SOVIET PHYSICS JETP VOLUME 29, NUMBER 2 AUGUST, 1969

CHEMICAL SHIFTS OF THE K_{α_1} X-RAY LINES DURING THE OXIDATION OF RARE EARTH METALS. THE ROLE OF THE f ELECTRONS

O. I. SUMBAEV, Yu. P. SMIRNOV, E. V. PETROVICH, B. S. ZYKOV, A. I. EGOROV, and A. I. GRUSHKO

A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences

Submitted September 24, 1968

Zh. Eksp. Teor. Fiz. **56**, 536–540 (February, 1969)

The energy differences between the K_{α_1} x-ray lines were measured for several rare-earth metals and their sesquioxides for the purpose of obtaining further information on the role of valence electrons with different orbital quantum numbers (the s, p, d, f electrons) in the chemical shift effect.[3-5] It was found that while the shifts for all trivalent rare-earth metals were approximately equal and relatively small, the shifts due to the oxidation of divalent metallic Eu and Yb to Eu_2O_3 and Yb_2O_3 were anomalously large and had a negative sign (cf. table). These anomalous shifts were attributed to changes in the number of f electrons during the oxidation of Eu and Yb; the constant $C_f = -760 \pm 30$ MeV (cf.[3-5]) was determined and found to differ considerably from the corresponding constants for sp and d electrons:

$$C_{sp} = +75 \pm 5 \text{ meV} \quad C_d = -115 \pm 10 \text{ meV}$$

This should make it possible easily to distinguish the f electrons from the sp and d electrons when the effect considered here is used as a method for investigating valence configurations of chemical bonds.[4]

INTRODUCTION

INVESTIGATIONS of the chemical shift of the inner levels of heavy atoms[1,2] have shown that the difference between the energies of the K_{α_1} x-ray lines ($2p_{3/2} \rightarrow 1s_{1/2}$) of an element (usually a metal) and its compound (usually an oxide or a compound with one of the elements in the oxygen group) satisfies a simple relationship[3-5] in the range $32 \lesssim Z \lesssim 74$:

$$\Delta E \equiv E_{Ox} - E_{Me} = \sum_l C_l \Delta m_l, \tag{1}$$

where $\Delta m_l = m_l^{(Me)} - m_l^{(Ox)}$ is the difference between the numbers of the l-type (l = s, p, d) electrons in the metal and its oxide; C_l represents the values of the shift corresponding to the removal of one l-type electron.

In the investigated range of values $\Delta m_l \lesssim 3$, the coefficients C_l are found to be independent of the value of Δm_l, i.e., the effect of the removal of n valence electrons of a given type is n times larger than the effect of the removal of one valence electron. The coefficients C_l are also independent of (or very weakly dependent on) the atomic number Z of the element and the principal quantum number of the valence electron, i.e., they are universal constants for all the investigated elements. In the case of the dependence of C_l on the orbital quantum number l, it is found that[3-5]

$$C_s \approx C_p \equiv C_{sp} = +75 \pm 5 \text{ meV} \quad C_d = -115 \pm 10 \text{ meV} \tag{2}$$

i.e., the effects of the removal of an s or p electron are approximately equal, whereas the effect of the removal of a d electron differs not only in the absolute value but also in its sign. This makes it possible to distinguish groups of sp and d electrons when the chemical shift is used as a method for the determination of the valence configurations of chemical bonds.[4,5]

A natural continuation of these investigations is the study of the role of the f electrons, i.e., a determination of the constant C_f. The radial wave function of the 4f electrons is described by a curve with a single maximum, which overlaps the wave function of the $2p_{3/2}$ (L_{III}) level much more than the function of the $1s_{1/2}$ (K) level so that naturally we would expect a negative sign for the constant C_f. The absence of satisfactory Hartree-Fock calculations for the f ions of heavy elements makes it impossible, at present, to obtain a quantitative theoretical value of this constant. The present paper describes an attempt to determine C_f experimentally.

