On the distance dependence of crystal-field parameters for Pr^{3+}: $LnCl_3$

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Abstract. The distance dependences of the intrinsic parameters $\overline{B}_k$ have been evaluated using the *ab initio* molecular-orbital MO theory for the Pr^{3+}–Cl$^-$ ion pair at different internuclear distances. The theoretical values for the corresponding power-law exponents are $t_4 = 6.0$ and $t_6 = 6.9$. The present result shows much better agreement for the theoretical variations of $\overline{B}_4(R)$ and $\overline{B}_6(R)$ with the experimental data than a previous theoretical calculation. The comparison of the present ion-pair system with the earlier theoretical and recent experimental results for the Pr^{3+}–F$^-$ ion-pair system shows similar distance dependences of the intrinsic parameters.

1. Introduction

Several studies on the crystal field of lanthanide ions in insulating compounds have been made recently under pressure [1, 2, 3]. High-pressure techniques provide a powerful tool to change the ligand geometry around the lanthanide ions continuously and it has been shown that all contributions to the crystal field can be described within the superposition model [4] in terms of pressure-induced changes in the structural parameters of the host crystals. Experimentally the distance dependences of the rank-4 and rank-6 intrinsic crystal-field parameters $\overline{B}_4(R)$ and $\overline{B}_6(R)$ of Pr^{3+} and Nd^{3+} in LnCl$_3$ have been determined only recently [3]. The average values of the power-law exponents t_4 and t_6 were found to be 6 and 5.5, respectively.

The earlier *ab initio* molecular-orbital (MO) calculation of the crystal-field parameters in PrCl$_3$ [5, 6] gave a reasonable agreement with values obtained experimentally. For the same system, Newman and Ng [7] made further improved calculations using an expansion of the ligand orbitals in terms of metal orbitals, considering the following contributions to the intrinsic parameters at different internuclear distances (i) point charge, (ii) charge penetration, (iii) exchange, (iv) p and s overlap and (v) p and s covalency. From the three theoretical values [7], the power-law exponents t_4 and t_6 can be estimated to be 10.7 and 10.9, respectively. However, these values are twice as large as the experimental data. It is not known whether this discrepancy between the theoretical and experimental results was therefore due to additional physical contributions at small internuclear distances or due to deficiencies of the model calculations. In the present work a new calculation is carried out for the same system to clarify this problem.

2. Numerical evaluation

The present calculation follows the LCAO–MO theory and uses the theoretical formalism decribed before in detail [5, 6]. The formalism is based on the same assumptions of the

superposition model. The superposition principle is applied only to the individual ligand contributions, so that all three-centre effects are neglected.

Two-centre integrals were evaluated using the ζ-function method developed by Barnett and Coulson [8]. All kinds of two-centre integrals between the central ion f orbital and the ligand s and p orbitals have been evaluated analytically, except the values for the exchange integrals, which were calculated numerically. For integrals over the ranges $(0,1)$ and $(0,\infty)$ containing a negative exponential function 12-point Gauss quadrature and 15-point Gauss–Laguerre quadrature approximations were used, respectively. An infinity series occurs in the exchange integral. The convergence of this series for the two-centre exchange integrals has already been analysed by Sahni and LaBudde [9] and it was noticed that the higher terms of this series are proportional to an inverse power of the index of summation. Therefore the series was terminated at the eighth term. The present computations were carried out on a PC with a specially developed Turbo Pascal program.

In evaluating the integrals Slater-type radial wave functions were used for Pr^{3+} and Cl^- [10, 6]. Both the one-electron orbital energies and the Madelung potentials on the positive and negative ions are needed for the overlap and covalency contributions. The Pr^{3+} 4f-orbital energy is taken to be -1.576 Hartree and the Cl^- orbital energies are $\epsilon_{3s} = -0.733$ Hartree and $\epsilon_{3p} = -0.150$ Hartree (cf. [7]). The Madelung potentials in the lanthanide chlorides were scaled with the metal–ligand distance R using the form 6.15 au$/R$ [5].

Table 1. Calculated matrix elements in cm^{-1} and overlap integrals ($\times 10^2$) for different internuclear distances R (au).

