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► To cite this version:

C. Linares, A. Louat. Interpretation of the crystal field parameters by the superposition and angular overlap models. Application to some lanthanum compounds. *Journal de Physique*, 1975, 36 (7-8), pp.717-725. <10.1051/jphys:01975003607-8071700>. <jpa-00208307>

HAL Id: jpa-00208307

<https://hal.science/jpa-00208307v1>

Submitted on 4 Feb 2008

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HAL Authorization

Classification
Physics Abstracts
8.140

INTERPRETATION OF THE CRYSTAL FIELD PARAMETERS BY THE SUPERPOSITION AND ANGULAR OVERLAP MODELS. APPLICATION TO SOME LANTHANUM COMPOUNDS

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(Reçu le 18 octobre 1974, révisé le 3 mars 1975, accepté le 18 mars 1975)

Résumé. — Le modèle de superposition est appliqué au calcul des paramètres intrinsèques $\bar{A}_2(R)$, $\bar{A}_4(R)$ et $\bar{A}_6(R)$ pour chacune des différentes distances des ligandes à l'ion dopant Eu^{3+} , dans les composés LaCl_3 , LaAlO_3 , La_2O_3 et $\text{La}_2\text{O}_2\text{S}$. Ces paramètres permettent de tirer des conclusions relatives à la covalence de ces matrices et de caractériser, dans certains cas, la liaison europium-ligande. D'autre part, on détermine, par le modèle du recouvrement angulaire, des paramètres σ^* dans le cas de composés faiblement covalents.

Abstract. — The superposition model is applied to the calculation of intrinsic parameters $\bar{A}_2(R)$, $\bar{A}_4(R)$ and $\bar{A}_6(R)$ for each europium-ligand distance in LaCl_3 , LaAlO_3 , La_2O_3 and $\text{La}_2\text{O}_2\text{S}$. These parameters allow one to draw conclusions regarding the covalency of these compounds and, in some cases, to characterize the europium-ligand bonding. On the other hand, for weakly covalent compounds, the σ^* parameters may be determined by the angular overlap model.

1. Introduction. — The crystal field parameters obtained from luminescence investigations of the Eu^{3+} ion in rare earth compounds are interpreted using the superposition approximation described by Newman [1] and the angular overlap model of Jørgensen [2]. Lanthanum compounds such as LaCl_3 , LaAlO_3 , La_2O_3 and $\text{La}_2\text{O}_2\text{S}$, are studied so that the distortion due to substitution of La^{3+} by Eu^{3+} is the same in all the lattices.

The first part of this work connects the superposition model with the classical theory of electrostatic point charges and gives intrinsic parameters relative to the ligand-europium bond in our compounds.

In the second part, the angular overlap model is summarized and values of σ^* radial parameters are determined.

2. Crystal field and superposition model. — 2.1 GENERAL OUTLINE. — The crystal field at a rare earth ion site in a solid is created by all the surrounding ions. This field has the site symmetry of the rare earth. From optical spectra, the operator equivalent (O_n^m) method of Stevens [3] permits one to determine the crystal field phenomenological parameters $B_{n(\text{exp})}^m$. Indeed the potential energy of 4f electrons may be written :

$$V = \sum_{n,m} B_n^m a_n O_n^m = \sum_{i,n,m} U_n^m B_n^m Z_n^m(\theta_i, \varphi_i) \quad (1)$$

$$a_n = \alpha, \beta, \gamma \quad \text{for } n = 2, 4, 6$$

where n and m refer to the 4f electron and to point symmetry, θ_i, φ_i are the angular coordinates of the i th 4f electron in relation to the rare earth ion taken as origin. In order to express V in terms of tesseral harmonics Z_n^m , a factor U_n^m must be introduced, the U_n^m used in this paper are given in table I.

Eq. (1) is very general, and no hypothesis is made on the physical significance of B_n^m which is purely phenomenological. Different models have been tested to represent the crystal field and the B_n^m values.

2.1.1 Electrostatic point charges model. — In this simplest approximation the surrounding ions are replaced by charges. The $V(R)$ electrostatic potential created by these charges at distance R , obeys Laplace's equation $\Delta V(R) = 0$ whose solution is :

$$V = \sum_{i,n,m} A_n^m r_i^n Z_n^m(\theta_i, \varphi_i). \quad (2)$$

TABLE I

n	m	U_n^m
2	0	$4\sqrt{5\pi/5}$
4	0	$16\sqrt{\pi/3}$
4	3	$4\sqrt{70\pi/105}$
6	0	$32\sqrt{13\pi/13}$
6	3	$16\sqrt{2\,730\pi/1\,365}$
6	6	$32\sqrt{6\,006\pi/3\,003}$

From eq. (1) and (2) it appears that the experimental B_n^m parameter is the product of an A_n^m parameter and a mean radial factor $\langle r^n \rangle$ of the 4f electron.