EXPERIMENTS AND RESULTS

We measured the energy differences between the K_{α_1} x-ray lines of rare-earth metals and their sesquioxides (Me_2O_3). The rare-earth elements in trivalent oxides can have configurations of the type $(\ldots 4f^n)6s^{1-i}6p^{1-i}5d^{1-i}$ or, for example, $(\ldots 4f^n)6s^{1-i}5d^{2(1-i)}$, where i is the degree of ionicity of the bonds. The valence configurations of trivalent metals can be similar, differing only in the degree of ionicity of the bonds.[1] The number of the f electrons in the metal and its oxide remains unchanged. The expressions for the expected effects are of the form

$$\Delta E = i(2C_{sp} + 1C_d) \quad \text{or} \quad \Delta E = i(1C_{sp} + 2C_d) \tag{3}$$

and so on, i.e., they contain only the known constants C_{sp} and C_d.

---

[1] The degree of ionicity of bonds in metals should naturally be assumed to be zero.

In the case of Eu and Yb, which are divalent in the metallic state, the situation may be somewhat different. We can expect the valence configurations $(\ldots 4f^7)6s^1 6p^1$ or $(\ldots 4f^7)6s^1 5d^1$ for Eu and, correspondingly, $(\ldots 4f^{14})6s^1 6p^1$ or $(\ldots 4f^{14})6s^1 5d^1$ for Yb and the presence of the energetically advantageous states with completely or half-filled f shells. To realize the trivalent state, one of the f electrons in the sesquioxides of these metals should become a valence electron, i.e., it should go over into a p or d state thereby giving rise to configurations of the $(\ldots 4f^6)6s^{1-i}6p^{1-i}5d^{1-i}$ or $(\ldots 4f^6)6s^{1-i}5d^{2(1-i)}$ type in Eu_2O_3 and of the $(\ldots 4f^{13})6s^{1-i}6p^{1-i}5d^{1-i}$ or $(\ldots 4f^{13})6s^{1-i}5d^{2(1-i)}$ type in Yb_2O_3.

The expressions for the expected effects should contain the constant C_f, in addition to the constants C_{sp} and C_d:

$$\Delta E = 2iC_{sp} + (i-1)C_d + C_f \quad \text{or} \quad \Delta E = iC_{sp} + (2i-1)C_d + C_f. \tag{4}$$

Thus, in the sequence of approximately equal shifts, described by relationships of the Eq. (3) type for the metal-sesquioxide pairs of all the rare-earth elements, we should expect anomalies in the case of Eu and Yb, whose sign and magnitude would allow us, using Eq. (4), to determine the sign and value of C_f.

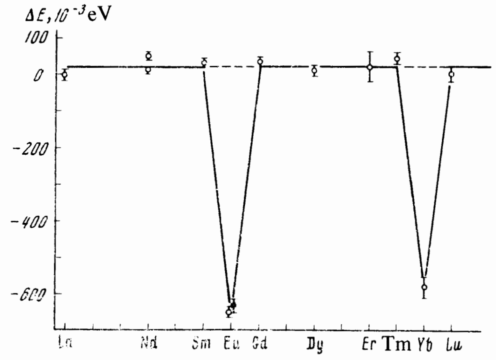
The experimental method was identical with that used in our previous investigations,[2-5] but the samples were usually placed in moisture-proof thin-walled dishes, their crystal structures were checked by x-ray diffraction, and in some cases the structure was determined before and after measurements.

The results are presented in the table and the figure. The letters A, B, C are used to denote the various crystallographic modifications of the oxides (cf., for example,[6]). The errors are the rms values, calculated from the deviations from the average results in each series of measurements (usually 10–20 series of measurements were carried out for each pair). The result for the Eu_2O_3-Eu pair was checked using new apparatus developed for investigations in the isotopic shift range;[7] the value obtained is denoted by an asterisk.

