The Influence of the Chemical State on K x-Ray Intensities*

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The x-ray intensities of the Kβ and KO lines relative to the Kα_1 transition were measured with high accuracy for the pairs La_2O_3-La, SmS-Sm, Sm_2O_3-Sm and Ta_2O_5-Ta. The Kβ_{13} and Kβ_{24} lines do not show significant intensity shifts. However, the intensity of the KO line is in La_2O_3 (15.0 ± 4.7)% higher, in SmS (6.9 ± 2.7)% lower and in Ta_2O_5 (12.5 ± 8.7)% higher than that emitted from the corresponding metal. These results can be reproduced by Dirac-Fock-calculations, where the KO-intensities show a typical dependence on the quantum numbers of the valence electrons. The observed shifts indicate a 4f−5d hybridization or promotion in metallic Lanthanum and suggest the missing of a 4f electron in metallic Samarium compared to the free atom.

1. Introduction

The study of energy shifts of K x-rays yields information about several nuclear and atomic properties [1]:

- Differences of nuclear charge radii can be determined from isotope shifts [2].
- Hyperfine splitting yields nuclear magnetic moments [3].
- Influences of the atomic structure and even dynamics can be studied [4].
- Chemical shifts can be used to determine the valence electrons in compounds and alloys [5].

These energy shifts are very small, typically $\lessapprox$ 1 eV for heavy elements, sometimes even $\leqq$ 10 meV. Therefore, their measurement requires high resolution.

In principle, also intensity shifts should occur. In practice, however, their determination is rendered very difficult by absorption effects within the samples. Intensity shifts of individual x-ray lines can be determined with the use of high-resolution spectrometers. In such measurements selfabsorption is the only major source of error.

In the present work we have attempted to search for intensity shifts of K x-rays in heavy elements in different chemical states, because the relatively large chemical shifts of K x-ray energies suggest that in such cases intensity shifts might become observable.

The measured x-ray intensity I from a photoexcited sample depends on four factors [6]:

$$I = J\, \varepsilon\, s\, p,$$

where J is proportional to the source strength, ε is the spectrometer efficiency, s describes excitation and absorption in the sample and p is the transition probability.

If we measure the fourfold ratio

$$V_4(K_j) = \frac{I(K_j,\text{compound})}{I(K\alpha_1,\text{compound})} \Big/ \frac{I(K_j,\text{metal})}{I(K\alpha_1,\text{metal})},$$

problems with the determination of the source strength and spectrometer efficiency are avoided. Of course, this method does not permit the observation of Kα_1 intensity shifts.

2. Apparatus

All measurements were carried out with a high-resolution curved crystal spectrometer [7] (Figure 1).

The resolution of the apparatus is ~25 eV at 50 keV in first order reflection, which has to be compared with a typical x-ray line width of 30 eV at this energy.

The x-ray source consisted of a pair of samples photoexcited by a 40 Ci source of ^{169}Yb at close distance.

The two samples, one metallic, the other a chemical compound, were mounted in a special source holder similar to the one in [8]. One sample (typically 5 mm × 1 mm × 0.01 mm) was located with its center 3 mm above the symmetry plane of the spectrometer, the other 3 mm below. Both samples were at a sample angle $\alpha = 28°$ with respect

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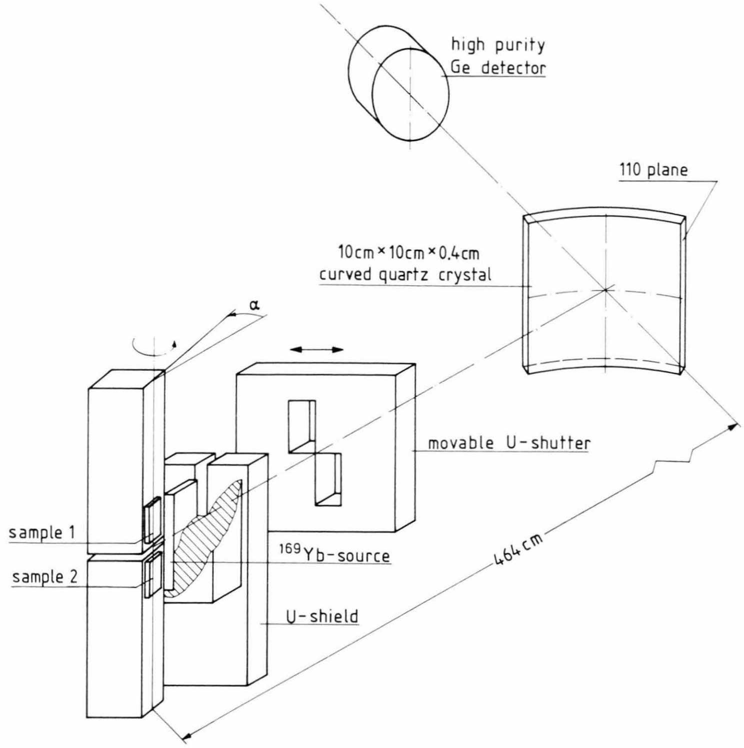

