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X-Ray Photoelectron Spectroscopy of Rare Earth Halides

Yoshinori UWAMINO,* Akira TSUGE, Toshio ISHIZUKA, and Hideo YAMATERA†
Government Industrial Research Institute, Nagoya, Hirate-cho, Kita-ku, Nagoya 462
†Department of Chemistry, Faculty of Science, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464
(Received January 22, 1986)

Rare earth (RE) halides (fluorides, chlorides, bromides, and iodides) have been studied by X-ray photoelectron spectroscopy. The binding energies (BE's) of the RE 3d and 4d peaks for the chlorides, bromides, and iodides are related to the atomic charge calculated on the basis of Pauling's scale of electronegativity (Pauling charge). Except for Y and Lu, the observed RE 3d and 4d BE's for the fluorides are lower than those expected. For Y and Lu, the observed RE 3d and 4d BE's for all halides are related to the Pauling charge. For the fluorides and chlorides, the BE's of the ligand peak show variations with increasing atomic number of RE's and a specific "tetrad effect" is observed in plots of BE versus RE atomic number and versus $1/R$ (where R is the mean distance from the ligand atom to the neighboring RE atom), except for the BE's of the F 1s peaks from the light RE fluorides. For the iodides and bromides, no or little characteristic variations are seen in the BE's of I and Br.

Rare earths (RE's) have been studied widely by X-ray photoelectron spectroscopy (XPS).[1–6] Satellite and multiplet peaks in the 3d and 4d spectra of RE compounds have been of paticular interest.[1,3–5] Although much attention has been devoted to the energy separations between the satellite and the main peak and between the multiplet components, there has been little consideration of absolute binding energies (BE's).

Jørgensen and Berthou measured absolute BE's of the inner and outer shells of RE elements and ligands in various RE compounds.[2] However, their calibrant (C 1s peak from mounting tape) is unsatisfactory for charge correction of nonconducting materials such as RE compounds.[7] Therefore, the BE values given by them 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 to one another in their chemical properties, slight differences in these properties may influence the BE's of ligands in RE compounds. Therefore, it is worthwhile measuring the BE's of such ligands.

Thus, we systematically measured the absolute BE's of the RE elements and ligands in RE oxides, sulfates, and oxalates.[6] For the oxides, appreciable differences were found in the BE's of O 1s peaks, and a specific "inclined W" form was 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 potential. In the present study, we examine whether the "inclined W" pattern appears or not for RE halides. In addition, we investigate the relation between the RE BE's and the electronegativities of halogen atoms. Thus we measured the BE's of the RE elements and ligands in a series of fluorides, chlorides, bromides, and iodides of RE's (including yttrium). The results of these measurements are discussed below.

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 eV). The X-ray power supply was operated at 7 kV and 40 mA. The pressure inside the sample chamber was below 5×10^{-5} Pa during the measurements. The resolution of the analyzer was set to give a full width at half-maximum (FWHM) of 1.9 eV for the Au $4f_{7/2}$ peak. The XPS data were obtained by digital accumulation using a Texas Instruments 980B minicomputer. The digital data were processed with 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.[8]

RE halide samples were prepared from 99.99% RE oxides (Shin-etsu Chemical Co.). The RE fluorides were precipitated from 1% nitric acid solutions by adding hydrofluoric acid and dried at 130 °C. The RE chlorides, bromides and iodides were prepared by dissolving the RE oxides in hydrochloric acid, hydrobromic acid, and hydroiodic acid, respectively, evaporating to dryness at 90 °C on a hot plate, and then drying in vacuum at room temperature for two days. Cerium iodide was not obtained by this method; therefore spectra are lacking on this compound.

All the powder samples were pressed at 200 kg cm^{-2} using a pellet die (Hitachi Ltd.) to give circular disks about 1 mm thick and 13 mm in diameter. All samples were fixed to the sample holder by means of double-sided adhesive tape.