For all the investigated elements (with the exception of Eu and Yb), we indeed obtained approximately equal values of the shifts.[2)] It is important to note that the average experimental value[3)]

$$\overline{\Delta E}/i = +27 \pm 7\ \text{meV}$$

agreed, within the limits of the experimental error, with the value calculated from the first of the relationships in Eq. (3) using the values of the constants found earlier [cf. Eq. (2)]:



Energy differences between the K_{α_1} x-ray lines of rare-earth metals and their sesquioxides: $\Delta E \equiv E_{Ox} - E_{Me}$.

$$\Delta E/i = +35 \pm 14\ \text{meV}$$

This supported quite clearly the $6s^1 6p^1 5d^1$ configuration for trivalent rare-earth metals and their oxides. This configuration fits a general sequence of the $6s^1 6p^1 5d^{(m-2)}$ type (where m is the valence), established earlier[4] for the transition metals in the sixth period (Ba-W sequence). The nearest possible configurations $6s^1 6p^2$ and $6s^1 5d^1$ would have given values for $\Delta E/i$ equal to, respectively, +225 ± 15 and −155 ± 20 meV.

The effects for Eu and Yb differed considerably in magnitude and sign. Assuming the $6s^1 6p^1$ configuration for metallic Eu and Yb, by analogy with the divalent neighbor Ba[4] and in agreement with the general sequence $6s^1 6p^1 5d^{(m-2)}$, and assuming that the sesquioxides of these elements have the same configuration as the other rare-earth oxides, $6s^1 6p^1 5d^1$, i.e., using the first of the two relationships in Eq. (4), we find the constant C_f, using the values of C_{sp} and C_d from Eq. (2):

$$C_{4f}^{(\text{Eu})} = -789 \pm 13\ \text{meV} \quad C_{4f}^{(\text{Yb})} = -727 \pm 31\ \text{meV}$$
$$\bar{C}_{4f} = -760 \pm 30\ \text{meV} \tag{5}$$

The values obtained do not depend strongly on the assumed variants of the structure. For example, the use of the second relationship in Eq. (4) gives the values

$$C_{4f}^{(\text{Eu})} = -626 \pm 13\ \text{meV} \quad C_{4f}^{(\text{Yb})} = -564 \pm 31\ \text{meV}$$
$$\bar{C}_{4f} = -600 \pm 30\ \text{meV} \tag{5$'$}$$

It is important to note that the values of the constant C_f differ markedly from C_{sp} and C_d, which makes it possible easily to observe any changes in the number or distribution of the f electrons associated with the formation of chemical compounds and to use the investigated chemical shift as a method for investigating such changes.

One of the simplest examples of this kind of application is the case of Ce and its dioxide: CeO_2-Ce. The simplest model of the structure of this compound is obtained on the assumption that metallic Ce is trivalent and has a valence configuration similar to that found for other trivalent metals $(\ldots 4f)6s^1 6p^1 5d^1$; if Ce is

---

[2)] During these measurements, we found that the value that we published earlier [4] for the La_2O_3–La pair was wrong. The error was due to the faulty construction of the protective Lucite dish used hermetically to seal a sample in the first experiment on La: the edge of the dish was in the field of view of our apparatus and this produced a large aberration shift which completely distorted the result.

[3)] The degree of ionicity i, calculated using Pauling's formula (cf. [4]), was assumed to be the same (0.86) for all the rare-earth oxides that we investigated.

Differences between energies of K_{α_1} lines of rare-earth metals and their oxides

Compound	Form of Oxide	$\Delta E = E_{Me_2O_3} - E_{Me}$, meV	$\Delta E/i$, meV
$La_2O_3 - La$	*A*	-3 ± 10	-3 ± 12
$Nd_2O_3 - Nd$	*A*	$+14 \pm 11$	$+16 \pm 13$
$Nd_2O_3 - Nd$	*C*	$+50 \pm 10$	$+58 \pm 12$
$Sm_2O_3 - Sm$	*B*	$+32 \pm 11$	$+37 \pm 13$
$Gd_2O_3 - Gd$	*C*	$+36 \pm 12$	$+42 \pm 14$
$Dy_2O_3 - Dy$	*C*	$+10 \pm 14$	$+12 \pm 16$
$Er_2O_3 - Er$	*C*	$+18 \pm 43$	$+21 \pm 50$
$Tu_2O_3 - Tu$	*C*	$+46 \pm 16$	$+53 \pm 19$
$Lu_2O_3 - Lu$	*C*	$+3 \pm 20$	$+3 \pm 23$
Average		$+23 \pm 7$	$+27 \pm 8$
$Eu_2O_3 - Eu$	*C*	-653 ± 12 -635 ± 20 *	-749 ± 12
$Yb_2O_3 - Yb$	*C*	-582 ± 30	-677 ± 35

