds. In[4] this method has been used to determine the valence configurations of metals in the Sr—Mo and Ba—W series, and in[16]—to determine the valence configurations of the majority of the trivalent rare-earth metals (REM) and their sesquioxides.

A theoretical calculation of the coefficients C_l can be carried out most accurately within the framework of self-consistent calculations of the type of the well-known Hartree-Fock model. If the self-consistent problem for an atom and ion of the given element is solved, then the quantities C_l can be simply expressed in terms of the orbital energies calculated in this problem:

$$C_l = (\varepsilon_{2p_{3/2}} - \varepsilon_{1s_{1/2}})_{l\text{-ion}} - (\varepsilon_{2p_{3/2}} - \varepsilon_{1s_{1/2}})_{\text{atom}}, \tag{3}$$

where $\epsilon_{2p_{3/2}}$ and $\epsilon_{1s_{1/2}}$ are the eigenenergies of the $2p_{3/2}$ and $1s_{1/2}$ states.

However, such calculations can only be carried out for free atoms and ions, whereas one measures the chemical shifts of Kα_1 lines for atoms in a crystal lattice in which the wave functions of the external (valence) electrons undergo considerable modifications compared with the free state. True, in determining the coefficients C_l from the chemical Kα_1 shifts we have allowed for the effects of the external surroundings by introducing corrections for the crystal structure in the magnitude of the degree of ionicity[3-5]; however, such allowance is of course very crude and one cannot in general expect necessarily agreement between the experimental constants C_l and those calculated for free atoms.

The situation is appreciably simpler for 4f atoms in rare-earth elements. These electrons differ in being located radially deep inside the atom; they are fully screened from external interactions by the filled 5s and 5p shells and their wave functions should not change appreciably on going from a free atom to the condensed state. It is therefore of obvious interest to determine experimentally the constant C_{4f} analogous to the C_{sp} and C_d constants. It is in this case that one can expect agreement between the experimental and theoretical values of the constants.

The possibility of an experimental determination of the C_{4f} coefficient is connected with the instability of the valence characteristic of certain rare-earth elements. The 4f electrons themselves, apparently, do not participate directly in the chemical bond since they are located rather deeply in the radial direction; however, their energy levels are very close to those of the valence 6s, 6p, and 5d electrons, so that mutual transitions can occur between them.[7] In such a transition accompanied by a change of valence there is a change in the number of 4f electrons, a fact which makes it possible to determine the constant C_{4f}. In[6] we made an attempt to determine the constants C_{4f}^{Eu} and C_{4f}^{Yb} using the experimental shifts of the Kα_1 lines between the divalent metallic Eu and Yb and their trivalent oxides. The numerical values of these constants depend, however, on the assumed distribution of valence electrons over the *l* states and are in this sense somewhat undetermined. Thus, if one assumes for metallic Eu and Yb the configuration $4f^n6s^16p^1$ in analogy with the neighboring divalent Ba,[4] and for the trivalent oxides of these elements a configuration coinciding with that of the other rare-earth oxides, $4f^{n-1}6s^{1-i}6p^{1-i}5d^{1-i}$[6] where i is the degree of ionicity of the bonds[1)], then we obtain for the constants C_{4f}^{Eu} and C_{4f}^{Yb} the values

$$C_{4f}{}^{Eu} = -798 \pm 22\,\text{meV},\quad C_{4f}{}^{Yb} = -736 \pm 35\,\text{meV} \tag{4}$$

If, on the other hand, one assumes that metallic Eu and Yb have the configuration $4f^n6s^15d^1$ and that the trivalent oxides of these elements have the configuration $4f^{n-1}6s^{1-i}5d^{2(1-i)}$, then one obtains somewhat different values of the constants C_{4f}:

$$C_{4f}{}^{Eu} = -629 \pm 17\,\text{meV} \quad C_{4f}{}^{Yb} = -567 \pm 33\,\text{meV} \tag{4'}$$

In our present work we have continued the investigation of the chemical shifts of the $K\alpha_1$ lines in rare-earth compounds in order to determine the actual variant for Eu and Yb as well as to obtain the constants C_{4f} for the largest possible number of rare-earth elements for the purpose of comparing them with the available theoretical calculations.