Results and Discussion

The 3d spectra for Y and La through Gd were measured. The $3d_{5/2}$ spectra of Y, La, Nd, and Gd are shown in Fig. 1. The spectra for Ce, Pr, Sm, and Eu were similar to those for La, Nd, Gd, and Gd, respectively. The Y 3d spectra of YF_3, YCl_3, YBr_3, and YI_3 are very similar to one another. For each of the other RE's, the RE $3d_{5/2}$ spectra of the chloride, bromide, and iodide are similar to one another, but

Table 1. BE's (in eV) of RE 3d Peaks

	Fluoride				Chloride				Bromide				Iodide			
	$3d_{3/2}$		$3d_{5/2}$		$3d_{3/2}$		$3d_{5/2}$		$3d_{3/2}$		$3d_{5/2}$		$3d_{3/2}$		$3d_{5/2}$	
Y		161.0		158.8		160.8		158.7		160.6		158.5		160.2		158.1
La	857.4s)	853.3	840.7s)	836.5	857.5s)	853.8	840.6s)	837.0	856.1s)	852.5	839.3s)	835.6	854.8s)	851.6	838.1s)	834.9
Ce	906.3	902.5s)	887.8	884.0s)	904.5	901.4s)	886.8	882.8s)	905.0	901.0s)	886.5	882.4s)		—a)		—a)
Pr		954.0		933.3	956.3	952.4s)	935.8	931.7s)	954.9	950.7s)	934.5	930.4s)	954.0	949.9s)	933.7	929.9s)
Nd		1006.1		982.9	1006.0	1002.1s)	983.5	979.7s)	1005.7	1001.5s)	983.3	979.0s)	1005.3	1000.9s)	982.2	977.7s)
Sm		1110.8		1083.5		1111.3		1084.2		1111.0		1083.9		1110.7		1083.8
Eu		1165.0		1135.0		1165.8		1136.0		1165.9		1135.4		1165.4		1134.9
Gd				1187.8				1188.6				1188.3				1187.7

s) Satellite peak. a) Cerium iodide sample was not obtained.

Table 2. BE's (in eV) of RE 4d Peaks

	Fluoride					Chloride			Bromide				Iodide				
La				106.9	104.0	109.5s)	106.5	103.4		108.9s)	106.3	103.4				106.8	103.7
Ce				113.7	110.1		112.4	108.9			113.5	110.1				—a)	—a)
Pr				120.3	115.9		119.4	115.4			119.5	115.4				119.3	115.1
Nd				125.7	121.5		125.3	121.3			124.8	121.0				124.9	120.8
Sm				136.6	131.8		137.1	132.3			136.8	132.0				136.3	131.5
Eu				142.5	137.2		142.8	137.4			142.4	136.9				142.1	136.5
Gd				148.4	143.3		149.0	143.7			148.9	143.5				148.4	143.1
Tb			178.7	154.8	149.9	177.9	155.0	149.8			154.8	149.5			176.9	154.7	149.6
Dy	211.0	183.4	173.1	163.3	157.4	180.3	158.0	154.8			157.6	154.5	209.5	185.1	178.5	157.4	154.2
Ho		190.5	177.8	168.9	163.1		177.7	163.1				162.5			187.5	166.3	162.1
Er		197.2	185.5	175.0	170.3	183.6	175.1	170.2				169.9		196.7	185.8	172.5	169.2
Tm			192.4	181.6	177.3		180.8	177.7				177.8		202.7	185.7	180.3	177.0
Yb		207.0	200.9	193.7	186.7			186.4	206.8	200.7	193.9	185.9		206.5	200.5	193.8	186.0
Lu				207.7	197.9		207.8	197.4			207.5	197.6				207.1	197.2

s) Satellite peak. a) Cerium iodide sample was not obtained.