	R					
	5.5812	5.2812	4.9812	4.6812	4.3812	4.0812
$\langle 4f\|s\rangle$	1.0055	1.3236	1.7197	2.2024	2.7749	3.4317
$\langle 4f\|\sigma\rangle$	1.4888	1.7728	2.0861	2.4188	2.7533	3.0610
$\langle 4f\|\pi\rangle$	0.9709	1.2526	1.6123	2.0691	2.6447	3.3632
$\langle 4f_0\|r_L^{-1}\|s\rangle$	1148.3	1613.5	2244.3	3088.2	4199.8	5639.6
$\langle 4f_0\|r_L^{-1}\|\sigma\rangle$	1564.4	2013.7	2570.3	3248.1	4056.9	4998.6
$\langle 4f_1\|r_L^{-1}\|\pi\rangle$	766.3	1057.6	1458.0	2006.5	2754.6	3770.4
$\langle 4f_0s\|ss\rangle$	1014.0	1404.7	1923.2	2599.3	3463.6	4542.1
$\langle 4f_0s\|\sigma s\rangle$	1470.0	1870.2	2354.7	2927.9	3586.3	4313.2
$\langle 4f_1s\|\pi s\rangle$	738.4	1011.8	1383.3	1885.4	2559.7	3458.2
$\langle 4f_0p\|sp\rangle$	930.9	1280.8	1740.7	2334.0	3082.9	4003.5
$\langle 4f_0p\|\sigma p\rangle$	1375.7	1734.8	2163.0	2660.4	3219.0	3817.0
$\langle 4f_1p\|\pi p\rangle$	707.0	962.8	1307.4	1768.9	2382.3	3190.5
$\langle 4f_0 4\bar{f}\|s4\bar{f}\rangle$	668.7	915.2	1239.7	1659.9	2192.6	2850.7
$\langle 4f_0 4\bar{f}\|\sigma 4\bar{f}\rangle$	1165.6	1442.9	1776.0	2169.2	2622.1	3125.7
$\langle 4f_1 4\bar{f}\|\pi 4\bar{f}\rangle$	689.0	909.0	1200.5	1584.3	2095.9	2766.8
$\sum_\tau \langle 4f_0\tau\|\tau 4f_0\rangle$	-120.5	-190.8	-282.3	-430.1	-647.3	-1021.0
T_2	1371.6	1618.8	1929.0	2323.7	2833.2	3502.1
T_4	114.3	150.5	201.4	273.9	379.3	535.6
T_6	20.3	29.7	44.3	67.3	104.2	164.2
$T_2(s)$	1368.0	1611.3	1913.3	2291.0	2765.6	3363.1
$T_4(s)$	110.9	143.5	186.8	244.4	320.2	418.1
$T_6(s)$	17.6	24.1	33.0	44.8	59.9	78.3
$T_2(p)$	1319.1	1534.7	1793.8	2105.3	2478.8	2923.8
$T_4(p)$	96.0	120.1	150.6	188.7	235.5	291.8
$T_6(p)$	12.9	16.9	22.0	28.3	35.9	44.4

The calculations were performed at six different internuclear distances from R_0 to R_n in 0.3 au steps, whereby $R_0 = 5.5812$ au corresponds to the metal–ligand separation of $LaCl_3$ at ambient conditions. All the necessary two-centre integrals are given in table 1. For brevity $4f_m$ refers to the 4f orbital with magnetic quantum number m and $\overline{4f}$ to the spherical part of the 4f wave function. The ligand wave functions are represented by $\tau = s$, σ and π. $T_k(\tau)$ represents the kth multipole interaction between the 4f electron and the ligand. T_k is the corresponding integral for the interaction between the 4f electron and a point charge at the ligand. Comparison with previous results [7] shows generally good agreement. Only the exchange integrals $\sum_\tau \langle 4f_0\tau || \tau 4f_0 \rangle$ have been calculated here and due to the close agreement with the previous results [7] these time-consuming calculations were not repeated for the other integrals, since it can be noticed from the result of Newman and Ng [7] that the ratios for the other exchange integrals $\sum_\tau \langle 4f_i\tau || \tau 4f_i \rangle$ ($i = 1, 2, 3$) with respect to the $i = 0$ integrals are nearly constant when distances decrease. These average ratios for $i = 1, 2, 3$ are 0.59, 0.28 and 0.15, respectively, and these estimates contribute a total uncertainty of less than 5% of the intrinsic parameters.

3. Results and discussion

The contributions of the five interaction mechanisms to the intrinsic crystal-field parameters $\overline{B}_k$ are presented in table 2. The distance dependences for the parameters $\overline{B}_4(R)$ and $\overline{B}_6(R)$ give $t_4 = 6$ and $t_6 = 6.9$ and are illustrated in figures 1 and 2, respectively, together with the experimental results [3]. The present calculation shows much better agreement for the variations of the total theoretical $\overline{B}_4(R)$ and $\overline{B}_6(R)$ with the experimental results than the previous theoretical data [7].
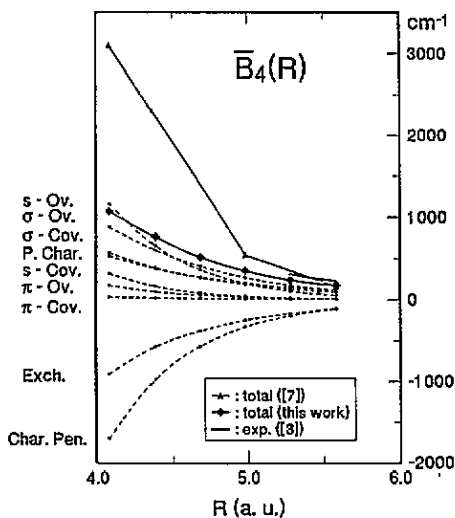

