X-RAY PHOTOELECTRON SPECTROSCOPY OF RARE-EARTH COMPOUNDS

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(First received 10 September 1983; in final form 3 January 1984)

ABSTRACT

A variety of rare-earth (RE) compounds (oxides, sulfates and oxalates) have been studied by X-ray photoelectron spectroscopy. Except for Eu, the binding energies (BE's) of the RE 3d and 4d peaks for the sulfates and oxalates are respectively almost equal to and 1.3—3.1 eV higher than those for the oxides. In the Eu 3d spectrum of europium(II) oxalate, distinct shake-down satellite peaks are present, and the BE's of these peaks are $\sim 10 \text{ eV}$ lower than the parent ones. For the oxides, appreciable differences are found in the BE's of the O1s peaks, and a specific "inclined W" form is observed in plots of BE versus 1/R (where R is the mean distance from the oxygen atom to the neighboring RE atom) and versus the RE oxidation—reduction potential (ORP). No characteristic differences are seen in the BE's (C1s, S 2s and S 2p) of the other ligands.

INTRODUCTION

Rare earths (RE's) have been studied widely by X-ray photoelectron spectroscopy (XPS) [1-16]. In this area, satellite formation in the XPS 3d spectra of RE compounds has been of particular interest [2, 3, 8-13]. The formation of satellites has been attributed to two mechanisms: shake-up [2] and electron transfer [3]. In reports concerning satellite formation, although much attention has been devoted to the energy separations between the satellite and main peaks, there has been little consideration of absolute binding energies (BE's).

In a systematic XPS study of 600 compounds containing 77 elements [6], Jørgensen and Berthou measured absolute BE's of the inner and outer shells

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of RE elements and ligands in various RE compounds. They corrected charge-up shifts for nonconducting materials by using the C 1s peak from mounting tape. However, use of the C 1s peak from mounting tape as a calibrant is unsatisfactory [17, 18]. Therefore, the BE values given by Jørgensen and Berthou [6] may involve some uncertainty. To discuss chemical shifts for RE elements, it is necessary to measure absolute BE's with greater accuracy. Although the RE elements show a striking similarity in terms of their chemical properties, only a slight difference in these properties may influence the BE's of ligands in RE compounds. Therefore, it is worthwhile measuring the BE's of such ligands.

It has been reported that a gold layer of constant thickness (~9Å path length through the layer) on a sample surface provides a good calibrant for charge correction [19]. Therefore, using such a gold layer as a calibrant, we measured the BE's of the RE elements and ligands in a series of oxides, sulfates and oxalates of RE's (including yttrium). The results of these measurements are discussed in this paper.

EXPERIMENTAL

The photoelectron spectra of the RE compounds were obtained using a JEOL JESCA-4 photoelectron spectrometer equipped with an Al $K\alpha$ X-ray source ($h\nu = 1486.6 \,\mathrm{eV}$). The X-ray power supply was operated at 8 kV and 40 mA. The pressure inside the sample chamber was below 1.1×10^{-8} torr during the measurements. The resolution of the analyzer was set to give a full width at half-maximum (FWHM) of $1.9 \,\mathrm{eV}$ for the Au $4f_{7/2}$ peak. The energy scale was calibrated to give this peak at 83.8 eV BE. The XPS data were obtained by digital accumulation using a Texas Instruments 980B minicomputer. The results were stored on magnetic tape for subsequent reduction using a Hewlett-Packard 9845B desk-top computer combined with the minicomputer. Data reduction consisted of smoothing of the raw data and curve synthesis using Gaussian peak shapes. The program was written in this laboratory in Hewlett-Packard BASIC.

Stock solutions (1%) of the RE elements were prepared by dissolving 99.99% RE oxides (Shin-etsu Chemical Co.) in 1*M* nitric acid. The RE oxalates were precipitated from the stock solutions by adding oxalic acid. The oxalates were filtered and dried at 140°C. The oxides were obtained by ignition of the oxalates at 1000°C in an electric furnace (Thermoline 10500). The RE sulfates were precipitated by adding stoichiometric sulfuric acid and 95% ethanol, filtered off, and dried at 300°C. All the powder samples were pressed at 200 kg cm⁻² using a pellet die (Hitachi Ltd.) to give circular disks ~ 1 mm thick and 13 mm in diameter. All samples were fixed to the sample holder by means of double-sided adhesive tape.