Fig. 1. The DuMond-type spectrometer of the Institut für Kernphysik with sample holder (at a sample angle α), movable U shutter, crystal and detector [7, 8].

to the direction of the beam to the spectrometer to minimize the systematic error due to the selfabsorption. A suitable Uranium shutter permitted the transmission of fluorescence radiation from only one sample at a time with frequent changes, so that the intensity measurements were carried out quasi-simultaneously with suitably gated detector-electronics. This procedure reduced the influence of all kinds of drifts both of the spectrometer and of the electronics. The Ge-detector allowed a more efficient background reduction than the commonly used NaI-counters.

The main problem was the proper treatment of selfabsorption. The energy dependence of x-ray absorption cross sections leads to trivial intensity shifts for samples of different geometry.

To correct for selfabsorption effects one has to know these cross sections and the sample geometry with sufficient accuracy.

With a computer program the selfabsorption shifts of relative $K\beta_{13}$-intensities were calculated. These data were compared with measurements on Sm_{met}- and Sm_2O_3-samples of different thicknesses and sample angle α. For angles α, where the sample geometry was well defined, good agreement was observed. We have, therefore, chosen a sample angle of 28°, a compromise between low selfabsorption and small geometrical linewidth.

A special situation exists for the KO absorption.

The KO-energy is very close to the K-absorption edge. Because of the natural linewidth of the KO-transition and the gradual rise of the K-edge they overlap. The energy difference and the K-edge structure depend on the chemical state [9]. Therefore, the KO-absorption cross sections can depend on the chemical state. To study this effect we have measured the absorption cross sections of photoionized Sm_{met} K x-rays in Sm_{met}-absorbers and of Sm_2O_3 K x-rays in Sm_2O_3-absorbers. The results, displayed in Fig. 2, show a remarkable difference of the KO-cross section from the lower edge value and they are even consistent with a difference between metal and oxide.

With a simple model, where the *K*-edge was approximated by a step function, we could reproduce the order of magnitude of this effect. This and the Sm-measurement yielded the following result: The KO-intensity shift is less affected by selfabsorption than the $K\beta_1$-shift, both relative to the $K\alpha_1$-line.

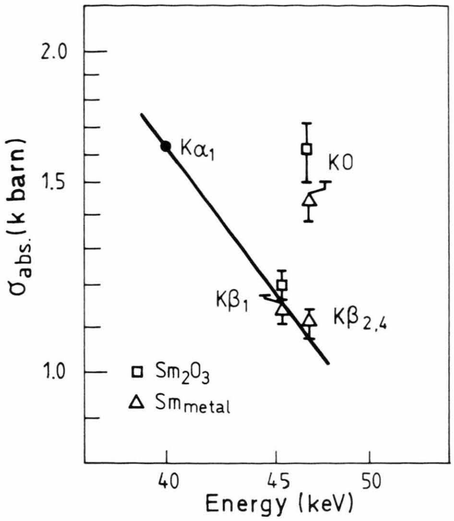

Fig. 2. Absorption cross sections for Sm_{met}-x-rays in Sm_{met} and Sm_2O_3-x-rays in Sm_2O_3. The $K\alpha_1$-line served as reference. The full line is from [10].

3. Measurements

The intensities of the $K\alpha_1$, $K\beta_{13}$, $K\beta_{24}$ and KO transitions were measured for the pairs listed in Table 1. The lines were recorded in 40–50 angle steps covering a range of about 3 FWHM. This wide range was necessary to determine the background correctly. The $K\alpha_1$-line was measured relatively often to detect drifts and irregularities (especially before and after every KO measurement). In the La measurement special care was taken to avoid errors introduced by oxidation of the La_{met} sample. Room background was measured at the KO angle positions.

All lines were measured repeatedly at positive and negative Bragg angles, the KO-line at least 8 times with up to 3 days measuring time per reflex.

Typical peak count rates ranged from $10\ s^{-1}$ for Sm-$K\alpha_1$ and $0.1\ s^{-1}$ for Sm-KO to $1\ s^{-1}$ for Ta-$K\alpha_1$ and $0.01\ s^{-1}$ for Ta-KO with a constant room background of about $0.08\ s^{-1}$.

Table 1. List of measured samples and configurations.