When the crystalline structure is known, the electrostatic parameters $B_{n(\text{elec})}^m$ can be calculated from the R_j , θ_j , Φ_j coordinates and the Q_j charge of each ion of the crystal [4]

$$B_{n(\text{elec})}^m = \frac{1}{U_n^m} e \frac{4\pi}{2n+1} \langle r^n \rangle \sum_j Q_j \frac{1}{R_j^{n+1}} Z_n^m(\theta_j, \Phi_j). \quad (3)$$

Unfortunately it is well established [5] that the $B_{n(\text{elec})}^m$ are very different from the experimental phenomenological parameters $B_{n(\text{exp})}^m$. Nevertheless, the ratios B_n^m/B_n^m are nearly the same in the two cases; so that the point charge model is better than one might imagine. Moreover, the electrostatic contribution of the ligands represents practically all (except for $B_{2(\text{elec})}^0$) the contribution of all the ions of the crystal.

This is why we have tested a more general model, accounting only for the ligands since their contribution is the most important.

2.1.2 Superposition model. — In this model, $\Delta V(r)$ is not equal to zero and B_n^m is not a known function of the distance r as in the case of a purely electrostatic field, and the parameters may include other contributions to crystal field (overlap, covalency...).

These ideas have been developed by Newman [1]. In the superposition model, the first assumption is that the total crystal field can be built up from the separate contributions of each ligand around the rare earth ion. The spherical symmetry of the ligands ensures that each contribution can be represented as a cylindrically symmetrical field $D_{\infty h}$ which is described by just three parameters $B_2^0(j)$, $B_4^0(j)$ and $B_6^0(j)$. These so called intrinsic parameters denoted by $\bar{A}_n(R_j)$ ⁽¹⁾ [$\bar{A}_2(R_j)$, $\bar{A}_4(R_j)$ and $\bar{A}_6(R_j)$], depend only on the distance R_j of the ligand from the lanthanide ion.

The phenomenological parameters B_n^m (Stevens notation) are expressed in terms of the $\bar{A}_n(R_j)$ by the formula :

$$B_n^m = \frac{U_n^0}{U_n^m} \sqrt{\frac{4\pi}{2n+1}} \sum_j \bar{A}_n(R_j) Z_n^m(\theta_j, \Phi_j) \quad (4)$$

⁽¹⁾ It can be noticed that the \bar{A}_n are connected to the I_n parameters previously introduced by Bethe [6] and Kibler [7] by :

$$\sqrt{\frac{4\pi}{2n+1}} I_n = U_n^0 \bar{A}_n$$

since

$$A_n^m \langle r^n \rangle = \sum_j \frac{4\pi}{2n+1} I_n(R_j) Y(\theta_j, \Phi_j).$$

Nevertheless, the outstanding merit of Newman's theory is to allow the experimental determination and interpretation of those intrinsic parameters depending only on the ligands.

or

$$B_n^m = \sum_j K_n^m(j) \bar{A}_n(R_j) \quad (5)$$

(provided that all the ligands are of the same type) K_n^m is called the coordination factor which depends only on the angular position of the ligands.

The merit of this model is to separate in B_n^m the angular part which is known from X-ray data and the radial part which is fitted to the experimental data.

In practice, a given type of ligand is at various distances from the rare earth ion; if these distances are not too different we can write [1] :

$$\bar{A}_n(R_j)/\bar{A}_n(R_k) = (R_j/R_k)^{t_n} \quad (6)$$

where the constant t_n has been computed. An intrinsic parameter $\bar{A}_n(R_0)$ at the mean distance R_0 of the coordinated ligands of the same type may also be determined.

Ligands often are of different types. If one type is denoted by T the expression (5) becomes :

$$B_n^m = \sum_{j,T} K_n^m(\theta_{j(T)}, \Phi_{j(T)}) \cdot \bar{A}_n(R_{j(T)}). \quad (7)$$

2.2 RESULTS. — In order to test the validity of the superposition model in our compounds we have calculated the parameters $B_{n(\text{elec})}^m$ from eq. (3).

These results which have already been published [8] are reported in table II. In this table $B_{n(\text{elec. tot.})}^m$ are compared to $B_{n(\text{elec. ligands})}^m$ and to $B_{n(\text{exp})}^m$. It can be seen that the electrostatic contribution of the ligands represents practically the total electrostatic field for $B_{4(\text{elec})}^m$ and $B_{6(\text{elec})}^m$; but the same is not the case with $B_{2(\text{elec})}^0$; the farthest ions contribution being important. The superposition model which is only concerned with the ligands may thus be applied to B_4^m and B_6^m .

Furthermore, the phenomenological parameters for $n = 4$ and 6 are different from the electrostatic ones and for these parameters the electrostatic contribution is not primordial. On the other hand, the electrostatic contribution of the ligands and the B_2^0 experimental parameter have about the same value; so an \bar{A}_2 intrinsic parameter can be calculated and it includes a large electrostatic contribution in agreement with Newman.

Electrostatic intrinsic parameters can be determined for \bar{A}_6 , \bar{A}_4 and also for \bar{A}_2 , and can be compared to the experimental intrinsic parameters.