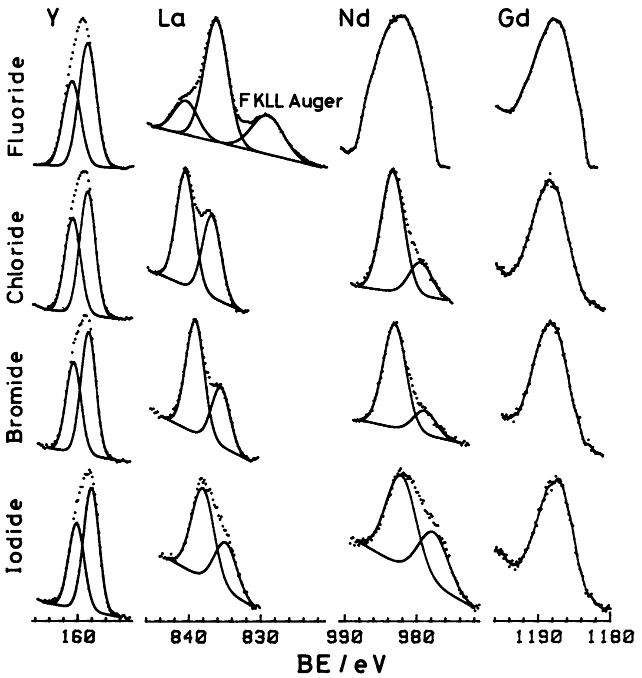

Fig. 1. Photoelectron spectra of the RE 3d$_{5/2}$ level for RE halides (RE=Y, La, Nd, and Gd). Dotted lines show observed spectra. Solid lines give deconvolutions of the main and satellite peaks. Y 3d$_{3/2}$ peak is shown at the higher BE site in each Y spectrum.

rather different from that of the fluoride. The different shape of the fluoride spectra are due to the low intensity of the satellite arising from the charge-transfer transition from the ligand anion to the 4f level of RE ion.[4] Distinct satellite peaks are recognized in the Nd 3d$_{5/2}$ spectra from the chloride, bromide, and iodide, but not in the spectra from the fluoride. For Gd, no distinct satellite peaks are recognized. For Nd and Gd, the FWHM's of the peaks from the fluorides are 1.3—2.0 times broader than those from the chlorides, bromides, and iodides.

The 4d spectra for all RE's were measured. The obtained spectra were similar to those given by Signorelli and Hayes[3] (the RE 4d spectra of several halides), and Suzuki et al.[4] (the RE 4d spectra of the fluorides, chlorides, and bromides of La and Ce). Satellite peaks were recognized in the La 4d spectra of the chloride and bromide. The RE 4d spectra for the halides of Tb through Yb were complex. Signorelli and Hayes have explained these complex structures by the electrostatic coupling of a 4d photohole with the unfilled 4f shell of RE.[3]

Tables 1 and 2 list the BE's of the 3d peaks and of the 4d peaks, respectively. Charging of the sample was corrected by regarding the C 1s peak from carbon contamination on the sample surface as located at 284.6 eV. The BE's of the measured satellite and multiplet peaks are also listed in Tables 1 and 2.

