



Modelling crystal-field interaction for f-elements in LaCl_3

V.V. Zhorin, G.K. Liu*

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

Abstract

The results of crystal field calculations in the framework of exchange charge model (ECM) are reported for trivalent lanthanide and actinide ions doped into LaCl_3 . Whereas the scalar strength of the model crystal field parameters is consistent with that previously determined by fitting the experimental data, the sign of the second-order parameter is found to be negative, in contrast to previous reports. The contribution from long-range electrostatic interactions exceeds that from the nearest neighboring ligands and leads to the negative sign of the second-order crystal field parameter. Other interaction mechanisms including overlap, covalency, and charge exchange are less important to the second order parameter, but dominate the fourth- and sixth-order parameters. This work provides a consistent interpretation of the previously controversial experimental results for both lanthanide and actinide ions in this classical host. © 1998 Elsevier Science S.A.

Keywords: Crystal field; Rare-earth ions; Actinide ions; Spectroscopy; Lanthanum trichloride

1. Introduction

Lanthanum trichloride is a classical ‘textbook’ host for f-element experimental and theoretical spectroscopy. Studies of this compound doped with lanthanide (4f) ions have provided a basis for the use of crystal-field modelling to describe the Stark splitting of 4f-electronic energy levels [1]. Most of the crystal field calculations were done using this host as a model to determine the contribution of different interactions to the observed splitting. Moreover, the set of free-ion parameters for LaCl_3 are often used as a starting point for fitting experimental data in other hosts.

In earlier crystal-field modelling, the most difficult part was to evaluate the long range electrostatic interaction represented by the second-order crystal-field parameter B_{20} . The first calculation of crystal field parameters for LaCl_3 was performed by Hutchings and Ray in 1963, and was based on a simple electrostatic model [2]. However, due to the poor convergence and a rudimentary point charge field evaluation, the obtained value for B_{20} was not reliable. As shown in Ref. [3], the point dipole and point quadrupole contributions to this parameter were strongly overestimated. Since this early work, numerous attempts have been made [4–6] to modify the electrostatic model [2] by including additional interactions, in order to get satisfactory agreement with experimental crystal-field parameters. In a review by Newman [4], up to ten different

interactions were considered. Since most of these later calculations were done in the framework of superposition model [4], which utilises only the nearest neighbour environment of a 4f ion, contributions from long range electrostatic interaction were assumed to be the same as that from Ref. [2]. In order to represent better the effects of long range electrostatic interactions, Malkin [3] developed an exchange charge model (ECM), which also includes other quantum chemical corrections such as electronic orbital overlap, covalency and charge exchange. No attempt to review the previous crystal field model for LaCl_3 on the basis of this ECM [3] has been published to date.

For lanthanide ions in LaCl_3 , a long time discrepancy between model crystal field and experiments was first realised in EPR studies of the ground state splitting of the S-state ions (Gd^{3+} and Eu^{2+}) in LaCl_3 [7–9]. The EPR assignment for the lowest of the four crystal field states in the $J=7/2$ free-ion ground state was $|M\rangle=\pm 1/2$, whereas the model crystal field predicted a $|M\rangle=\pm 7/2$ ground state. This prediction is the direct result of a positive second order crystal field parameter B_{20} . Whereas numerous efforts were made to introduce additional interaction mechanisms to balance the difference between the existing model crystal field and the EPR results, the problem has not been resolved. Recently, more sophisticated spectroscopic experiments, such as Zeeman and spectral hole-burning experiments on the excited states of Am^{3+} in LaCl_3 , have been performed [10–12]. These experiments showed that the existing model crystal field [13] is

*Corresponding author.

inconsistent with experimental observation for the $J=1$ states (5D_1), which splits into a non-Kramers doublet ($\mu=1$) and a singlet ($\mu=0$) states. The model predicts that the doublet has lower energy level, whereas it was observed at 9 cm^{-1} above the singlet in the Zeeman experiment. This result was further confirmed by the hyperfine energy-level structure obtained in spectral hole-burning experiments. The same experiments on Am^{3+} doped into CaWO_4 [11] gave the reverse order for the two sublevels of the $J=1$ state, which is in agreement with the model crystal field established for lanthanides in CaWO_4 . In order to resolve the discrepancy for $\text{Am}^{3+}:\text{LaCl}_3$, it is necessary to assume that the sign of the second-order parameter is negative. However, the theoretical basis of a negative B_{20} for this system is unclear.