THE EXPERIMENTAL AND THE RESULTS

All the measurements were carried out on the previously described experimental setup by the usual method.[3-6,8] Samples of hygroscopic compounds and rare-earth metals were placed in moisture-resistant, small, thin-walled containers; the structures of the investigated compounds were checked by means of x-ray diffraction. The results of the measurements are presented in Table I. The same table also includes results from a previous paper.[6] The letters "A", "B", and "C" denote the crystallographic modifications of the oxides (see, for example,[9]). The errors are mean-square errors obtained from the deviations of the individual measurement series from the average results (usually 10–20 series for each pair).

In a previous study[6] we determined the valence configurations of the majority of trivalent REM. In this work we determine the valence configurations of a further three REM—Pr, Tb, and Ho. The measured shifts of the $K\alpha_1$ lines for the Me_2O_3—Me pairs of the investigated elements (see Table I) are close to the calculated value $\Delta E = +39 \pm 19$ meV obtained under the assumption that trivalent REM have a $6s^16p^15d^1$ configuration. The closest possible configurations $6s^16p^2$ and $6s^15d^2$ would yield the values $\Delta E = +208 \pm 26$ meV and $\Delta E = -130 \pm 19$ meV respectively. Thus, one should assume for Pr, Tb, and Ho, as also for the remaining trivalent REM, the configuration $4f^n6s^16p^15d^1$.

For some trivalent rare-earth elements we measured the shifts for the MeF_3—Me (Sm, Gd, Tu, and Lu) and $MeCl_3$—Me (Sm) pairs. The shifts $\Delta E/i$ are close to those for the Me_2O_3—Me pairs attesting to the weak dependence of the reduced chemical shift (divided by the degree of ionicity i) on the nature of the partner in the bond.

Table I. Chemical shifts of the $K\alpha_1$ lines in rare-earth compounds

No.	Compounds		$\Delta E = E_A - E_B$, meV	i_A	No.	Compounds		$\Delta E = E_A - E_B$, meV	i_A
	A	*B*				*A*	*B*		
1	La_2O_3	La	-3 ± 10	0.89	18	Gd_2O_3 «*C*»	Gd	$+36 \pm 12$	0.85
2	CeO_2	Ce	-457 ± 15	0.87	19	GdF_3	Gd	-13 ± 15	0.94
3	Pr_2O_3	Pr	-20 ± 15	0.89	20	Tb_2O_3 «*C*»	Tb	$+19 \pm 15$	0.85
4	$PrO_{1,824}$	Pr	-263 ± 9		21	$TbO_{1,66}$	Tb	-268 ± 17	
5	Nd_2O_3 «*A*»	Nd	$+14 \pm 11$	0.87	22	$TbO_{1,73 \pm 0,02}$	Tb	-394 ± 18	
6	Nd_2O_3 «*C*»	Nd	$+50 \pm 10$	0.85	23	Dy_2O_3 «*C*»	Dy	$+10 \pm 14$	0.85
7	Sm_2O_3 «*B*»	Sm	$+32 \pm 11$	0.85	24	Ho_2O_3 «*C*»	Ho	$+1 \pm 17$	0.85
8	SmF_3	Sm	-44 ± 10	0.94	25	Er_2O_3 «*C*»	Er	$+18 \pm 43$	0.85
9	$SmCl_3$	Sm	-28 ± 11	0.89	26	Tu_2O_3 «*C*»	Tu	$+46 \pm 16$	0.85
10	$SmCl_2$	Sm	$\left\{\begin{array}{l}+545 \pm 12\\+615 \pm 12\end{array}\right.$	0.90	27	TuF_3	Tu	$+46 \pm 24$	0.94
					28	YbO_3 «*C*»	Yb	-582 ± 30	0.87
11	Eu_2O_3 «*C*»	Eu	-644 ± 13	0.87	29	YbF_3	Yb	-557 ± 27	0.95
12	EuF_3	Eu	-664 ± 12	0.95	30	Yb_2S_3	Yb	-520 ± 25	0.69
13	$EuCl_3 \cdot 6H_2O$	Eu	-623 ± 15	0.86	31	$YbCl_2$	Yb	-7 ± 30	0.90
14	$EuBr_3 \cdot 6H_2O$	Eu	-644 ± 20	0.84	32	Lu_2O_3 «*C*»	Lu	$+3 \pm 20$	0.85
15	$EUI_3 \cdot 6H_2O$	Eu	-618 ± 21	0.80	33	LuF_3	Lu	-48 ± 38	0.94
16	EuF_2	Eu	-1 ± 11	0.96					
17	EuF_3	EuF_2	-631 ± 15						