2.2.1 Intrinsic electrostatic parameters. — Those parameters may be calculated by the following formula [9]

$$\left. \begin{aligned} \bar{A}_2(R)_{\text{elec}} &= \frac{1}{2} Kq \frac{\langle r^2 \rangle}{R^3} \\ \bar{A}_4(R)_{\text{elec}} &= \frac{1}{8} Kq \frac{\langle r^4 \rangle}{R^5} \\ \bar{A}_6(R)_{\text{elec}} &= \frac{1}{16} Kq \frac{\langle r^6 \rangle}{R^7} \end{aligned} \right\} \quad (8)$$

TABLE II

Parameters	LaCl ₃	LaAlO ₃	La ₂ O ₃	La ₂ O ₂ S
B_2^0 (elec ligands)	133	— 69	— 252	— 29.7
B_2^0 (elec total)	— 397	— 97	— 110	— 3.7
B_2^0 (exp)	89	— 85	— 350	37
B_4^0 (elec ligands)	— 9.35	34.5	18.6	46.9
B_4^0 (elec total)	— 13.3	21.1	19.8	42.3
B_4^0 (exp)	— 38	55	65	99.8
B_4^3 (elec ligands)	—	926	— 2 387	— 1 650
B_4^3 (elec total)	—	550.3	— 2 390	— 1 522
B_4^3 (exp)	—	1 100	— 4 500	— 2 768
B_6^0 (elec ligands)	— 1.26	— 10.4	9.8	6.62
B_6^0 (elec total)	— 1.65	— 13.4	11.3	5.77
B_6^0 (exp)	— 51	— 75	25	26.9
B_6^3 (elec ligands)	—	123.5	88.9	88.0
B_6^3 (elec total)	—	158.6	82.5	82.6
B_6^3 (exp)	—	850	240	307
B_6^6 (elec ligands)	12.4	— 105.2	91	87.7
B_6^6 (elec total)	16.2	— 133.9	100.7	96.6
B_6^6 (exp)	495	— 800	280	345

TABLE III

Compound	La ³⁺ site symmetry	Ligands	R Å	θ^0	Φ^0		
LaCl ₃	C _{3h} [10] (D _{3h}) ⁽²⁾	3 Chlorine	2.97	90	— 70.4	59.6	179.6
		3 —	2.99	43.13	— 118.1	1.9	121.9
		3 —	2.99	136.87	— 118.1	1.9	121.9
LaAlO ₃	D ₃ [11]	3 Oxygen	2.55	90	— 30	90	210
		3 —	2.68	35.35	— 115.1	4.9	124.9
		3 —	2.68	144.65	— 64.9	55.1	175.1
		3 —	2.82	90	— 90	30	150
La ₂ O ₃	C _{3v} [12]	3 Oxygen	2.420	70	— 60	60	180
		1 —	2.420	0	—	—	—
		3 —	2.691	122.3	— 120	0	120
La ₂ O ₂ S	C _{3v} [13]	3 Oxygen	2.423	74.7	— 60	60	180
		1 —	2.424	0	—	—	—
		3 Sulfur	3.037	129.7	— 120	0	120

(²) An 5°6 inverse rotation of *OxOy* axis around *Oz* transforms the C_{3h} symmetry into a higher pseudo symmetry D_{3h}, in order to cancel the *B*₆^{−6} parameter.

where $\overline{A}_n(R)_{elec}$ is in cm^{−1}, *R* and *r* being expressed in cm and *K* chosen equal to -116×10^{-5} (*q* = − 2 for O^{2−} and S^{2−}; *q* = − 1 for Cl[−]). *R* values are in table III, $\langle r^n \rangle$ values are those of Freeman and Watson [14].
Results are given in table IV.

Eq. (8) show that
$$\overline{A}_n(R_j)_{elec}/\overline{A}_n(R_K)_{elec} = (R_j/R_K)^{n+1} . \tag{9}$$

This formula (9) is the same as the formula (6) of the superposition approximation but here *t_n* = *n* + 1.

TABLE IV

Compound	R Å	$\bar{A}_2(R)$ (cm ⁻¹) elec	$\bar{A}_4(R)$ (cm ⁻¹) elec	$\bar{A}_6(R)$ (cm ⁻¹) elec
LaCl ₃	$R_1 = 2.97$	515	8.6	0.58
	$R_2 = 2.99$	505	8.3	0.55
LaAlO ₃	$R_1 = 2.55$	1 627	36.8	3.35
	$R_2 = 2.68$	1 397	28.7	2.37
	$R_3 = 2.82$	1 203	22.2	1.65
La ₂ O ₃	$R_1 = R_2 = 2.420$	1 902	48	4.85
	$R_3 = 2.691$	1 396	28.2	2.3
La ₂ O ₂ S	$R_1 = R_2 = 2.423$	1 900	47.3	4.75
	$R_{3s^2} = 3.037$	960	15.2	0.98

As in the superposition model, the electrostatic contribution is not negligible, the t_n coefficients must be nearly 3, 5 and 7 for t_2 , t_4 and t_6 respectively.

2.2.2 Intrinsic parameters. — The application of the superposition model allows us to calculate three intrinsic parameters for each ligand in a given lattice. The crystal field parameters are B_2^0 , B_4^0 , B_4^3 , B_6^0 , B_6^3 and B_6^6 when the symmetries are those described in table III. (In D_{3h} symmetry $B_4^3 = B_6^3 = 0$.) For each compound, table V gives the experimental

law t_n for different host crystals. It can be seen that the choice of t_n is not critical (all the values chosen give similar results).