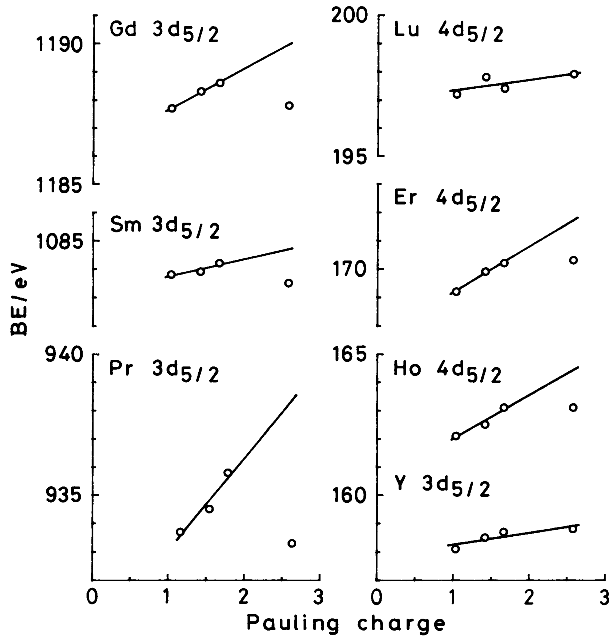

Fig. 2. Correlations of the BE's of the RE 3d$_{5/2}$ and RE 4d$_{5/2}$ (RE=Y, Pr, Sm, Gd, Ho, Er, and Lu) with Pauling charge for each RE halide.

Jørgensen and Berthou[2] have reported the BE's of RE 3d and 4d peaks in a series of RE fluorides except for the fluorides of Dy, Ho, and Tm. The BE's of the RE 3d and 4d peaks listed in Tables 1 and 2 are 2.4—7.2 eV lower than those reported by them. The disagreement can be attributed to the difference in the calibrant used for charge correction.

In Tables 1 and 2, appreciable differences appear in the BE's of the RE 3d and 4d peaks for each RE element. Generally, chemical shifts in XPS are related to the atomic charge calculated on the basis of Pauling's scale of electronegativity (Pauling charge).[9] Figure 2 shows the dependence of the BE's of RE 3d$_{5/2}$ or 4d$_{5/2}$ peaks on the Pauling charge for Y, Pr, Sm, Gd, Ho, Er, and Lu (electronegativity values were quoted from Ref. 10). For Y with 4f levels far above the filled shell and Lu with a completely filled 4f shell, the BE's of Y 3d$_{5/2}$ and Lu 4d$_{5/2}$ peaks increase with an increase in Pauling charge for all compounds. For other RE's with a partly filled 4f shell, the BE's of RE 3d$_{5/2}$ and 4d$_{5/2}$ peaks increase in the order, iodide$<$bromide$<$chloride, but the peaks from the fluorides appear at lower BE's than expected. Why the solid lines in Fig. 2 show different slopes is a problem of further investigation.

The spectra of the ligands (F 1s, Cl 2s, Cl 2p, Br 3s, Br 3p$_{1/2}$ and $_{3/2}$, Br 3d, I 3p$_{1/2}$ and $_{3/2}$, I 3d$_{3/2}$ and $_{5/2}$, and I 4d) in all RE halides were obtained. The spectrum for each RE was simple and no significant differences were observed between the ligand spectra of different RE's. Table 3 lists the BE's of the ligand peaks. The Br 3d and I 4d peaks were not resolved

Table 3. BE's (in eV) of F 1s, Cl 2s, Cl 2p, Br 3s, Br 3p, Br 3d, I 3p, I 3d, and I 4d Peaks

	Fluoride	Chloride		Bromide				Iodide				
	F 1s	Cl 2s	Cl 2p	Br 3s	Br $3p_{1/2}$	Br $3p_{3/2}$	Br 3d	I $3p_{1/2}$	I $3p_{3/2}$	I $3d_{3/2}$	I $3d_{5/2}$	I 4d
Y	684.8	269.6	199.0	256.1	189.1	182.3	69.1	930.3	874.4	630.5	619.0	49.5
La	684.6	269.5	198.8	255.8	188.8	182.0	68.8	930.2	874.2	630.4	618.9	49.4
Ce	684.6	269.5	199.0	255.7	188.7	181.9	68.7	—a)	—a)	—a)	—a)	—a)
Pr	684.8	269.4	198.7	255.6	188.6	181.9	68.6	929.9	874.2	630.4	619.0	49.5
Nd	684.8	269.4	198.8	255.7	188.6	182.0	68.8	930.0	874.3	630.4	618.9	49.6
Sm	684.8	269.4	198.9	255.7	188.7	182.0	68.8	930.2	874.4	630.5	619.0	49.5
Eu	684.4	269.5	199.0	255.6	188.6	182.0	68.7	930.3	874.6	630.4	619.0	49.6
Gd	684.8	269.7	199.0	255.8	188.9	182.2	69.0	930.2	874.4	630.5	619.0	49.7
Tb	684.5	269.5	199.0	255.8	188.7	182.0	68.8	930.4	874.6	630.5	619.1	49.6
Dy	684.6	269.6	199.0	255.8	188.7	182.1	69.0	930.4	874.5	630.5	619.0	49.6
Ho	684.5	269.5	199.0	255.8	188.8	182.0	68.9	930.3	874.4	630.5	619.0	49.6
Er	684.6	269.5	199.0	255.8	188.7	182.2	68.9	930.4	874.6	630.5	619.0	49.3
Tm	684.6	269.6	199.1	255.9	188.9	182.1	69.0	930.0	874.3	630.4	618.9	49.5
Yb	684.9	269.7	199.1	255.8	188.8	181.9	68.8	930.2	874.4	630.4	618.9	49.6
Lu	685.0	269.8	199.2	256.0	188.9	182.3	69.1	930.1	874.5	630.5	619.0	49.5

