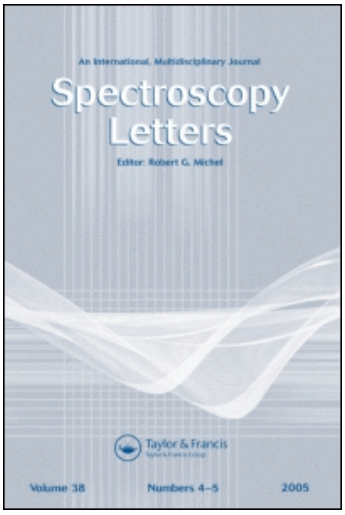

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STUDY ON COVALENT BONDING OF 4f ORBITAL AND LIGAND

KEY WORDS: Lanthanide, 4f orbital, covalent bonding

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Abstract

A new parameter $\bar{b}$ characterizing covalent behaviour of 4f orbit has been developed on the basis of spectral properties of trivalent lanthanides and used to tested the interaction between 4f electrons and ligands for many of the lanthanides compounds. The factors influencing covalent bonding and changing law of covalency have been discussed by the new parameter.

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Introduction

Owing to partially filled and weakly bonding nature of 4f orbits, Lanthanide compounds have particular optical, electric and magnetic properties and potential applications, so great interests have been taken in the studies on basic theory and application of these compounds[1-5]. Bonding feature of 4f orbits has been argued all along. Some authors believed that 4f orbits provided much contribution to bonding between lanthanide and ligands[1-2]. The others considerd they did not participate in bonding[3]. Quantitative studies about covalent degree invoving 4f orbit in lanthanide compounds have seldom been carried out[4]. Zhang[5] ever discussed covelent behavior of trivalent europium in some compounds, but he did not report the factors influencing covalent bonding.

Authors believed that lanthanide ions can form complexes by ionic linkage with ligand, but with weak covalency [6-8]. As further study, in this paper, bonding behaviours of lanthanides are quantitatively discussed, covalent parameter originally proposed by Zhang[5] is modified and the factors affecting covalent bonding and changing regularity of covalency are discussed by new parameter.

Theory

Crystal field interaction gives rise to nephelauxetic effect, splitting of energy levels and J-mixing effect. Among these three effects, nephelauxetic effect simultaneously depands on central field covalency and symmetry -restraining covalency. But in lanthanide series, central field covalency is predominent. For solid lanthanide compounds only nephelauxetic effect and J-mixing effect can result in

shift of absorption bands,so deducting J-mixing effect, the band shift induced by nephelauxetic effect, which just characters covalency of 4f orbit ligand bond, are able to be evaluated.

J-mixing effect can be calculated by following expressions

$$\Delta E_J = (2J+1)^{-1} \sum_K S_k^2 \sum_{J'} (\Psi_{J'} \| U^{(k)} \| \Psi_J)^2 (E_J - E_{J'})^{-1} \quad (1)$$

$$S_k^2 = \sum_g ((2k+1)^{-1} | B_{kq} |^2) \quad (2)$$

where S_k is crystal field intensity parameter and B_{kq} crystal field parameter. Induced matrix elements are taken from references[9,10].

If 4f and ligand orbits mix, the wave function of 4f orbit is written as

$$\Psi_J = a^{1/2} \phi_J + b^{1/2} \phi_L \quad (3)$$

where ϕ_J is 4f orbit immediate coupling wave function and ϕ_L ligand wavefunction. By *treating* $b^{1/2} \phi_L$ *as a perturbation , eigenvalues are obtained by formula*

$$E(J) = aE_J - a\, b\, \beta^2 (E_L - E_J)^{-1} \quad (4)$$

and

$$b = < \phi_J | H' | \phi_L > \quad (5)$$

where H' is perturbation Hamiltonian. If $< \phi_J | \phi_L > = 0$, considering normalization of Ψ_J, a+b=1. Eq(4) is rewritten as

$$E(J) = E_J - bE_J - b\, \beta^2 (E_L - E_J)^{-1} + b^2 \beta^2 (E_L - E_J)^{-1} \quad (6)$$

Neglecting higher order infinitesimal eq(6) can simplified as

$$E(J) = E_J - bE_J \tag{7}$$

E(J) characters the energy levels of lanthanide ion involving covalent bonding excluding J-mixing effect.