As an example, in order to prove the precision of our calculations, we report (table VII) those made for LaAlO₃. In this table we give, for several values of t_n , the intrinsic parameter $\bar{A}_n(R)$ derived from the different experimental B_n^m . We have chosen the constants t_n for which the calculated values of $\bar{A}_n(R)$ are the closest. This choice is confirmed by the comparison between the experimental and calculated values of B_n^m :

$$B_n^m{}_{\text{calc}} = \sum_j K_n^m(j) \bar{A}_n(R_j). \quad (10)$$

TABLE V

Compound	LaCl ₃	LaAlO ₃	La ₂ O ₃	La ₂ O ₂ S
B_n^m cm ⁻¹				
B_2^0	89	— 85	— 350	37
B_4^0	— 38	55	65	100
B_4^3	—	1 100	— 4 500	— 2 768
B_6^0	— 51	— 75	25	27
B_6^3	—	850	240	307
B_6^6	495	— 800	280	345

crystal field parameters in Stevens's notation. LaCl₃ parameters are those of Dieke [15]; as for LaAlO₃, we have reidentified some levels by taking into account the excitation spectrum, and some of our previously published parameters [16] must therefore be corrected. La₂O₃ parameters have been determined by one of us [17]. Finally, for La₂O₂S, we have taken the new B_n^m parameters of Sovers given by Newman [18].

Coordination factors have been calculated in the case of Cl⁻, O²⁻ and S²⁻ ligands, from X-ray data given in table III. The intrinsic parameters of an Eu³⁺-ligand bond can be determined from that data. Table VI summarizes intrinsic parameters for each europium-ligand distance and also the power

The precision is less satisfactory for \bar{A}_6 than for \bar{A}_4 . However, for all the compounds studied, this precision is good. In table VIII compounds are classified according to the mean value R_0 of the europium-ligand separation. We give the corresponding intrinsic parameters and the energy of the ⁵D₀ level of Eu³⁺ ion (except for La₂O₂S because there are two different ligands O²⁻ and S²⁻). We note that the parameters \bar{A}_2 and \bar{A}_4 increase when R_0 decreases. This is not surprising because \bar{A}_4 and specially \bar{A}_2 are sensitive to the electrostatic field whose variation is linear in $1/R$. Moreover, the position of the ⁵D₀ level is reduced when R_0 decreases from LaCl₃ to La₂O₂S. These facts show that covalency probably increases from LaCl₃ to La₂O₂S [19].

On the other hand, a comparison of $\bar{A}_{2\text{elec}}$ with \bar{A}_2 parameters (tables IV and VI), shows that $\bar{A}_{2\text{elec}}$ is greater than \bar{A}_2 , for LaCl₃ and LaAlO₃, though a smaller value of $\bar{A}_{2\text{elec}}$ may be expected. We think that in these compounds, the electrostatic screening strongly reduces the electrostatic field near the doping ion; there is therefore a strong reduction of the parameter $\bar{A}_{2\text{elec}}$ relative to its calculated value. In less ionic compounds, such as La₂O₃ and La₂O₂S, screening does not play an important part. For the \bar{A}_4 and \bar{A}_6 parameters, $\bar{A}_{n\text{elec}}$ has always a much

TABLE VI

Compound	R	t_2	$\overline{A}_2(R)$ cm^{-1}	t_4	$\overline{A}_4(R)$ cm^{-1}	t_6	$\overline{A}_6(R)$ cm^{-1}
LaCl ₃	R_1	4-5	370 ± 20	5-7	35.0 ± 1.5	5-7	21 ± 2
	R_2		360 ± 20		33.4 ± 1.5		20 ± 2
LaAlO ₃	R_1	5-6	$1\,000 \pm 200$	11-12	62.5 ± 1	11-12	28.3 ± 1
	R_2		800 ± 200		35 ± 1		16.4 ± 0.2
	R_3		600 ± 150		19 ± 1		9.4 ± 0.5
La ₂ O ₃	$R_1 = R_2$	5-6-7	$3\,750 \pm 500$	9-10 (11)	107.5 ± 1.5	9-10-11	14 ± 0.5
	R_3		$2\,000 \pm 30$		39 ± 3		4.8 ± 1
La ₂ O ₂ S	$R_1 = R_2$	—	—	—	88 ± 0.5	—	18.5 ± 0.5
	R_{3s^2-}				22 ± 3		4.3 ± 0.8

TABLE VII₁

LaAlO₃

t_2	3			4			5			6			7		
$\overline{A}_2(R_1)$	2 143			1 450			1 095			834			653		
$\overline{A}_2(R_2)$	2 048			1 269			863			618			472		
$\overline{A}_2(R_3)$	1 765			1 057			673			457			300		
B_2^0 exp	— 85														
B_2^0 calc	257			30			— 74			— 89			— 20		
t_4	5			7			10			11			12		
	From		Mean	From		Mean	From		Mean	From		Mean	From		Mean
	B_4^0	B_4^3	Value	B_4^0	B_4^3	Value	B_4^0	B_4^3	Value	B_4^0	B_4^3	Value	B_4^0	B_4^3	Value
$\overline{A}_4(R_1)$	58.6	43.8	51.2	61.4	48.4	54.9	63.9	56.2	60.1	64.4	59	61.7	64.8	62	63.4
$\overline{A}_4(R_2)$	45.7	34.1	39.9	43.3	34.1	38.7	38.9	34.1	36.5	37.3	34.1	35.7	35.6	34.1	34.9
$\overline{A}_4(R_3)$	35.4	26.5	31	30.3	23.9	27.1	23.4	20.5	22	21.3	19.5	20.4	19.4	18.5	18.9
B_4^0 exp	55														
B_4^0 calc	48.1			49.3			51.8			52.7			53.9		
B_4^3 exp	1 100														
B_4^3 calc	1 288			1 248			1 170			1 150			1 122		