a) Cerium iodide sample was not obtained.

into their $d_{3/2}$ and $d_{5/2}$ peaks. Jørgensen and Berthou[2] have reported the BE's of F 1s peaks for the fluorides of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Yb, and Lu. The BE's of the F 1s peaks listed in Table 3 are 3.0—5.5 eV lower than those reported by Jørgensen and Berthou. The disagreement can be attributed to the difference in the calibrant used for charge correction.

For each RE halide, an intensity ratio of the halogen peak (F 1s, Cl 2s, Br $3p_{3/2}$, and I $3d_{5/2}$) to O 1s peak ranged from 27.0 to 8.2, after peak intensity was normalized with photoelectric cross sections,[11] mean free paths for photoelectron,[12] and efficiencies of detection of the electron. This demonstrates that the formation of halide oxides, if any, on our sample surface was not serious for the present XPS studies.

For the RE oxides, we have reported the "inclined W" pattern in the plots of the BE's of O 1s peaks versus $1/R$ and versus the RE oxidation potential.[6] The pattern is identical with the "tetrad effect"[13] that is the minute irregularity in the variation of complex formation constants[14] and unit cell volumes[15] as a function of lanthanoid atomic number. Figure 3 shows the relationships between the BE's of the F 1s, Cl 2s, Br $3p_{3/2}$, and I $3d_{5/2}$ peaks and the atomic number for lanthanoids. For the RE fluorides and chlorides, the solid lines connecting the points for La, Gd, and Lu (with spherical configurations) show that the BE of the F 1s and Cl 2s peak increases with an increase in RE atomic number. This result agrees with those shown for the BE's of O 1s peaks for the RE oxides.[6] The points for the other RE's deviate from the solid lines except for light RE fluorides. The pattern reflects electronic configurations of RE elements and is called "tetrad effect." We can not at present give a good reason for the absence of "tetrad effect" for the fluorides of Ce through Eu. For the RE iodide and bromide, the BE's of the I $3d_{5/2}$ and Br $3p_{3/2}$ peaks show no or hardly meaningful dependence on the RE atomic number. It has been reported that the magnitude of the chemical shift for each element decreases with an increase in ionic radii.[16] The large radius of the bromide and iodide ion may be the reason for the very small chemical shift of iodine and bromine atom.