An ~ 6 Å layer of gold was deposited onto each sample as a calibrant. In

our instrument, because the input lens of the energy analyzer is set at 45° to the sample surface, photoelectrons ejected from the sample and traversing the gold layer have a path length within it $\sqrt{2}$ times the thickness of the deposited film, i.e., ~ 9 Å. Details of the gold decoration onto the samples have been given elsewhere [19]. For exact charge correction, the calibrant peak (Au $4f_{7/2}$) was measured before and after every XPS measurement. More than two samples were measured for every compound.

RESULTS AND DISCUSSION

The $3d_{5/2}$ spectra of Y, La, Ce, Pr, Nd, Sm, Eu and Gd are shown in Fig. 1. For cerium oxide, the Ce $3d_{5/2}$ and $3d_{3/2}$ peaks were not resolved using the apparatus employed in this study. Therefore, the Ce $3d_{3/2}$ spectrum is also shown in Fig. 1. Spectra extending beyond the BE of the Gd $3d_{5/2}$ peak could not be obtained, since the apparatus did not have the capacity to measure BE's in excess of 1200 eV.



Fig. 1. Photoelectron spectra of the RE $3d_{5/2}$ level for RE oxides, sulfates and oxalates (RE = Y, La, Ce, Pr, Nd, Sm, Eu, Gd). Deconvolutions of the main and satellite peaks are given by solid lines. In the spectra of Nd₂O₃, the peak of lowest BE is assigned to the O *KLL* Auger peak.

Tatsumi et al. [13] reported XPS spectra of RE $3d_{5/2}$ peaks for RE hydroxides from La to Gd. The spectra shown in Fig. 1 are similar to those given by Tatsumi et al. except for the cerium compounds and for europium oxalate. Praline et al. [15] reported that the spectrum of Ce(III) given by Tatsumi et al. should be assigned to Ce(IV) species. The Ce(III) spectrum given by Tatsumi et al. is similar to the Ce(IV) spectrum of CeO₂ shown in Fig. 1, and not to the Ce(III) spectra of Ce₂(SO₄)₃ and Ce₂(C₂O₄)₃. Therefore, we agree with the conclusions of Praline et al.

Distinct satellite peaks are apparent in the spectra for every compound of La, Ce, Pr and Nd, and for europium oxalate. For the other compounds, the satellite peaks disappear into the background levels.

In Table 1, the BE's of the 3d peaks for Y, La, Ce, Pr, Nd, Sm and Gd are listed. Each sample's charging was corrected by regarding the $4f_{7/2}$ peak from each gold deposit as being located at 83.8 eV. The BE's of the measured satellite peaks are also listed in Table 1. Each BE difference between the parent and satellite peaks is in agreement with the value reported by Berthou et al. [9] within the limits of experimental error. For CeO₂, the BE's of all the peaks obtained are listed in Table 1, since the computer used in this laboratory did not permit deconvolution of the Ce 3d spectrum.

The RE $3d_{5/2}$ BE's for the sulfates are nearly equal to those for the oxalates except for the europium compounds. They are 1.3-2.7 eV higher than those for the oxides. The BE's of the Ce $3d_{5/2}$ peaks for Ce₂(SO₄)₃ and Ce₂(C₂O₄)₃ are 1.3 eV higher than that (885.8 eV) for Ce₂O₃, as reported previously by Praline et al. [15].