Based on ECM, we have recently performed a series of theoretical calculations on the crystal field parameters for trivalent lanthanide (4f) and actinide (5f) ions in LaCl_3 [14]. The analysis provided in this paper focuses on the controversial sign and value for the second-order crystal field parameter B_{20} . It is shown that the calculation of conditionally convergent sums in the electrostatic contribution results in a negative B_{20} for the La site in LaCl_3 .

2. Model calculation with ECM

In ECM, the effective Hamiltonian for electrons localised at an f-element ion is written as [3]

$$H = H^{(q)} + H^{(s)}, \quad (1)$$

where

$$H^{(q)} = \sum_{p,k} B_{pk}^{(q)} O_{pk} \quad (2)$$

is the energy of an electron in the field of point charges of the lattice, p is the rank (or order) of crystal field parameters $B_{pk}^{(q)}$, and k denotes components (from $-p$ to p), O_{pk} are Stevens spherical polynomials [3]. Representing the exchange charge interaction, $H^{(s)}$ is the energy associated with the overlap of the electron wavefunctions of the f-element ion with the wave functions of the ligand electrons,

$$H^{(s)} = \sum_{p,k} B_{pk}^{(s)} O_{pk}, \quad (3)$$

where

$$B_{pk}^{(s)} = B_{pk}^{(s)}(S_s, S_\sigma, S_\pi, G_s, G_\sigma, G_\pi),$$

and $S_s = \langle n30|300\rangle$, $S_\sigma = \langle n30|310\rangle$, $S_\pi = \langle n31|311\rangle$ are the overlap integrals of 4f or 5f ion wavefunctions with 3s, 3p ligand wavefunctions $|nlm\rangle$, and n, l, m are quantum numbers.

The ‘exchange charge’ contribution includes effects of covalency overlap and exchange, and depends on three dimensionless adjustable parameters G_s, G_σ , and G_π [3]

that ‘scale’ the overlap integrals. These three adjustable parameters depend on the radial wavefunctions used in the calculations of the overlap integrals and are constants for isostructural crystals for a given pair of ions [3].

Calculations of electrostatic contribution for the fourth- and sixth-order parameters can be performed simply by summing over a few neighbouring coordination shells of the f ion. However, special attention should be paid to the calculation of the conditionally convergent sums in the second-order parameters. In this case, the Ewald method is required in order to obtain correct results [3].

Our calculation was performed by using crystallographic data for a single crystal of LaCl_3 . The crystal lattice of LaCl_3 is hexagonal (the space group is $C_{6h}^2-P6_3/m$) with a bimolecular unit cell [15]. For convenience of interpretation, we write the electrostatic part of the second-order parameters as

$$B_{2k}^{(q)} = (1 - \sigma_2) \langle r^2 \rangle \sum_l L_{2k}(l), \quad (4)$$

where $0 < \sigma_2 < 1$ is a Sternheimer constant introduced to allow for linear shielding of the external electrostatic field acting on the valence electrons by the filled electronic shells of the f ion, and $\langle r^2 \rangle$ is the radial integral for the f ion and is calculated together with $\langle r^4 \rangle$ and $\langle r^6 \rangle$ using Hartree–Fock numerical functions with relativistic corrections for the 4f and 5f ions, and l denotes different sublattices. The lattice sum $L_{2k}(l)$ depends on the positions and charge of crystal lattice ions only. The values of $L_{2k}(l)$ are the same for all f-element ions in a given crystal environment. The calculated values of $L_{2k}(l)$ for LaCl_3 are listed in Table 1. The x and z axes of the reference coordinate are parallel to the crystallographic a and c axes,

Table 1
Lattice sums for second-order parameters ($\text{cm}^{-1}/\text{\AA}^2$)

Ion position $l(x, y, z)^a$	$L_{20}(l)$	$L_{22}(l)$	$L_{2-2}(l)$
La(1) 2/3; 1/3; 1/4	−4985	0	0
La(2) 1/3; 2/3; 3/4	−489	0	0
Cl(1A) $u; v; 1/4$	−469	−3826	559
Cl(1B) $-u; -v; 3/4$	1945	2276	2158
Cl(2A) $-v; u-v; 1/4$	−469	2396	3033
Cl(2B) $v; v-u; 3/4$	1945	732	−3049
Cl(3A) $v-u; u; 1/4$	−469	1428	−3592
Cl(3B) $u-v; -u; 3/4$	1945	−3006	891
Total	−1046	0	0

^a $u=0.287a_0$, and $v=0.382a_0$, where a_0 is the lattice constant [15].