TABLE VII₂

LaAlO₃

t_6	5				7				10				11				12			
	From			Mean	From			Mean	From			Mean	From			Mean	From			Mean
	B_6^0	B_6^3	B_6^6	Value	B_6^0	B_6^3	B_6^6	Value	B_6^0	B_6^3	B_6^6	Value	B_6^0	B_6^3	B_6^6	Value	B_6^0	B_6^3	B_6^6	Value
$\overline{A}_6(R_1)$	21.9	21	23.8	22.2	23.9	23.2	25.5	24.2	27.1	26.9	27.9	27.3	28.1	28.3	28.6	28.3	29.2	29.7	29.3	29.4
$\overline{A}_6(R_2)$	17.1	16.4	18.6	17.3	16.9	16.4	18	17.1	16.4	16.4	17	16.6	16.3	16.4	16.5	16.4	16.1	16.4	16.1	16.2
$\overline{A}_6(R_3)$	13.3	12.7	14.4	13.4	11.8	11.4	12.6	11.9	9.9	9.8	10.2	10	9.3	9.4	9.4	9.4	8.7	8.9	8.7	8.8
B_6^0 exp	— 75																			
B_6^0 calc	— 75.5				— 75.8				— 75.7				— 75.6				— 75.5			
B_6^3 exp	850																			
B_6^3 calc	899				886				860				851				841			
B_6^6 exp	— 800																			
B_6^6 calc	— 747.3				— 759.6				— 786.4				— 793				— 804			