If neglecting covalent difference between distinct energy levels b is directly expressed as

$$b = (\Delta E_J - \Delta E(J))(\Delta E_J)^{-1} \tag{8}$$

where ΔE_J is the energy difference between the terms of $4f^n$ configuration for free ion. This parameters has the same meaning as that proposed by Zhang[5]. In fact, bonding nature of 4f orbits are different relative to the various energy levels of $4f^n$ configuration. Therefore this parameter should be redefined . For J' energy level, eq(9) is also vivid

$$E(J') = E_{J'} - b' E_{J'} \tag{9}$$

eq(9) minus eq(7) gives

$$\Delta E(J)= \Delta E_J - b' E_{J'} + bE_J \tag{10}$$

A new parameter is defined by

$$\bar{b} = (b' E_{J'} - bE_J)(\Delta E_J)^{-1} \tag{11}$$

then $$\Delta E(J) = \Delta E_J - \bar{b}\Delta E_J \quad (12)$$

Eq(12) is rewritten as

$$\bar{b} = (\Delta E_J - \Delta E(J))(\Delta E_J)^{-1} \quad (13)$$

The parameter, $\bar{b}$ reflects covalent magnitude, more reasonably than parameter b, depends on the natures of lanthanide ion and ligand and the energy levels of $4f^n$ configuration as well.

Results and Discussion

Degree of covalency in praseodymium(III) and erbium(III) compounds is discussed. To illustrate the influence of different energy levels of $4f^n$ configuration on degree of covalency, covelent parameter $\bar{b}$ are calculated by using the energy difference between $^4I_{13/2}$, $^4I_{11/2}$, $^4G_{11/2}$ levels and ground state $^4I_{15/2}$ for trivalent erbium and the energy difference between $^3P_0$ and $^3H_4$(ground state) for trivalent praseodymium. The energy levels and crystal field parameters are available from references[11-23] and total crystal field intensity parameters are calculated by the formula

$$S = (1/3 \sum_k S_k^2)^{1/2} \quad (14)$$

The calculated results are given in Tables 1-4.

TABLE 1
Total crystal field intensity parameters of various crystal Pr(III) compounds.

Crystal	Total crystal field intensity parameters	Crystal	Total crystal field intensity parameters
$PrCl_3$	182.23	$Cs_2NaRECl_6$	449.38
$Pr(OH)_3$	273.31	Y_2O_3	850.57
$Pr(NO_3)_3 \cdot 6H_2O$	353.10	$ThBr_4$	342.36
PrP_5O_{14}	355.29	$LaAlO_3$	673.23
Pr^{3+} : LaF	392.15	YPO_4	325.92
$LaCl_3$	167.28	$LuPO_4$	355.14
$LaBr_3$	149.31		

TABLE 2
Total crystal field intensity parameters of various crystal Er(III) complexes.

Crystal	Total crystal field intensity parameters	Crystal	Total crystal field intensity parameters
$Er(OH)_3$	128.72	$Y_3Ga_5O_{12}$	513.01
$KEr(WO_4)_2$	280.46	$Y_3Al_5O_{12}$	541.56
$ErVO_4$	345.22	Y_2O_2S	317.72
Er3+ : $LaBr_3$	111.08	$RECl_3 6H_2O$	207.72
$LaCl_3$	119.45	RE_2O_3	281.90
LaF_3	264.13	CdF_2	518.84
$Y(OH)_3$	131.42	$GaCl_3$	125.68
YF_3	280.70	$ScCl_3$	407.41
YCl_3	296.43	$InCl_3$	417.49
Y_2O_3	568.79	$LuPO_4$	235.34
YPO_4	257.89	$KGa(WO_4)_2$	269.84
YVO_4	286.24	$HfSiO_3$	306.62
$YAlO_3$	371.21	$RE_3Al_5O_{12}$	516.21
KY_3F_{10}	326.50	$LiYF_4$	333.90