Sample pair	Configuration of free atoms Xe-core [11]	Valence of compound
La_2O_3-La_{met}	$5d^16s^2$	3
SmS-Sm_{met}	$4f^66s^2$	2
Sm_2O_3-Sm_{met}	$4f^66s^2$	3
Ta_2O_5-Ta_{met}	$4f^{14}5d^36s^2$	5

4. Results

The measured data were analyzed as described elsewhere [6]. The results are shown in Table 2. The errors include statistical and fit errors and systematic errors caused by selfabsorption and drifts. The $K\beta_{13}$-fourfold ratios are equal to unity within errors. Also the $K\beta_{24}$-ratios do not show any significant shift. However, the KO-lines show sizeable intensity differences. The KO-intensity in La_2O_3 is (15.0 ± 4.7)% higher, in SmS (6.9 ± 2.6)% lower than that from the metal. The very low KO-line intensities in the Ta experiment led to uncertainties that do not reveal an unambiguous shift. It is interesting to note that there is no shift at all for the pair Sm_2O_3-Sm.

Table 2. Experimental values of $\dfrac{I(K_j,\text{compound})}{I(K_j,\text{metal})} \bigg/ \dfrac{I(K\alpha_1,\text{compound})}{I(K\alpha_1,\text{metal})}$ in % .

	La_3O_3-La	SmS-Sm	Sm_2O_3-Sm	Ta_2O_5-Ta
$K\alpha_1$	100	100	100	100
$K\beta_{13}$	101.0 ± 2.0	100.2 ± 1.6	99.0 ± 1.6	101.2 ± 1.7
$K\beta_{24}$	98.8 ± 2.7	98.0 ± 2.8	96.8 ± 2.7	103.8 ± 14.0
KO	115.0 ± 4.7	93.1 ± 2.6	101.6 ± 3.7	112.5 ± 8.5

5. Comparison with Theoretical Calculations

In the following we try to explain the experimental results within a simple model of the chemical bond.

For this purpose we used an atomic multiconfiguration Dirac-Fock program (MCDF), developed by Grant and coworkers [12].

This program builds up the electronic wave functions as linear combinations of given electronic configurations with fixed values for parity and total angular momentum. Breit interaction, vacuum polarization and electron selfenergy are taken into account. The nucleus is described by a two-parameter Fermi distribution.

Within this program chemical binding can only be described by different valence shell occupations, representing the limit of pure ionic bond. Covalent bond and breaking of spherical symmetry by the other atoms cannot be considered.

We took all possibilities to couple the electron hole angular momentum to the ground state angular momentum. Different couplings for the ground state affected the calculated intensities by less than 5×10^{-4}.

Table 3. Comparison of calculated relative transition probabilities (upper part of table) with experimental data (error ≦ 2%) [14] listed in the lower part. The calculated data in the left column for each element were obtained in the present work. The data in the right columns were calculated by Scofield [13].

		Lanthanum		Samarium		Tantalum	
		MCDF	RHF [13]	MCDF	RHF [13]	MCDF	RHF [13]
Theory	$K\alpha_2$	54.44	54.49	55.26	55.23	57.42	57.35
	$K\alpha_1$	100	100	100	100	100	100
	$K\beta_3$	9.85	9.63	10.21	10.02	10.88	10.70
	$K\beta_1$	19.08	18.68	19.78	19.38	21.00	20.68
	$K\beta_4$	2.07	2.04	2.20	2.17	2.46	2.42
	$K\beta_2$	4.06	3.98	4.29	4.28	4.80	4.69
Exp.	$K\alpha_2$	54.45		55.2		57.4	
	$K\beta_1$	–		–		21.4	

Table 4. Calculated relative KO-intensities (in %) for different configurations.

Lanthanum		Samarium		Tantalum	
configuration	intensity	configuration	intensity	configuration	intensity
$4f^15d^16s^1$	0.883	$4f^66s^2$	0.908	$4f^{14}5d^36s^2$	1.042
$4f^16s^2$	0.905	$4f^66s^1$	0.916		
$5d^26s^1$	0.956	$4f^66s^0$	0.927		
$5d^16s^2$	0.978	$4f^55d^16s^2$	0.973	$4f^{14}5d^06s^0$	1.154
$5d^16s^1$	0.986	$4f^56s^2$	1.005		
$5d^16s^0$	0.997	$4f^56s^1$	1.016		
$5d^06s^2$	1.014	$4f^56s^0$	1.029		
$5d^06s^1$	1.026				
$5d^06s^0$	1.041				

All calculations were performed for the elements La, Sm and Ta. The transition probabilities for $K\alpha_{1,2}$ and $K\beta_{1,2,3,4}$-lines were calculated for the following configurations (Xe-core):

La $5d^16s^2$, $5d^16s^0$, $5d^06s^0$,

Sm $4f^66s^2$, $4f^66s^0$, $4f^56s^0$,

Ta $4f^{14}5d^36s^2$, $4f^{14}5d^06s^0$.