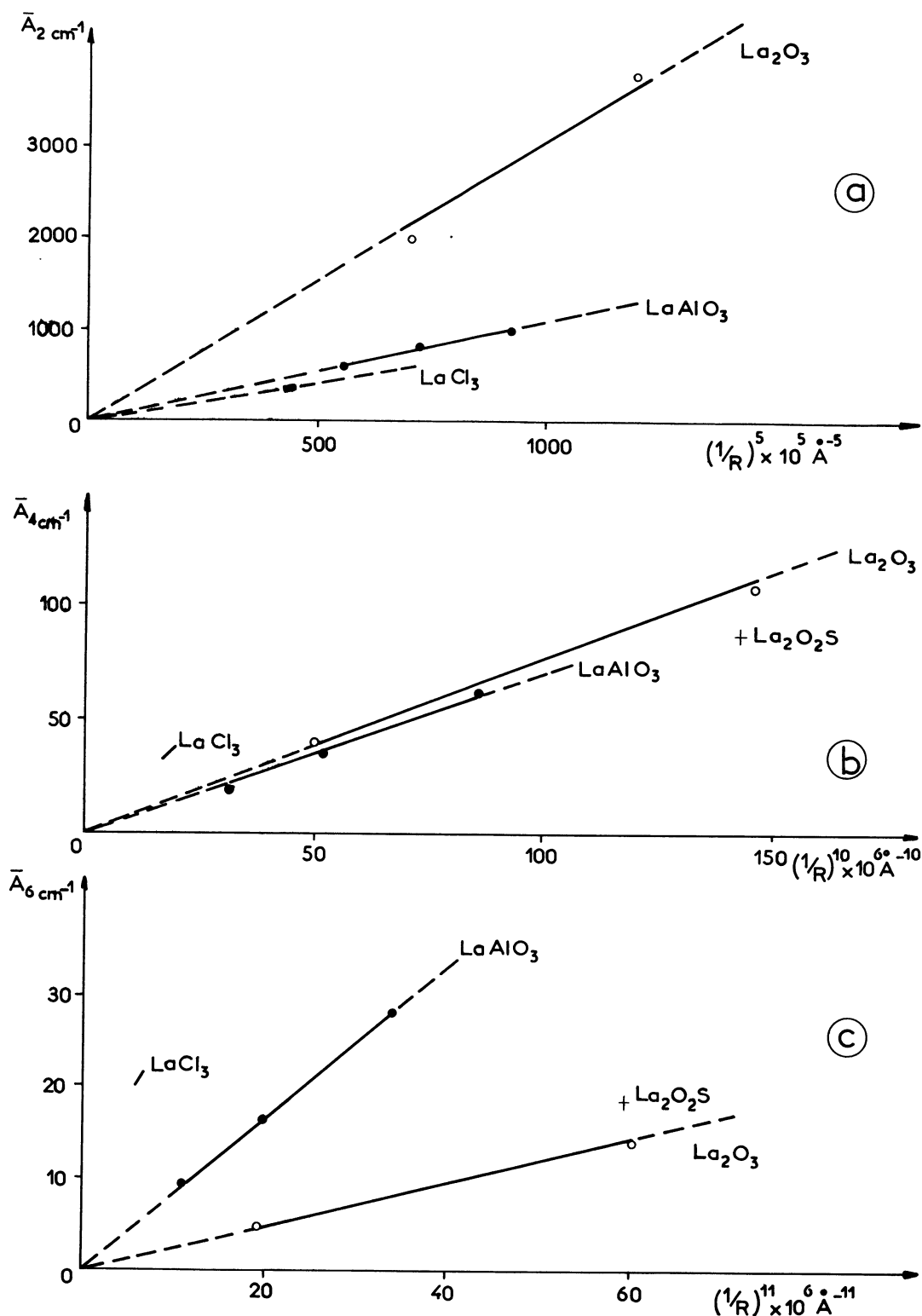


FIG. 1. — The variation of the intrinsic parameter $A_n(R)$ as a function of $(1/R)^n$. (The full lines represent the experimental range.)

lower value than A_n , which agrees with Newman's observation on other compounds [1] : the screening effect is negligible for \bar{A}_4 and \bar{A}_6 parameters.

At last, in order to have a general view of our results, figures 1(a, b, c) show the parameters \bar{A}_2 , \bar{A}_4 and \bar{A}_6 for all the ligands in a given compound

plotted as a function of $1/R^5$ for \bar{A}_2 , $1/R^{10}$ for \bar{A}_4 and $1/R^{11}$ for \bar{A}_6 . These different curves are obviously straight lines according to formula (6) (excepted for \bar{A}_4 and \bar{A}_6 of LaCl_3 , t_4 and t_6 being different from 10 and 11). It appears that the slope of the line concerning oxygen ligands, in the three compounds LaAlO_3 ,

TABLE VIII

Compound Parameter	LaCl ₃	LaAlO ₃	La ₂ O ₃	La ₂ O ₂ S
$\bar{A}_2(R_0) \text{ cm}^{-1}$	365	800	3 000	—
$\bar{A}_4(R_0) \text{ cm}^{-1}$	34	35	70	88
$\bar{A}_6(R_0) \text{ cm}^{-1}$	20.5	16.4	8.6	18.5
$^5D_0 \text{ energy (cm}^{-1}\text{)}$	17 267	17 235	17 219	—
$R_0 \text{ Å}$	2.98	2.68	2.54	2.423

La₂O₃ and La₂O₂S, is about the same for the \bar{A}_4 parameters, whereas it is quite different for \bar{A}_2 and \bar{A}_6 ; the classification order is reversed for these two last parameters. It may be noted that this classification seems to be connected with covalency since LaAlO₃ is always near LaCl₃ whose ionicity is well known so that LaAlO₃ is the most ionic among the compounds studied. Concerning the \bar{A}_4 parameter a single straight line is found; and it seems that its slope may characterize the europium-ligand bond.

TABLE IX

Theoretical value	R	\bar{A}_2/\bar{A}_4	\bar{A}_4/\bar{A}_6	\bar{A}_2/\bar{A}_6
	—	2.2	1.4	3.1
LaCl ₃	R_1	10.5	1.67	17.6
	R_2	10.7	1.67	18
	R_1	16	2.21	35.4
LaAlO ₃	R_2	22.8	2.12	48.6
	R_3	31.4	1.82	63.8
	$R_1 = R_2$	—	4.75	—
La ₂ O ₂ S	R_{3s^2}	—	5.1	—
	$R_1 = R_2$	34.8	7.7	268
La ₂ O ₃	R_3	51.3	8.1	418

The superposition model provides further information. It is known (Jørgensen [20]) that for weakly covalent compounds (central ion electrons are on the ligands), the angular overlap model can be used. In this case, the intrinsic parameter ratios have special values which can be calculated from Kibler's papers [21, 22]

$$\left. \begin{aligned} \bar{A}_2/\bar{A}_4 &= 4 \times 5/9 = 2.2 \\ \bar{A}_4/\bar{A}_6 &= 2 \times 9/13 = 1.4 \\ \bar{A}_2/\bar{A}_6 &= 8 \times 5/13 = 3.1 \end{aligned} \right\} \quad (11)$$

Table VIII lists these ratios for the compounds studied. Except for \bar{A}_4/\bar{A}_6 , the ratios are quite different from the theoretical values. Since the B_2^0 parameter (and afterwards \bar{A}_2) is sensitive to distant ions contributions, we shall consider \bar{A}_4/\bar{A}_6 as the most significant ratio. For LaCl₃ and LaAlO₃, this ratio is close to the theoretical value; the angular overlap model can then be used for these two compounds.

3. Angular overlap model. — 3.1 GENERAL OUTLINE. — In this model we are interested in the relative extent of the σ antibonding influence of the ligands X on f orbitals of the central rare earth ion M.

In the case where all the ligands of the same type are at the same distance from the europium ion, each overlap integral S_{MX} can be expressed in terms of a common radial parameter since σ orbitals have axial symmetry. Moreover, as this model is a partially delocalized one, the electrons of each ligand stay concentrated close to that ligand, while 4f electrons may remove on MX axis; so their angular coordinates are those of the ligands (θ_j, Φ_j). The overlap integral may therefore be written as a product of a radial dependent quantity by a parameter which depends only on the angular coordinates of the ligand, Ξ is that last term.