TABLE 3
Shifts of energy levels, difference between levels and degree of covalency in doped-Pr crystal

Crystal	Shifts caused by J-mixing effects		Difference between the levels and ground levels		Degree of covalency(%)
	$^3H_4$	$^3P_0$	E_{exp}	E(J)	
Pr^{3+} :LaF_3	-22.33	3.28	20725.00	20699.39	3.23
$LaCl_3$	-4.57	0.19	20385.43	20380.67	4.72
$LaBr_3$	-3.51	0.18	20282.34	20278.65	5.19
$Cs_2NaRECl_6$	-18.48	12.77	20281.50	20250.25	5.33
Y_2O_3	-68.63	19.84	19378.00	19289.53	9.82
$ThBr_4$	-13.49	4.03	20122.33	20104.81	6.01
$LaAlO_3$	-75.98	5.39	20414.00	20332.63	4.94
YPO_4	-14.01	3.78	20264.44	20246.65	5.34
$LuPO_4$	-18.08	3.61	20236.00	20214.31	5.49
$PrCl_3$	-5.57	0.24	20357.44	20351.63	4.85
$Pr(OH)_3$	-9.95	-2.65	20341.67	20334.37	4.93
$Pr(NO3)_3 \cdot 6H_2O$	-18.35	-6.77	20729.41	20717.83	3.14
PrP_5O_{14}	-20.37	2.63	20639.22	20616.22	3.62

It is shown that 4f orbits have weak contribution to covalent bonding between lanthanide(III) and ligand indeed. The higher the energy levels, the stronger the covalency, and the degree of covalency in heavy rare earth compounds is relatively lower than in light rare earth compounds (Table 3-4). The fact likely results from lanthanide contraction, 4f election clouds of light rare earth atoms is of larger expansion than that of heavy atoms in series. The same conclution was supported by the work by Ryan,et al[24].

Bonding behaviours of 4f orbits for different Lanthanide(III) ions change in the same ligand order, say LaF_3< $LaCl_3$ < $LaBr_3$ in Er(III) and Pr(III) doped LaX_3

TABLE 4
Shifts of energy levels, difference between levels and degree of covalency in doped-Er crystal*

Crystal	Shifts caused by J-mixing effect			Difference between the levels and ground level				Degree of Covalency(%)	
	$^4I_{15/2}$	$^4I_{13/2}$	$^4G_{11/2}$	$^4I_{13/2}$		$^4G_{11/2}$		$^4I_{13/2}$	$^4G_{11/2}$
				E_{exp}	E(J)	E_{exp}	E(J)		
Er^{3+}:									
LaF_3	-3.10	-2.18	1.13	6482.07	6481.15	26238.50	26364.27	0.07	0.10
$LaCl_3$	-0.71	-0.51	0.20	6481.56	6481.36	26271.39	26270.48	0.07	0.40
$LaBr_3$	-0.48	-0.33	0.21	6475.14	6474.99	26180.03	27179.34	0.17	0.75
YCl_3	-2.00	-1.20	1.96	6466.84	6466.04	26104.23	26100.27	0.30	1.04
YF_3	-2.47	-1.54	1.44	6483.43	6482.50			0.05	0.32
Y_2O_3	-7.25	-3.99	7.03	6458.21	6454.95	26074.50	26060.20	0.48	1.20
$RECl_3$ $6H_2O$	-1.23		0.85			26297.56	26295.48		0.31
YPO_4	-2.06		1.32			26250.47	26247.09		0.49
YVO_4	-2.41		1.67			26177.52	26173.44		0.77
$YAlO_3$	-4.67	-3.10	2.60	6469.26	6467.69	26155.25	26147.98	0.28	0.86
$LuPO_4$	-1.75		1.10			26246.57	26243.82		0.50
$HfSiO_3$	-2.22		2.01			26219.42	26215.19		0.61
$Y_3Al_5O_{12}$	-9.15	-6.01	5.82	6441.45	6438.36	26168.67	26153.70	0.47	0.84
$RE_3Al_5O_{12}$	-8.72	-5.81	5.18	6464.98	6462.08	26104.63	26090.73	0.37	1.08
$Y_3Ga_5O_{12}$	-0.18	-5.40		6466.69	6463.91			0.34	
$LiYF_4$	-3.35	-2.16		6476.36	6475.17			0.17	
$GdCl_3$	-0.68	-0.48		6479.31	6479.11			0.10	
Y_2O_2S	-2.36	-1.40		6426.54	6425.58			0.93	
CaF_2	-10.08	-6.85		6479.70	6476.47			0.15	
$KGd(WO_4)_2$	-2.49	-1.56		6477.87	6476.94			0.14	
$ScCl_3$	-3.93		3.66			26120.90	26113.31		1.00
$InCl_3$	-4.19		3.82			26109.60	26101.59		1.04
$Y(OH)_3$	-1.06					26261.90	26260.25		0.44
KY_3F_{10}	-2.43	-1.34	2.30	6481.11	6480.02	26344.08	26339.35	0.09	0.14
$ErVO_4$	-3.63		2.35			26125.93	26119.95		0.97
Er_2O_3	-4.02	-2.95	1.14	6458.21	6457.14	26063.17	26058.01	0.44	1.20