Table 2
Contributions to L_{20} from different coordination shells LaCl_3 ($\text{cm}^{-1}/\text{\AA}^2$)

Coordination shell number	Ion	Number of ions in shell	L_{20}
1	Cl	9	1300
2	La	2	-4155
3	Cl	3	-973
4	La	6	1782

respectively. Since all $L_{21}(l)$ and $L_{2-1}(l)$ are zeros, they are not listed.

It can be seen from Table 1, that the negative sign for the total value of L_{20} is largely due to the negative contribution from the lanthanum sublattices, although three of the chlorine sublattices also give negative contributions to L_{20} . To understand the source of the positive sign for B_{20} in previous work, we calculated the contributions from several coordination shells by direct summation over the lattice. Results are listed in Table 2.

In calculations of the overlap integrals, it was found that, because of the more diffuse nature of the chlorine 3p orbital, the dominant contribution is from the S_π integrals, which are significantly larger than that for oxygen or fluorine ions. Therefore, in calculation of $B_{pk}^{(s)}$, we used a simplified ECM model, in which $G_s = G_\sigma = G$. Thus we have only two varied parameters: G and G_π .

For comparison with previous work, we chose two systems, Nd^{3+} and Am^{3+} doped, respectively, into LaCl_3 . The calculated crystal field parameters, $B_{pk} = B_{pk}^{(q)} + B_{pk}^{(s)}$, are listed in Table 3 in comparison with the previously determined values [13,16]. All the previously determined crystal field parameters are from the least squares fitting of experimental data to the simplified model

of D_{3h} effective point symmetry. It is evident that the most dramatic change is the sign of B_{20} , and the leading contribution is from the electrostatic interaction. The calculated values for the fourth- and sixth-order parameters are not much different from those established by fitting of the experimental spectra to a point charge model of D_{3h} symmetry. For the sixth-order parameters, one can compare the calculated value of $[(B_{66})^2 + (B_{6-6})^2]^{1/2}$ for C_{3h} model, which is 382 cm^{-1} for Nd^{3+} and 834 cm^{-1} for Am^{3+} , with the fit value of B_{66} for the D_{3h} model. It is also anticipated that, because of the more extended nature of the 5f electrons, the fourth- and sixth-order crystal field parameters for the actinide ion Am^{3+} are about two times of that for the lanthanide ion Nd^{3+} .

3. Discussion

In addition to ECM calculation, we have reanalysed the crystal field energy level structure of Am^{3+} in LaCl_3 by using the same least squares fitting program as Carnall did in his systematic analyses of trivalent actinide ions in LaCl_3 [10]. By reversing the assignments of the two Stark levels for the $J=1$ multiplets (5D_1 and 7F_1) in two ($\mu=0, 1$) crystal-field submatrices, we obtained B_{20} with opposite signs and other parameters with no significant changes. As anticipated, assigning a lower energy level to the $\mu=0$ singlet resulted in a negative B_{20} . The fit parameters and deviations listed in Table 4 are from two fittings with different assignments. Fit 1 was with Carnall's original assignment for the first 35 experimental levels. Fit 2 was with assignment of 5D_1 and 7F_1 with the values from laser excitation experiments ($\mu=0$ singlet has lower energy than that of $\mu=1$ doublet) [10,12] and reassignment of

Table 3
Crystal field parameters for Nd^{3+} and Am^{3+} in LaCl_3 crystal (cm^{-1})

pk	$B_{pk}^{(q)}$		$B_{pk}^{(s)}$		B_{pk} (ECM, C_{3h})		B_{pk} (fit to D_{3h})	
	Nd^{3+}	Am^{3+}	Nd^{3+}	Am^{3+}	Nd^{3+}	Am^{3+}	Nd^{3+} [11]	Am^{3+} [10]
20	-117	-122	39	81	-78	-41	81	121
40	-21	-55	-57	-142	-78	-197	-42	-73
60	-3	-10	-41	-80	-44	-90	-44	-118
66	20	68	279	588	299	656	439	1066
6-6	-13	-44	-226	-471	-239	-515	-	-

Table 4
Free-ion and crystal-field parameters of $\text{Am}^{3+}:\text{LaCl}_3$ (in cm^{-1}) resulted from two fittings with different assignments^a

	F^2	F^4	F^6	P^2	ζ	B_{20}	B_{40}	B_{60}	B_{66}	$\Delta^5D_1(\text{cla})^b$	σ^c
Fit 1	52788	43098	28247	766	2536	96	-76	-101	1146	-19	29
Fit 2	52629	41431	29413	804	2545	-61	-149	-94	1110	10	26

^a Other free-ion parameters are fixed at the same values in Table 1 of Ref. [10].