The Eu $3d_{5/2}$ spectrum of europium oxalate is quite different from those of the oxide and sulfate, as can be seen from Fig. 1. The spectrum of the oxalate consists of two distinct peaks separated by $\sim 10 \, \text{eV}$. The spectrum may be attributed to Eu(II) species. Fadley et al. [1] and Jørgensen and Berthou [6] reported a strong chemical shift (by $\sim 10 \,\mathrm{eV}$) of the Eu $3d_{5/2}$ peak between Eu(II) and Eu(III), and the latter authors assigned the peak of higher BE to Eu(III). However, we cannot agree, for the following reasons. If the peak of higher BE were to be assigned to $Eu_2(C_2O_4)_3$, the BE of that peak should be nearly equal to the value for $Eu_2(SO_4)_3$. However, the BE is actually $\sim 1.5 \,\mathrm{eV}$ lower than that for $\mathrm{Eu}_2(\mathrm{SO}_4)_3$. In addition, it is unlikely that the chemical shift of the Eu $3d_{5/2}$ peak on going from Eu(II) to Eu(III) would be as high as 10 eV. It has been reported that the chemical shifts of the Ce $3d_{5/2}$ peak on going from Ce(0) to Ce(III) and Ce(IV) are 2.6 and 4.6 eV, respectively [15], and that of Sm $3d_{5/2}$ on going from Sm(0) to Sm(III) is far less than $10 \, \text{eV}$ [10]. It is reasonable to estimate that the chemical shift of an RE $3d_{5/2}$ peak on going from RE(II) to RE(III) will be smaller than that on going from RE(0) to RE(III). Therefore, in the Eu $3d_{5/2}$ spectrum of europium oxalate shown in Fig. 1, we have assigned the peak of higher BE as the parent Eu(II) peak, and that of lower BE as a shake-down satellite.

TABLE 1 BE'S (in eV) OF RE 3d PEAKS

	Oxide				Sulfate				Oxalate			
	3d ₃ ,	5	3d5	3/2	3d	3/2	3d5	2/2	3d	3/2	3d	5/2
۲	158	6.	156	3.8	16	1.4	159	9.8	16	1.6	15	9.5
La	855.4	851.4	838.6	834.6	857.0	853.9	840.3	837.2	856.9	853.7	840.2	837.0
ථ	16	7.2 907.	.9 901.7		905.7	902.3	887.0	883.6	905.9	902.3	887.1	883.6
	68	9.3 889.	.8 883.1	5								
ፚ	954.4	949.1	933.4	928.7	956.3	952.7	935.9	932.3	955.9	952.1	935.6	931.8
ΡN	1005.6	1001.1	982.9	978.4	1007.5	1003.3	984.7	980.6	1007.2	1003.2	984.5	980.5
Sm	1111	2	1084	t.1	111	2.5	108	5.4	111	2.4	108	5.3
nЭ	1165	.4	1135	5.4	116	7.4	113'	7.7	1165.8	1155.9	1136.2	1126.4
Gd			1187	7.5			118	8.6			118	9.6

^a As the computer used in this laboratory did not permit the deconvolution of the Ce 3d spectrum for CeO₂, the BE's of all the peaks obtained are listed.



Fig. 2. Photoelectron spectra of the RE 4d level for RE oxides, sulfates and oxalates (RE = La, Ce, Eu, Tb, Yb, Lu).

The 4d spectra of several RE's (La, Ce, Eu, Tb, Yb and Lu) are shown in Fig. 2, and the BE's of all RE 4d peaks obtained are listed in Table 2. As we were not able to deconvolute the complex spectra of all RE compounds except for Lu, the data listed in Table 2 do not always represent accurate BE's for the parent and satellite peaks. However, they are sufficient for a comparison of the BE's of RE 4d peaks for the sulfates, oxalates and oxides. The 4d spectra for the oxide, sulfate and oxalate of each RE are similar to each other except for those of Ce and Eu. No remarkable difference in BE is seen between the oxalates and sulfates except for Eu. The BE of each of the sulfate and oxalate peaks is 1.3-3.1 eV higher than the corresponding value for the oxides. The Eu 4d spectrum of the europium oxalate sample is quite different from those of the oxide and sulfate. As discussed above in relation to the Eu $3d_{5/2}$ spectrum, we assign the peaks of lower BE to shake-down satellites of Eu(II). The Ce 4d spectrum of CeO_2 is as complex as the 3d spectrum. The S 2p peak (169.3-169.9 eV) overlaps with the RE 4d peak in the spectra of the sulfates of Tb, Dy, Ho, Er and Tm.