* Only results for $^4I_{13/2}$ and $^4G_{11/2}$ are presented.

host(Table3-4). Covalent degree principally depends on the properties of donor atoms which directly bond trivalent lanthanide. In addition, other atoms adjacent to donor atoms in host also influence bonding nature of 4f-orbits. Generally, the smaller the electronegativity of the adjacent atoms, the stronger the covalent bond between 4f orbit and ligand. Covalency in some similar composition hosts decreases in the order $AlO_3^{3-} > VO_4^{3-} > SiO_3^{2-} > PO_4^{3-}$ and $Al_5O_{12}^{9-} > Ga_5O_{12}^{9-}$, but the adjacent atom electronegativities are 1.61, 1.63, 1.90, 2.19 and1.81 for Al, V, Si, P and Ga respectively[25].

Besides, the covalency in Ln^{3+}doped hosts is relative to the properties of substituted lanthanide(III) ions, too. The gradually decreasing radii of substituted ions produces a strongly increasing covelency of 4f orbit ligand bond. From Table 4 $LaX_3 < YX_3$, $LaCl_3 < GdCl_3 < InCl_3$ and from Table 3 $YPO_4 < LuPO_4$ and $LaCl_3 < PrCl_3$ corresponding ionic radii are 0.88, 1.061, 0.81, 0.938, 0.848 and 1.013Å for Y(III), La(III), In(III), Gd(III), Lu(III) and Pr(III). That is because the trivalent lanthanides share so similar chemical and physical properties that ion substitution by each other don't bring about remarkable distortion of crystal, hence the covalency of 4f orbit ligand bond is decided to a large extent by the distance of lanthanide ion to donor atom and the longer the distance the less the covalency. Since trivalent erbium and yttrium are of similar radii, covalent parameters of corresponding compounds are almost identical. Covalent differences between Er^{3+} : $YAlO_3$ and Er^{3+}:$Y_3Al_5O_{12}$, Er^{3+} : $LiYF_4$ and Er^{3+} : KY_3F_{10} can be derived from crystal lattice differences.

It is important to note that covalent characteristic of 4f orbit -ligand bond is not directly correlative to stability of lanthanide compounds. For the compounds with similar composition and structure as the stability increase, covalency becomes weaker. There is a typical example, lanthanide trihalide stabilities weaken in the

order (fluoride> chloride>bromide)[26], contrarily covalency increased in the same order (fluoride<chloride<bromide). Trivalent lanthanide forms ionic linkage with inorganic ligand through static electric interaction[27] and covalent characteristic is very weak. As a result the stability of compouunds mainly depend on intensity of the ionic bond. According to the Pearson classification scheme[28], trivalent lanthanides are classified as hard acids, hence they are apt to form stable compounds with hard bases. Considering that hardness of halide weakens with enbancement of atomic number, the conclusion above is right. It is obvious that covalency hasn't direct correlation to total crystal field intency parameters either. Reference[29] ever pointed out that the temperature and pressure induce the shift of absorptin bands, this phenomenon could be explained from lattice distortion.

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