These configurations may play a role in the chemical binding of these elements. The calculated $K\alpha_{1,2}$-intensities differed by less than 10^{-4}, the $K\beta_{1,2,3,4}$ by less than 10^{-3} for these configurations. Such changes are far below our detection limit, and the results of our measurement are in complete agreement with expectation, see Table 2.

The relative intensities calculated with this program for the different K x-rays with free atom configurations are compared with older relativistic Hartree-Fock calculations [13] and with experimental data [14] in Table 3.

The relative KO-intensities were calculated for different configurations of Lanthanum, Samarium and Tantalum. They show a characteristic trend: the less electrons in the valence shells, the higher the KO intensity.

As a general rule we find: one electron less in the 6s-, 5d- and 4f-shell increases the KO-intensity by

Table 5. Calculated and experimental La KO-intensity shifts.

Metallic configuration	Remarks	V_4(KO) [%]
$5d^16s^2$	free atom, according to Herbst [16], also metallic configuration	106.4
$5d^26s^1$	suggested by Herbst [17], to represent the strong 5d-character	108.9
$4f^16s^2$	these were regarded to find possible 4f-influences	115.0
$4f^15d^16s^1$		117.9
	experiment	115.0 ± 4.7

Table 6. Calculated and experimental Sm KO-intensity shifts.

Metallic configuration	Remark	V_4(KO, SmS)	V_4(KO, Sm_2O_3)
$4f^6 6s^2$	free atom configuration	102.0	113.3
$4f^5 5d^1 6s^2$	metallic configuration according to Herbst [16]	95.2	105.7
$4f^5 5d^0 6s^0$	valence electrons are not localized	90.1	100.0
	experiment	93.1 ± 2.6	101.6 ± 3.7

1.0–1.5%, 3.5–4.5% and 11.0–12.0%, respectively. Table 4 shows the relative KO-intensities for different La-, Sm- and Ta-configurations. With reasonable assumptions about the oxide configuration a comparison with the experimental results will give information about the atomic configuration of localized electrons in the metal.

Because La_2O_3 has to a good approximation ionic bond (ionicity 87% [15]) we adopt the configuration $5d^0 6s^0$.

The comparison with experimental data for Lanthanum is shown in Table 5. The calculations indicate a 5d-4f hybridization or promotion in the metallic state of Lanthanum, a possibility also discussed by Keller [18].

The ionicity of Sm_2O_3 amounts to 85% [15], so that we may assume the configuration $4f^5 6s^0$. Sm has only 30% ionicity, but because of the small influence of the 6s-electrons we assume the configuration $4f^6 6s^0$.

A comparison of calculated values of V_4(KO) for some metallic configurations with experimental results is shown in Table 6. This demonstrates the missing of a 4f-electron in metallic Samarium as compared to the free atom.

Assigning $4f^{14} 5d^3 6s^2$ to metallic Tantalum and $4f^{14} 5d^0 6s^0$ to Ta_2O_5, we can reproduce the experimental results:

$$V_4(\text{calc.}) = 110.7\% , \quad V_4(\text{exp.}) = (112.5 \pm 8.7)\% .$$

6. Comparison with Other Experiments

To our knowledge there are up to now only a few investigations regarding the $K\beta/K\alpha$ intensity shift at 3d-elements ($Z = 21-29$) performed with semiconductor spectrometers [19–23]. In these experiments the intensities are higher and no problems with edge-absorption arise.

Because mainly the 3d-electrons participate in the bond, the $K\beta$-transition plays a similar role as "outer" K-transition as the KO-line in our experiment. The $K\beta/K\alpha$ intensity ratio depends on the chemical valency up to 20% [19] and can differ by 10% for compounds of the same valency [19]. The results for K_2CrO_4 from Tamaki [19] and Lazzarini [20] are in disagreement by about 2.5 standard deviations. There is also a remarkable influence of the excitation mechanism [24]. But finally they seem to have one feature in common with our results:

The fewer electrons in the valence shell, the stronger the "outer" K-transition.

7. Conclusion

We have shown both experimentally and theoretically the dependence of the KO-intensity on the chemical state. A comparison of experiment and theory yields information about the atomic configuration of the metallic samples. The configurations thus determined support conclusions from solid state physics [16, 18].

The theoretically predicted dependence of the other K-transitions lies below our detection limits.

Thus the investigation of relativ KO-intensities can be an independent method to determine valence configurations. However high accuracy in the experiment is essential.

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