Special attention has been given in our work to those rare-earth elements which manifest a different valence in different compounds. These are—Ce, Pr, and Tb which can manifest a valence of 3 or 4, and Sm, Eu, and Yb which can manifest a valence of 2 or 3. As has been noted in the Introduction, the change in the valence is related to a change in the number of 4f electrons. Because of this it turns out to be possible to determine the constant C_{4f} for the indicated elements. Let us consider these cases in more detail.

1. Cerium. In the metallic state Ce exhibits the valence 3, characteristic for rare-earth elements. It is natural to assume that the distribution of valence electrons over the *l* states in metallic cerium is the same as in the remaining trivalent REM, i.e. that metallic Ce has the configuration $4f^16s^16p^15d^1$. However, in CeO_2 cerium exhibits the valence 4 releasing the last 4f electron to one of the valence levels and forming a stable state with zero 4f electrons. The four valence electrons in CeO_2 should distribute themselves among the three valence levels—6s, 6p, and 5d. The possible configurations are $4f^06s^{1-i}6p^{1-i}5d^{2(1-i)}$, $4f^06s^{1-i}6p^{2(1-i)}5d^{1-i}$, $4f^06s^{1-i}6p^{3(1-i)}$, $4f^06s^{1-i}5d^{3(1-i)}$, and $4f^05d^{4(1-i)}$. Making use of relations (1) and (2) one can write down expressions for the expected shifts between metallic Ce and CeO_2. Depending on the assumed configuration of CeO_2 these expressions will be of the form

$$\Delta E = C_{4f}{}^{Ce} + 2iC_{sp} + (2i-1)C_d = C_{4f}{}^{Ce} + 54 \tag{5a}$$

or

$$\Delta E = C_{4f}{}^{Ce} + (3i-1)C_{sp} + iC_d = C_{4f}{}^{Ce} + 28 \tag{5b}$$

etc. Using the experimental value of the shift for the CeO_2—Ce pair, we find hence for C_{4f}^{Ce} the values (in meV); -511 ± 24, -485 ± 24, -460 ± 23, -537 ± 25, and -562 ± 25. It is seen that the values of the constant C_{4f}^{Ce} do not depend very strongly on the choice of the valence configuration of CeO_2. This is due to the fact that CeO_2 is an ionic compound with a degree of ionicity close to 1 (i = 0.87); the valence electrons are to a large extent removed from the Ce atom and their

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[1)] As the ionicity scale we always use the same scale of Pauling [10] in which the degrees of ionicity are calculated according to the formula $i = 1 - m \exp[-\frac{1}{4}(\Delta x)^2]/n$ where m is the valence, n is the coordination number, and Δx is the electronegativity difference of the partners in the compound.[11]

distribution over the l states has little effect on the magnitude of the chemical shift determined mainly by the change in the number of 4f electrons.