tetravalent in the oxide, then its configuration can be, by analogy with neighboring Hf,[4] $(\ldots 4f^0)6s^{1-i}6p^{1-i}5d^{2(1-i)}$. Then, we can expect the CeO_2-Ce shift to obey the relationship

$$\Delta E = 2iC_{sp} + [1 - 2(1 - i)]C_d + C_f.$$

Substituting $i = 0.86$ (mentioned earlier in the paper), as well as the values of C_{sp}, C_d from Eq. (2) and $\overline{C}_f$ from Eq. (5), we obtain

$$\Delta E = -710 \pm 30 \text{ meV}$$

Naturally, we should not expect an exact quantitative agreement in view of the approximate nature of the model and because the effect of the removal of the first f electron (Ce) may differ from the effects of removal of the seventh (Eu) and fourteenth (Yb) f electrons, which have been used to find the value of $\overline{C}_f$. However, we may expect a qualitative or even semiquantitative agreement whose degree would give us an idea of the accuracy of the method. We recently obtained an experimental value

$$\Delta E(CeO_2 - Ce) = -460 \pm 15 \text{ meV}$$

which is in satisfactory agreement with the predicted value.

The authors are grateful to Professor D. M. Kaminker for his interest in this investigation, and to V. I. Marushenko and A. S. Ryl'nikov for their part in the control measurements on Eu.

We are very grateful to V. B. Glushkova for advice on the method of preparation of a number of oxides and for kindly supplying some of them.

---

[1] O. I. Sumbaev and A. F. Mezentsev, Zh. Eksp. Teor. Fiz. 48, 445 (1965) [Sov. Phys.-JETP 21, 295 (1965)].

[2] O. I. Sumbaev, A. F. Mezentsev, V. I. Marushenko, E. V. Petrovich, and A. S. Ryl'nikov, Zh. Eksp. Teor. Fiz. 50, 861 (1966) [Sov. Phys.-JETP 23, 572 (1966)].

[3] E. V. Petrovich, O. I. Sumbaev, V. S. Zykov, Yu. P. Smirnov, A. I. Egorov, and A. I. Grushko, Zh. Eksp. Teor. Fiz. 53, 796 (1967) [Sov. Phys.-JETP 26, 489 (1968)].

[4] O. I. Sumbaev, E. V. Petrovich, Yu. P. Smirnov, A. I. Egorov, V. S. Zykov, and A. I. Grushko, Zh. Eksp. Teor. Fiz. 53, 1545 (1967) [Sov. Phys.-JETP 26, 891 (1968)].

[5] E. V. Petrovich, O. I. Sumbaev, V. S. Zykov, A. I. Egorov, Yu. P. Smirnov, and A. I. Grushko, Zh. Eksp. Teor. Fiz. 55, 745 (1968) [Sov. Phys.-JETP 28, 385 (1969)].

[6] V. B. Glishkova, Polimorfizm okislov redkozemel' nykh élementov (Polymorphism of Oxides of Rare-Earth Elements), Nauka, Leningrad, 1967.

[7] O. I. Sumbaev, A. F. Mesentsev (Mezentsev), V. I. Marushenko, and A. S. Rilnikov (Ryl'nikov, Mezhdunarodnyi simpozium po strukture yadra, Dubna, 1968, Soobshcheniya uchastnikov (Papers presented at International Symposium on Nuclear Structure, Dubna, 1968), p. 179.

Translated by A. Tybulewicz
68