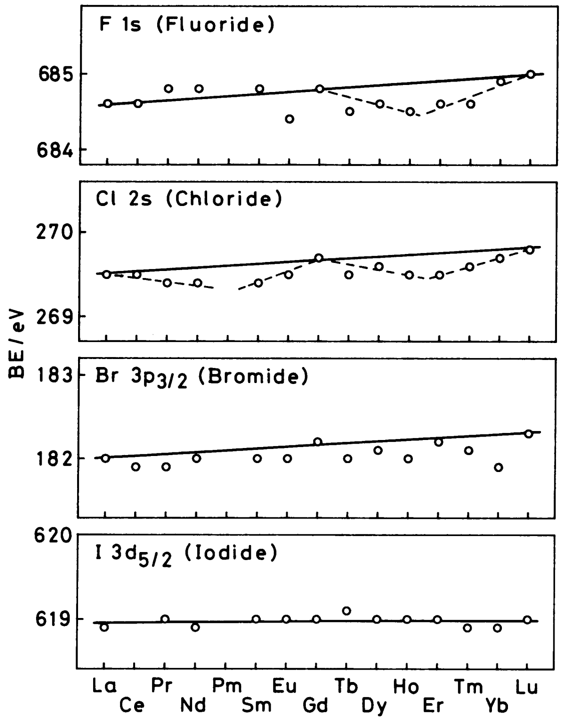

Fig. 3. BE's of the F 1s, Cl 2s, Br $3p_{3/2}$, and I $3d_{5/2}$ peaks as a function of the lanthanoid.

For the RE oxides, a correlation has been

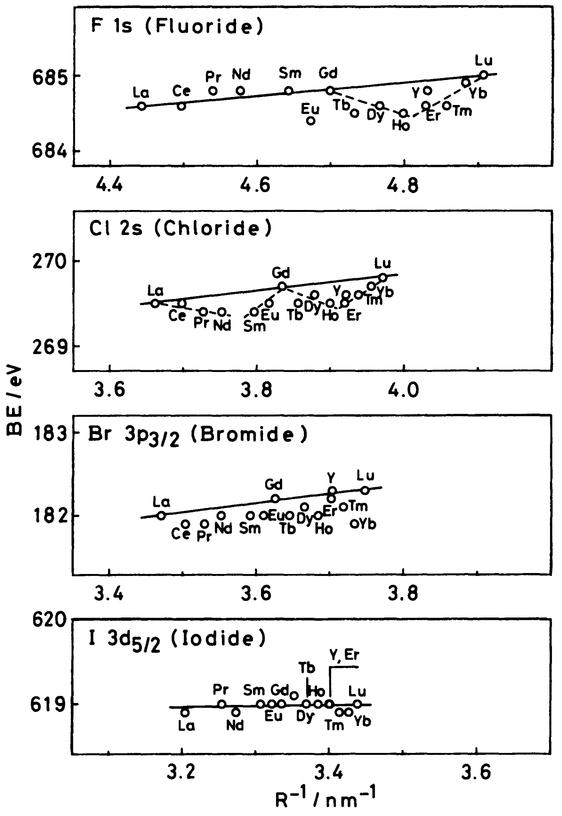

Fig. 4. Correlations of the BE's of the F 1s, Cl 2s, Br $3p_{3/2}$, and I $3d_{5/2}$ peaks with $1/R$ for each RE halide.

recognized between the BE of the O 1s peak and the mean distance from oxygen atom to the RE atom.[6] Figure 4 shows the relationships between the BE's of the F 1s, Cl 2s, Br $3p_{3/2}$, and I $3d_{5/2}$ peaks and $1/R$ for RE halides (R values quoted from Ref. 17). Solid lines were drawn so as to connect approximately the points for La, Gd, and Lu in the same manner as shown in Fig. 3. For the fluoride and the chloride, the BE's of the halogen peaks increase with an increase in $1/R$. This result agrees with those reported by Nefedov et al.[18] for the O 1s peaks for 37 kinds of oxides and the F 1s peaks for 20 kinds of fluorides. The plot for the BE's of the Cl 2s peaks show a "tetrad effect." The F 1s BE's of Gd through Lu show a similar trend. For the iodide, the BE's of the I $3d_{5/2}$ peaks show no meaningful dependence on the $1/R$. The Br $3p_{3/2}$ peaks of the bromide show a pattern intermediate between Cl 2s and I $3d_{5/2}$.

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