In analogy with tetravalent Hf,[4] we consider the first of the above configurations $4f^0 6s^{1-i} 6p^{1-i} 5d^{2(1-i)}$ the most likely, and we take the constant C_{4f}^{Ce} to have the value

$$C_{4f}^{Ce} = -511 \pm 24 \text{ meV} \tag{6}$$

2. Praseodymium and terbium. In the metallic state Pr and Tb are trivalent. Their valence configurations have been established in this work (see above); Pr has the configuration $4f^2 6s^1 6p^1 5d^1$, and Tb has the configuration $4f^8 6s^1 6p^1 5d^1$. On being annealed in air Pr and Tb are partly oxidized to the tetravalent state producing oxides with the composition MeO_x where $1.5 < x < 2.0$; these can be considered as a mixture of the trivalent and tetravalent oxides. We obtained mixed oxides of the composition $PrO_{1.824}$ (35 percent Pr_2O_3 and 65 percent PrO_2) and $TbO_{1.66}$ (67 percent Tb_2O_3 and 33 percent TbO_2)[2)] by direct combustion in air of metallic Pr and Tb at a temperature of ~800°C. The oxide composition was determined by gravimetric analysis.

If it is assumed, as in the case of Ce, that the tetravalent oxides of Pr and Tb have the configurations $4f^1 6s^{1-i} 6p^{1-i} 5d^{2(1-i)}$ and $4f^7 6s^{1-i} 6p^{1-i} 5d^{2(1-i)}$ respectively, then the expressions for the expected $K\alpha_1$ shifts will be of the form

$$\begin{aligned} \Delta E(PrO_{1.824} - Pr) &= 0{,}35(2iC_{sp} + iC_d) + 0{,}65[C_{4f}^{Pr} + 2iC_{sp} \\ &\quad \times (2i-1)C_d] = 0.65C_{4f}^{Pr} + 49; \\ \Delta E(TbO_{1.66} - Tb) &= 0{,}67(2iC_{sp} + iC_d) + 0.33[C_{4f}^{Tb} + 2iC_{sp} \\ &\quad \times (2i-1)C_d] = 0.33C_{4f}^{Tb} + 44. \end{aligned} \tag{7}$$

Substituting in these the experimental values of the shifts, we obtain for the constants C_{4f}^{Pr} and C_{4f}^{Tb}:

$$C_{4f}^{Pr} = -480 \pm 30 \text{ meV} \quad C_{4f}^{Tb} = -940 \pm 80 \text{ meV} \tag{8}$$

Mixed oxides of Pr and Tb can also be obtained by thermal decomposition of the corresponding carbonates. We thus obtained a Tb oxide with a composition $TbO_{1.73 \mp 0.02}$. The amount of TbO_2 in the mixture was determined by titration. Using the experimental value of the shift of the pair $TbO_{1.73 \mp 0.02}-Tb$ one can, as above, determine the constant C_{4f}^{Tb}. The obtained value of

$$C_{4f}^{Tb} = -960 \mp 90 \text{ meV} \tag{8'}$$

is in good agreement with that obtained above.

3. Europium and ytterbium. The constants C_{4f}^{Eu} and C_{4f}^{Yb} have already been determined in our previous work[6] on the basis of measurements of the shifts for the pairs Eu_2O_3-Eu and Yb_2O_3-Yb. In the metallic state Yb and Eu are divalent; their two valence electrons should be distributed over the 6s, 6p, and 6d valence states producing one of the possible valence configurations $6s^1 5d^1$, $6s^1 6p^1$, $6p^2$, and $5d^2$. Which of these configurations is actually established can be determined by measuring the chemical shift of the $K\alpha_1$ lines between metallic Eu and Yb and their divalent ionic compounds. We measured the shifts for the EuF_2-Eu and $YbCl_2-Yb$ pairs. The expected shifts $\Delta E/i$ calculated from relations (1) and (2) are -35 ∓ 14 meV for the configuration $6s^1 5d^1$, $+160 \mp 20$ meV for the configurations $6s^1 6p^1$ and $6p^2$, and -230 ± 20 meV for the configuration $5d^2$. The experimental values $\Delta E/i = -1 \mp 11$ meV for the EuF_2-Eu pair and $\Delta E/i = -8 \mp 33$ meV for the $YbCl_2-Yb$ pair provide evidence favoring the $6s^1 5d^1$ configuration. The trivalent oxides of Eu and Yb have apparently the same configuration as the other rare-earth elements, i.e., the configuration $6s^{1-i} 6p^{1-i} 5d^{1-i}$,[6] since they differ in no way in their physical properties (lattice parameters, structure of the infrared spectra, etc) determined by the nature of their chemical bond from the other rare-earth oxides.[7,9] Using the indicated configurations, we obtain from the experimental $K\alpha_1$ shifts for the pairs Eu_2O_3-Eu and Yb_2O_3-Yb the following values of the constants C_{4f}^{Eu} and C_{4f}^{Yb}:

$$C_{4f}^{Eu} = -604 \pm 18 \text{ meV}, \quad C_{4f}^{Yb} = -542 \pm 32 \text{ meV}, \quad \bar{C}_{4f}^{Eu,\,Yb} = -573 \pm 30 \text{ meV}, \tag{9}$$

which differ somewhat from the variants cited in[6] [relations (4) and (4′) of the Introduction].

The obtained values of the constants are practically independent of the ionicity scale. In fact, the expression for the expected shift between metallic Eu and Yb and their trivalent ionic compounds is of the form

$$\Delta E = C_f + (2i-1)C_{sp} + iC_d \tag{10}$$

or, if one uses the values of the constants C_{sp}, C_d, and $\bar{C}_{4f}$ from (2) and (9),

$$\Delta E = -653 + 45i, \tag{10'}$$

whence it is seen that the magnitude of the shift varies in all by 7 percent when the degree of ionicity varies between 0 and 1. The measured shifts for the trivalent europium halide—europium have in fact turned out practically to coincide (see Table I).

A similar result has been obtained for Yb for which we measured the shifts for the pairs YbF_3-Yb and Yb_2S_3-Yb. If we make use of these measurements for determining the constants C_{4f}^{Eu} and C_{4f}^{Yb}, then we obtain the following values:

From the shift for the pairs	C_{4f}^{Eu}, meV	C_{4f}^{Yb}, meV
EuF_3-Eu:	-627 ∓ 17	—
$EuCl_3 \cdot 6H_2O-Eu$:	-582 ∓ 19	—
$EuBr_3 \cdot 6H_2O-Eu$:	-602 ∓ 23	—
$EuI_3 \cdot 6H_2O-Eu$:	-574 ∓ 24	—
YbF_3-Yb:	—	-520 ∓ 31
Yb_2S_3-Yb:	—	-471 ∓ 30

(11)

Finally, we measured the shift of the $K\alpha_1$ lines for the pair of compounds EuF_3-EuF_2. In these compounds with almost 100 percent ionic bonding ($i = 0.96$ for EuF_2 and $i = 0.95$ for EuF_3) the valence electrons are almost completely removed from the Eu atom and the magnitude of the shift is practically equal to the constant C_{4f}^{Eu}. The measured value of the shift for the pair EuF_3-EuF_2 is $\Delta E = -631 \mp 15$ meV which is in good agreement with the values of the constant C_{4f}^{Eu} obtained above [relations (9) and (11)].

The average values of the constants $\bar{C}_{4f}^{Eu}$ and $\bar{C}_{4f}^{Yb}$ from all the measured pairs of compounds are found to be

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[2)] The percentages indicate the fractions of the initial metals in the corresponding oxides.

$$\bar{C}_{4f}{}^{\mathrm{Eu}} = -603 \mp 10\ \mathrm{meV} \quad \bar{C}_{4f}{}^{\mathrm{Yb}} = -511 \pm 21\ \mathrm{meV} \tag{12}$$

4. Samarium. In the metallic state Sm is trivalent. Its valence electrons are distributed over the l states in such a way that the $4f^5 6s^1 6p^1 5d^1$[6] configuration is established; however, Sm can form compounds in which it exhibits a valence of 2. When Sm goes over from the trivalent to the divalent state one of its valence electrons apparently escapes to the 4f shell, and the remaining two electrons are distributed over the 6s, 6p, and 6d valence levels with the formation of one of the possible configurations: $4f^6 6s^1 5d^1$, $4f^6 6s^1 6p^1$, and $4f^6 5d^2$. We obtained samarium dichloride by reduction of anhydrous samarium trichloride with metallic samarium. The synthesis was carried out twice with a 10-percent and with a 100-percent excess of Sm relative to that required stoichiometrically.