If covalency is weak, the hypothesis of Wolfsberg-Helmholz [23] can be applied: a non diagonal element H_{MX} of the energy matrix is proportional to S_{MX}^2 i.e. to the product of the square of the radial term (noted σ^*) by Ξ^2 (angular parameter); as it is the same for the diagonal elements, the energy may be written:

$$E \sim \sigma^* \Xi^2. \quad (12)$$

In order to find the radial term σ^* which characterizes the chemical bond, we need to calculate Ξ^2 and E .

TABLE X

$$\begin{aligned} \psi_{z^2} &= \sqrt{7/2}(5 \cos^3 \theta - 3 \cos \theta) \\ \psi_{z^2} &= \sqrt{42/4} \sin \theta (5 \cos^2 \theta - 1) \cos \Phi \\ \psi_{z^{-1}} &= \sqrt{42/4} \sin \theta (5 \cos^2 \theta - 1) \sin \Phi \\ \psi_{z^2} &= \sqrt{105/2} \sin^2 \theta \cos \theta \cos 2 \Phi \\ \psi_{z^{-2}} &= \sqrt{105/2} \sin^2 \theta \cos \theta \sin 2 \Phi \\ \psi_{z^2} &= \sqrt{70/4} \sin^3 \theta \cos 3 \Phi \\ \psi_{z^{-3}} &= \sqrt{70/4} \sin^3 \theta \sin 3 \Phi \end{aligned}$$

— First, for Ξ^2 we need the 7 wave functions of the 4f electron normalized to 4π (table X).

The j th ligand contribution to Ξ^2 parameter of a given orbital such as ψ_{z^2} is:

$$\Xi_{z^2}^2 = \psi_{z^2}(\theta_j, \Phi_j) \cdot \psi_{z^2}(\theta_j, \Phi_j) \quad (13)$$

the corresponding orbital energy for all the N ligands is given by:

$$W = \Xi_{z^2}^2 \sigma^* = \sum_{j=1}^N \psi_{z^2}(\theta_j, \Phi_j) \cdot \psi_{z^2}(\theta_j, \Phi_j) \cdot \sigma^*. \quad (14)$$

The site symmetry in our compounds is not very high and for some orbitals, non diagonal elements appear:

$$\Xi^2 = \sum_{j=1}^N \psi_{z^2}(\theta_j, \Phi_j) \cdot \psi_{z^2}(\theta_j, \Phi_j) \quad (15)$$

u and v vary between -3 and $+3$.

In this case, orbital energies are found by solving the associated determinant.

The sum of Ξ^2 values of all orbitals is $N(2l + 1)$ where N is the number of ligands and $2l + 1$ is the degeneracy of the shell (here, $l = 3$).

In our compounds, the ligands are not at the same distance but those distances are not very different so that we can use a law in $(R_0/R)^8$ [24] (R_0 is the mean distance).

— Secondly, the orbital f energy E (formula (12)) can also be calculated from the crystal field theory. We need to determine matrix elements

$$\langle \psi_{z_3^y} | V | \psi_{z_3^y} \rangle$$

TABLE XI

$$\begin{aligned} \langle \psi_{z_3^0} | V | \psi_{z_3^0} \rangle &= \frac{8}{15} B_2^0 + \frac{16}{11} B_4^0 + \frac{1600}{429} B_6^0 \\ \langle \psi_{z_3^1} | V | \psi_{z_3^1} \rangle &= \frac{2}{5} B_2^0 + \frac{8}{33} B_4^0 - \frac{400}{143} B_6^0 \\ \langle \psi_{z_3^2} | V | \psi_{z_3^2} \rangle &= -\frac{56}{33} B_4^0 + \frac{160}{143} B_6^0 \\ \langle \psi_{z_3^3} | V | \psi_{z_3^3} \rangle &= -\frac{2}{3} B_2^0 + \frac{8}{11} B_4^0 - \frac{80}{429} B_6^0 + \frac{160}{429} B_6^0 \\ \langle \psi_{z_3^{-3}} | V | \psi_{z_3^{-3}} \rangle &= -\frac{2}{3} B_2^0 + \frac{8}{11} B_4^0 - \frac{80}{429} B_6^0 - \frac{160}{429} B_6^0 \\ \langle \psi_{z_3^0} | V | \psi_{z_3^3} \rangle &= -\frac{2\sqrt{10}}{55} B_4^3 + \frac{16\sqrt{10}}{429} B_6^3 \\ \langle \psi_{z_3^1} | V | \psi_{z_3^2} \rangle &= \frac{2\sqrt{10}}{165} B_4^3 + \frac{8\sqrt{10}}{143} B_6^3 \end{aligned}$$

(V is the crystal potential). Table XI reports these matrix elements for the symmetries of our compounds. In the formulae of this table, the parameters B_n^m are given by the optical spectra. Energies found in this way are relative to the baricenter. In order to identify antibonding energies with those of crystal field, baricenter of the $\Xi^2 \sigma^*$ has to be determined.

3.2 RESULTS. — Calculations have been performed for LaCl_3 , LaAlO_3 and also for La_2O_3 . Tables XII, XIII and XIV summarize the results. The antibonding energies relative to the baricenter $\Xi^2 \sigma^*$ (b.) are reported in the 4th column of these tables.