The spectra of the ligands (O 1s, C 1s, S 2s and S 2p) in three lanthanum compounds are shown in Fig. 3. The spectral patterns for the other RE compounds were similar to those shown in Fig. 3. The S 2p doublet peak was

TABLE 2 BE'S (in eV) OF RE 4d PEAKS

	Oxide		Sulfate		Oxalate	
La B	105.3	101.9	107.3	104.2	107.5	104.4
లి	125.1 121.4 115.	.9 111.9 108.5	113.1	109.6	113.4	109.5
ጜ	126.9 119.8 1	115.7 112.1	120.8	116.6	120.6	116.6
PN	123.1	119.2	126.4	122.3	125.8	121.9
Sm	135.7	130.8	137.3	132.7	137.6	132.6
Eu	141.1	135.4	142.9	137.3	143.9 142.6 13	7.0 134.9 129.3
Gd	146.7	141.6	148.8	143.6	149.6	144.2
đŢ	163.9 156.	7 148.9	155.8	150.3	179.0 15	5.7 150.7
Å	208.6 181.1 1	170.1 155.6	182.5 161.9	158.2 156.3	212.3 183.8 17	3.8 158.3 155.8
Но	189.1 175.5 1	166.9 161.1	190.0	162.6	191.4 178.5	167.7 163.1
卤	195.6 182.9 1	174.3 168.6	195.4	185.9	197.7 185.9	177.1 170.5
n Tu	214.6 202.4 1	190.8 176.4	190.0 18	1.3 178.1	217.3 202.3	191.4 178.1
¥Ъ	205.6 199.5 1	193.0 185.0	208.7 201.3	194.7 187.1	207.8 200.9	195.1 187.1
Lu	206.1	196.3	208.1	198.3	208.3	198.5



Fig. 3. Photoelectron spectra of the atoms of the ligands (O 1s, C 1s, S 2s and S 2p) of lanthanum compounds. The C 1s spectra show a peak at lower energy, assignable to hydrocarbon contamination.

not resolved into $2p_{1/2}$ and $2p_{3/2}$ peaks. The O 1s spectra for the oxides consist of two peaks separated by ~3 eV. The peak of higher BE may be attributed to water absorbed during the formation of the sample pellets, because Burroughs et al. [11] found that similar peaks of higher BE in the O 1s spectra of RE oxides disappeared on heating at 1000°C for 1 h in vacuum. Instead of heating the samples, we separated the two peaks by data reduction using a desk-top computer..

Table 3 lists the BE's of the O 1s and C 1s peaks for the oxalates, of the S 2s, S 2p and O 1s peaks for the sulfates, and of the O 1s peaks for the

	O 1 <i>s</i>			C 1s	S 2s	S 2p
	Oxide	Sulfate	Oxalate	Oxalate	Sulfate	Sulfate
Y	530.0	532.8	533.5	290.1	233.5	169.9
La	529.9	532.8	533.0	289.8	233.2	169.4
Ce	529.7	532.1	532.8	289.9	232.5	168.6
Pr	528.9	532.9	533.1	289.8	233.5	169.6
Nd	529.3	533.0	533.2	289.9	232.7	169.9
Sm	530.2	532.6	533.1	290.3	233.4	169.7
Eu	530.0	532.6	532.8	289.5	233.1	169.2
Gd	530.4	532.6	533.2	289.9	233.0	169.2
Tb	529.1	532.7	533.3	290.0	233.2	169.3
Dy	5 29.4	532.8	533.4	290.1	233.4	169.6
Но	529.9	532.6	533.2	289.9	233.1	169.3
Er	529.9	532.8	533.0	290.1	233.4	169.9
Tm	530.3	532.8	533.0	289.8	233.5	169.6
Yb	531.0	532.9	533.0	289.8	233.7	169.9
Lu	530.8	532.9	533.4	289.9	233.6	169.9

TABLE 3BE'S (in eV) OF O 1s, C 1s, S 2s AND S 2p PEAKS

oxides. For CeO_2 , the BE's of the O 1s peaks are 529.7 and 532.6 eV. These values are in good agreement with the BE's reported by Praline et al. [15] (529.6 and 532.7 eV). For Yb_2O_3 , the value (531.0 eV) shown in Table 3 agrees well with that reported by Lang et al. [7] (530.8 \pm 0.2 eV). Jørgensen and Berthou [6] reported the BE's of S $2p_{3/2}$ peaks for the sulfates of Y, La, Ce, Pr, Nd, Eu, Gd, Yb and Lu. Except for Nd₂(SO₄)₃, the BE's of the S 2p peaks shown in Table 3 are 1.1-2.5 eV lower than those reported by Jørgensen et al. The disagreement can be attributed to the difference in the calibrant used for charge correction.