We measured the chemical shifts relative to metallic Sm for each of the resulting compounds ($SmCl_2$I and $SmCl_2$II). If one assumes the configuration of Sm in $SmCl_2$ to be the same as in the divalent compounds of Eu and Yb, i.e., $4f^6 6s^{1-i} 5d^{1-i}$, then the expression for the expected shift will be of the form

$$\Delta E = -C_{4f}{}^{\mathrm{Sm}} + i(C_{sp} + C_d) + C_{sp} = -C_{4f}{}^{\mathrm{Sm}} + 49. \tag{13}$$

Taking into account the fact that the constant C_{4f} should be negative, one would have expected a positive shift for the pair $SmCl_2$–Sm. The experimental shifts proved indeed to be positive (see Table I), and the magnitudes of the shifts differed somewhat depending on the method of obtaining the $SmCl_2$. This is apparently connected with the fact that for a 10-percent excess of Sm complete reduction of $SmCl_3$ to $SmCl_2$ does not occur.

Using the experimental values of the shifts for the pairs $SmCl_2$I–Sm and $SmCl_2$II–Sm, we obtain from (13) for the constant C_{4f}^{Sm}

$$C_{4f}{}^{\mathrm{Sm}}(\mathrm{I}) = -496 \mp 24\ \mathrm{meV} \quad C_{4f}{}^{\mathrm{Sm}}(\mathrm{II}) = -566 \mp 24\ \mathrm{meV} \tag{14}$$

In calculating C_{4f}^{Sm} we assumed that $SmCl_2$ has the configuration $4f^6 6s^{1-i} 5d^{1-i}$; however, the choice of the valence configuration is of little importance here because of the large degree of ionicity of $SmCl_2$ ($i = 0.9$). The other two possible configurations would yield the following values of C_{4f}^{Sm}: for $4f^6 6s^{1-i} 6p^{1-i}$

$$C_{4f}{}^{\mathrm{Sm}}(\mathrm{I}) = -516 \mp 24\ \mathrm{meV} \quad C_{4f}{}^{\mathrm{Sm}}(\mathrm{II}) = -586 \mp 24\ \mathrm{meV} \tag{15a}$$

and for $4f^6 5d^{2(1-i)}$

$$C_{4f}{}^{\mathrm{Sm}}(\mathrm{I}) = -477 \mp 25\ \mathrm{meV} \quad C_{4f}{}^{\mathrm{Sm}}(\mathrm{II}) = -547 \mp 25\ \mathrm{meV} \tag{15b}$$

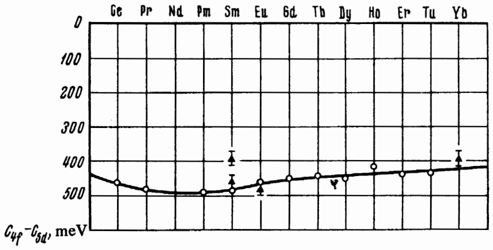
Below we present the values of the constants C_{4f} which we have obtained:

Element:	Ce	Pr	Sm	Eu	Tb	Yb
C_{4f}^{exp}, meV	−511±24	−480±30	−566±24 −496±24	−603±10	−940±80 −960±90	−511±21

Since the 4f electrons are least affected by the external surroundings, these values can be compared directly with those calculated for free atoms.