For LaCl_3 and LaAlO_3 the calculation of the σ^* parameter yields values whose dispersion is weak regardless of the original equation chosen : the mean value is 27 cm^{-1} and 22 cm^{-1} for LaCl_3 and LaAlO_3 respectively. In some recent studies [25] on erbium orthovanadates and orthophosphates, this σ^* parameter is about 40 cm^{-1} .

The angular overlap model is therefore valid for LaCl_3 and LaAlO_3 doped with Eu^{3+} , weakly covalent compounds.

As far as La_2O_3 is concerned, it is not possible to find a mean value of σ^* , the dispersion being too

TABLE XII

 LaCl_3

Basis functions	Irreducible representation	$\Xi^2 \sigma^*$ cm^{-1}	$\Xi^2 \sigma^*(b)$ cm^{-1}	W_{CF} cm^{-1}	σ^* cm^{-1}
$\psi_{z_3^0}$	A_2'	$0.6 \sigma^*$	$-8.4 \sigma^*$	-198	23.6
$\psi_{z_3^1}$	E'	$14.1 \sigma^*$	$5.1 \sigma^*$	169	32.5
$\psi_{z_3^2}$	E''	$9 \sigma^*$	$0 \sigma^*$	7	—
$\psi_{z_3^3}$	A_2'	$16.1 \sigma^*$	$7.1 \sigma^*$	107.2	15.1
$\psi_{z_3^{-3}}$	A_1'	$0.1 \sigma^*$	$-8.9 \sigma^*$	-262	29.4

TABLE XIII

 LaAlO_3

Basis functions	Irreducible representation	$\Xi^2 \sigma^*$ cm^{-1}	$\Xi^2 \sigma^*(b)$ cm^{-1}	W_{CF} cm^{-1}	σ^* cm^{-1}
$\psi_{z_3^{-3}}$	A_1	$27.4 \sigma^*$	$15 \sigma^*$	408.7	27.2
Mixing $\left\{ \begin{array}{l} \psi_{z_3^0}, \psi_{z_3^3} \end{array} \right.$	A_2	$0.6 \sigma^*$	$-12.4 \sigma^*$	-253	20.4
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	A_2	$1.6 \sigma^*$	$-10.8 \sigma^*$	-179	16.6
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	E	$2.1 \sigma^*$	$-10.3 \sigma^*$	-260	25.2
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	E	$26.7 \sigma^*$	$14.3 \sigma^*$	271.5	19

TABLE XIV

 La_2O_3

Basis functions	Irreducible representation	$\Xi^2 \sigma^*$ cm^{-1}	$\Xi^2 \sigma^*(b)$ cm^{-1}	W_{CF} cm^{-1}	σ^* cm^{-1}
$\psi_{z_3^{-3}}$	A_2	$0 \sigma^*$	$-7.7 \sigma^*$	171.5	-22.3
Mixing $\left\{ \begin{array}{l} \psi_{z_3^0}, \psi_{z_3^3} \end{array} \right.$	A_1	$6 \sigma^*$	$-1.7 \sigma^*$	-390	230
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	A_1	$27.6 \sigma^*$	$19.9 \sigma^*$	770	39
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	E	$1 \sigma^*$	$-6.7 \sigma^*$	-276	41
Mixing $\left\{ \begin{array}{l} \psi_{z_3^1}, \psi_{z_3^2} \end{array} \right.$	E	$9 \sigma^*$	$1.3 \sigma^*$	0	—

important; this oxide cannot be considered as weakly covalent.

These conclusions are in good agreement with those obtained from the superposition model.

4. Conclusion. — The superposition model is applied to the lanthanum compounds : LaCl_3 , LaAlO_3 , La_2O_3 and $\text{La}_2\text{O}_2\text{S}$. Intrinsic parameters are determined for each europium-ligand distance. These calculations have shown that the model holds well in our lattices and gives fair precision. It is especially interesting to study the intrinsic parameters as a function of $(1/R)^n$. The main result is that the slope of the straight lines obtained for each compound increases for \bar{A}_2 when the compounds are tabulated in ascending order for the distances R_0 . It is clear that this order is reversed when \bar{A}_6 is considered, so that the classification order seems to be related to the degree of covalency. Moreover, for the \bar{A}_4 parameters, the slope of the straight lines is about the same for all lattices. Thus it is more than likely that this slope is characteristic of the europium ligand bonding.

The angular overlap model can be applied to weakly covalent compounds for which $\overline{A}_4/\overline{A}_6$ ratio is about 1.4. This model gives good results for LaCl_3 and LaAlO_3 in which the σ^* radial parameter is close to 25 cm^{-1} . The fact that this model cannot be applied to La_2O_3 shows clearly that this oxide is too covalent. A further study for other lattices will allow us to decide whether or not σ^* is connected with the ligand nature.

The outstanding merits of these two models is,

after reducing the number of parameters, to allow a comparison of compounds of different symmetries; this was not possible with the only phenomenological crystal field parameters.

Acknowledgments. — We are indebted to Mr. D. J. Newman of the Queen Mary College of London for helpful discussions and for the communication of results concerning La_2O_3 X-ray data prior to publication.

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