In Table 3, appreciable differences appear in the BE's of the O 1s peaks for the oxides. Generally, chemical shifts in XPS are related to the atomic charge calculated on the basis of Pauling's scale of electronegativity. However, the differences in BE found here cannot be explained by the differences in electronegativity among the RE's.

For the O 1s peaks for 37 kinds of oxides and the F 1s peaks for 20 kinds of fluorides, Nefedov et al. [20] have confirmed a correlation between the BE of the XPS peak of an atom carrying a negative charge and the mean distance from this atom to the neighboring one. Figure 4 shows the relationship between the BE of the O 1s peak and 1/R, where R is the distance from the oxygen atom to the neighboring RE atom, for a series of RE oxides (R values quoted from Ref. 21: since R values for the nonstoichiometric oxides Pr_6O_{11} and Tb_4O_7 could not be estimated, plots for Pr and Tb are absent in Fig. 4). The solid line connecting the points for La, Gd and Lu (with spherical electron configurations) shows that the BE of the O 1s peak increases with an increase in 1/R. This result agrees with those obtained by Nefedov et al. [20]. The BE's for the other RE oxides deviate from the solid



Fig. 4. Correlation of the BE of the O 1s peak with 1/R for RE oxides.

line. The pattern of the plots in Fig. 4 must reflect some intrinsic properties of the 4f group elements. The pattern is a kind of "inclined W" [22].

Figure 5 shows the relationship between the BE's of the O 1s peaks for the oxides, of the C 1s peaks for the oxalates, and of the S 2s and S 2p peaks for the sulfates, and the oxidation—reduction potential (ORP) of each RE element ($RE \rightleftharpoons RE^{3+}$, ORP values quoted from Ref. 23). For the oxides, the solid line connects the points for La, Gd and Lu in the same manner as shown in Fig. 4. The BE's of the O 1s peaks decrease with an increase in ORP. The BE's for the other RE oxides deviate from the solid line. In a compound, a metal atom with higher ORP is more liable to transfer electrons to ligand atoms; this makes the BE of the ligand atom lower. This idea explains the fact that the BE of the ligand atom decreases with an increase in ORP of the RE atom. The pattern of the plots for the oxides again has the form of an "inclined W".

The BE's of the C 1s peaks for the oxalates and of the S 2s and S 2p peaks



Fig. 5. Correlations of the BE's of the O 1s, C 1s, S 2s and S 2p peaks with ORP for each RE compound.

for the sulfates show no meaningful dependence on the RE ORP except for cerium sulfate. Since C and S atoms are not directly bonded to RE atoms, their BE's may not be influenced appreciably by the RE atoms. We are unable to offer an appropriate explanation for the deviation of the BE for cerium sulfate. No characteristic differences are seen in the BE's of the O 1s peaks for the oxalates or sulfates. These BE's are almost the same as those of O 1s peaks resulting from absorbed water in the oxides. The O 1s peaks for the sulfates and oxalates may be attributed to absorbed water or water of crystallization included in the samples.

CONCLUSIONS

The XPS studies of RE compounds (oxides, sulfates and oxalates) reported here may be summarized as follows:

(1) except for Eu, the BE's of the RE 3d and 4d peaks for the sulfates are almost equal to those for the oxalates, and 1.3-3.1 eV higher than those for the oxides;

(2) in the Eu 3d spectrum of europium(II) oxalate, distinct shake-down satellite peaks are apparent, and the BE's of these peaks are $\sim 10 \text{ eV}$ lower than the parent ones;

(3) in spite of the striking similarity of the RE elements in terms of their chemical properties, appreciable differences appear in the BE's of the O 1s peaks for the oxides: an "inclined W" pattern in evident in plots of the O 1s BE versus 1/R or ORP;

(4) no characteristic differences are seen in the BE's of the C 1s, S 2s and S 2p peaks for the oxalates and sulfates.

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