COMPARISON OF EXPERIMENT AND THEORY

As has already been noted in the Introduction, a theoretical determination of the constants C_l requires self-consistent calculations of the wave functions for the atom and for the l ion of the given element. At present such calculations can apparently be carried out for all elements of the periodic table; little published data is, however, available for elements with $Z > 36$, including the rare-earth elements which are of interest to us, and the available few calculations are at times carried out with insufficient accuracy for our purpose (for example, the calculations for Tb in the monograph of Herman and Skillman[12]). The relative accuracy with which the orbital energies required for obtaining the constants C_l must be calculated is of the order of 10^{-6}–10^{-7}, since the errors in the determination of the experimental constants C_l are of the order of a few hundredths of an electron volt while the energies of the $1s_{1/2}$ state in the region $32 \lesssim Z \lesssim 74$ considered by us are of the order of several dozen kilo-electron volts.



Comparison of theoretical and experimental differences of the constants $C_{4f} - C_{5d}$. Continuous curves with circles – theoretical, triangles – experiment.

It has recently become possible for us to compare our experimental values of the constants C_{4f} with theoretical values calculated by Waber (private communication and[13]) within the framework of a self-consistent model employing the Dirac equation with allowance for exchange interaction according to one of Slater's variants. The energy difference of the $K\alpha_1$ lines for the calculated rare-earth configurations $4f^n 6s^2$ and $4f^{n-1} 5d^1 6s^2$ is equal in our notation to the difference of the constants C_{4f} and C_{5d}.

The calculated differences are shown in the Figure by circles and by the continuous curve; in the second column of Table II we present the numerical values of these differences for the elements of interest to us. We can obtain similar differences of the constants by using the experimental values of C_{4f} and the value C_d from relation (2). These differences are given in the third and fifth columns of Table II. A direct comparison with the calculated differences between the constants can only be carried out for Sm, Eu, and Yb. The point is that the calculated configurations correspond to divalent (II) and trivalent (III) states of rare-earth elements. For Sm, Eu, and Yb we measured the chemical shifts of the $K\alpha_1$ lines precisely between the divalent and trivalent states of these elements. For Ce, Pr, and Tb we measured the chemical shifts between trivalent and tetravalent (IV) states of the indicated elements, i.e., shifts between the configurations $4f^{n-1} 5d^1 6s^2$ and $4f^{n-2} 5d^2 6s^2$. In forming the tetravalent state the second of the f electrons in Waber's initial configuration is removed; the shifts on removing the first and second f electrons need by no means be equal.

The experimental differences of the constants

Table II. Comparison of theoretical and experimental values of $C_{4f} - C_{5d}$

Element	II → III			III → IV
	$C_{4f} - C_{5d}$, meV		Deviation from theory, percent	$C_{4f} - C_{5d}$, meV
	theory	experiment		experiment
Sm	—430	—381±26 —451±26	+23 +6	
Eu	—464	—488±14	—5	
Yb	—430	—396±23	+8	
Ce	—463			—396±26
Pr	—480			—365±32
Tb	—444			—825±80 —845±90

$(C_{4f} - C_{5d})_{exp}$ for the elements Sm, Eu, and Yb are plotted in the figure as triangles. As is seen from the Figure and from Table II, very good agreement is observed with the calculated differences of the constants. For Ce, Pr, and Tb such a comparison will become possible when the calculation analogous to the one carried out will be performed for the configurations $4f^{n-1}5d^1 6s^2$ and $4f^{n-2}5d^2 6s^2$ of the indicated elements.

CONCLUSION

The conclusion of the previous paper[6] that the shifts of the $K\alpha_1$ lines appearing when the 4f electron is removed from the atom (the constants C_{4f}) differ sharply from the corresponding shifts when the sp- and d-symmetry electrons are removed is confirmed. This makes it possible to utilize the chemical shift of the $K\alpha_1$ lines as a method of investigating phenomena connected with the change in the number of 4f electrons.

The quantitative agreement of the experimental and theoretical constants C_{4f} attests to the fact that the effect of the field on the 4f electrons is indeed not large, and the basic mechanism of the investigated effect of the chemical shift of the $K\alpha_1$ lines is the mutual screening mechanism taken into account within the framework of the self-consistent model used in the theoretical calculations.

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133