^b $\Delta^5D_1 = E(\mu=1) - E(\mu=0) = 9 \text{ cm}^{-1}$ from experiment.

^c σ is the standard deviation [10], 35 observed levels were fit.

some other levels after the first iteration of fitting procedures. With this result, we have shown that the sign of B_{20} may not significantly affect the overall crystal field spectrum of a trivalent 5f ion in LaCl_3 , but determines the ordering of $J=1$ multiplets. For Am^{3+} in LaCl_3 , the ordering of the $J=1$ multiplets observed in spectral hole burning and Zeeman experiments [10–12] supports the ECM calculation which results in a negative B_{20} . There is neither an alternative explanation nor additional mechanisms for the observed characteristics of this $J=1$ state. For other states, the effects induced by changing the sign of B_{20} are balanced by variation of the fourth- and sixth-order parameters.

Generally, the ordering of levels in each Stark multiplet depends on all crystal field parameters. However, for the $J=1$ states of the ions that have an even number of f electrons, and the $J=3/2$ states of the ions that have an odd number of f electrons, the Stark splitting of these states is dominated by the second order crystal field parameter. Using the crystal field parameters resulting from our ECM calculations together with the free-ion interaction parameters provided by previous work [13], we have also performed calculations on the Stark splitting of the electronic states of Pr^{3+} and Nd^{3+} ions in LaCl_3 [14]. A reasonable agreement was achieved between our calculation and the previous fitting of the experimental data with a point charge model based on an effective D_{3h} site symmetry. Based on our model calculation, it is clear that the second order crystal field parameter characterises the long range electrostatic coupling as well as the nearest neighbouring interactions. The large contributions from the La shells leads to a negative $B_{20}^{(q)}$, whereas a smaller positive value for $B_{20}^{(s)}$ was obtained. The total value of B_{20} ($=B_{20}^{(q)} + B_{20}^{(s)}$) is negative for lanthanide and actinide ions in LaCl_3 . We have shown that, for 4f and 5f ions in LaCl_3 , it is not appropriate with any crystal field model to include only the nearest neighbour ions for second-order parameter calculation, because such an approximation results in a wrong sign for B_{20} . It is necessary to point out that the change in crystal lattice structure due to the f-element ion substitution does not change the sign of B_{20} , whereas it might have pronounced effect on the fourth- and sixth-order parameters.

Our conclusion about the sign of B_{20} is supported also by an early experiment [17], in which it was shown that the experimental value of B_{20} for Np^{3+} in the isostructural LaBr_3 is negative. This negative B_{20} was explained by introducing a correction [6], which closely resembles the shielding of crystal field by the filled out shell s and p orbitals of the f-element ion. This correction is included in our calculation by the Sternheimer constant σ_2 . Since the point charge electrostatic contribution from the crystal lattice already gives a negative sign for B_{20} , it is not necessary to introduce additional corrections of uncertain significance.

Another consequence of the negative B_{20} for lanthanide

and actinide ions in LaCl_3 is that the mechanisms previously evaluated for the ground state splitting of the S-state ions including Gd^{3+} , Eu^{2+} , and Cm^{3+} in LaCl_3 become questionable. Since a negative B_{20} results in a $\mu=1/2$ ground state, many of the higher order mechanisms previously introduced for interpreting the EPR experiments could be over estimated [7]. More detailed analysis is needed for this special case.

We did not evaluate contribution from higher electrostatic multipoles (point dipoles, quadrupoles and so on), because this procedure is far from being exact for two main reasons: (1) the values of ion polarisability in crystals can only be determined with a limited precision; (2) there is no convergence for multipole series (dipole and quadrupole contributions have the same order). This was clearly demonstrated by Garcia and Faucher [18] in comparing their calculation of crystal field interaction in $\text{Nd}^{3+}:\text{LaCl}_3$ with earlier results published by Newman [4]. These two studies reached no agreements on the dipole and quadrupole contributions. For instance, the quadrupole interaction contribution into B_{20} is -1410 cm^{-1} according to Refs. [2] and [4], but it is 206 cm^{-1} according to Ref. [18]. More thorough theoretical and experimental investigations are certainly required for resolving this discrepancy.

Acknowledgements

Work was performed under the auspices of the Office Basic Energy Science, Division of Chemical Sciences, US Department of Energy under contract number W-31-109-ENG-38. We would like to thank our colleagues, particularly J.V. Beitz and L. Soderholm, for their insights and comments. Zhorin is on leave from Kuban State University, Krasnodar, 350040, Russia.

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