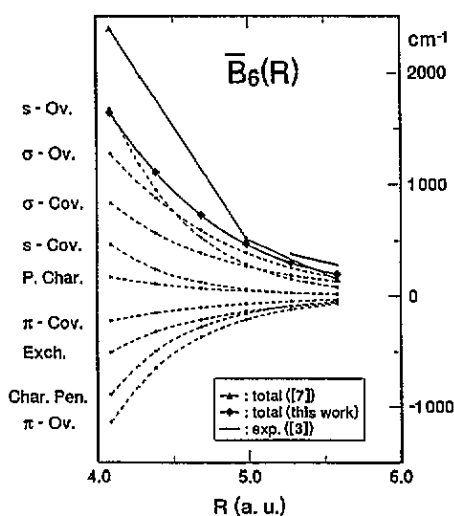Figure 1. A comparison between the experimental and theoretical variation of the intrinsic parameter $\overline{B}_4(R)$.

Figure 2. A comparison between the experimental and theoretical variation of the intrinsic parameter $\overline{B}_6(R)$.

It is especially noticed that the positive π contributions to overlap and covalency vary only slightly with distance in the whole region for $\overline{B}_4$. In the case of $\overline{B}_6$ the negative

Table 2. Calculated contributions to the intrinsic parameters $\overline{B}_k$ (cm^{-1}) of the $Pr^{3+}-Cl^-$ ion pair for different internuclear distances R (au).

				R			
		5.5812	5.2812	4.9812	4.6812	4.3812	4.0812
$\overline{B}_2$	point charge	1371.6	1618.8	1929.0	2323.7	2833.2	3502.1
	charge penetration	− 322.2	− 519.4	− 842.5	−1375.6	−2261.8	−3747.5
	exchange	− 130.0	− 205.8	− 304.5	− 463.9	− 698.2	−1101.2
	s overlap	30.2	58.2	109.8	202.9	366.2	643.9
	p overlap	88.9	143.4	230.6	368.9	586.9	928.3
	s covalency	5.6	11.4	23.1	46.2	91.1	177.8
	p covalency	62.1	89.6	129.8	88.6	275.7	406.4
$\overline{B}_4$	point charge	114.3	150.6	201.4	273.8	379.3	535.6
	charge penetration	− 116.8	− 196.6	− 333.5	− 570.1	− 980.9	−1697.9
	exchange	− 107.4	− 170.1	− 251.7	− 383.4	− 577.0	− 910.2
	s overlap	54.4	104.7	197.7	365.3	659.1	1159.0
	p overlap	123.0	193.4	301.6	464.9	706.6	1056.1
	s covalency	10.2	20.6	41.7	83.1	163.9	320.0
	p covalency	94.0	135.3	195.4	283.4	413.5	609.5
	total	171.7	237.9	352.4	517.0	764.6	1072.2
$\overline{B}_6$	point charge	20.3	29.8	44.3	67.4	104.2	164.2
	charge penetration	− 49.9	− 88.2	− 156.6	− 279.2	− 496.6	− 890.6
	exchange	− 60.0	− 95.0	− 140.5	− 214.1	− 322.2	− 508.2
	s overlap	78.6	151.4	285.6	527.7	952.2	1674.1
	p overlap	93.4	132.3	178.1	219.5	226.4	129.9
	s covalency	14.7	29.9	60.2	120.0	236.8	462.2
	p covalency	95.4	136.2	195.2	281.6	409.6	603.4
	total	192.5	296.3	466.4	723.0	1108.3	1635.0

π contributions vary, however, more steeply with decreasing R. Due to this effect the contribution of the p orbitals is largely cancelled. The rapid negative increase in π and charge penetration contribution with decreasing distance is responsible for the smaller effective power-law exponent t_6 in the present calculation. The cancellation of the π and σ contributions can finally lead to negative values of the intrinsic parameter $\overline{B}_6$ at small internuclear distances as observed experimentally in covalently bonded systems and metals [11], in which the contact contributions are very important. In fact, the pressure induced variations of the crystal field are satisfactorily described by these effects.

Comparison with the work of Newman and Ng [7] shows good agreement at R_0. Major discrepancies occur, however, in the overlap and covalency contributions at smaller distances. Both contributions are overestimated by Newman and Ng [7] at smaller distances. In the present formalism, both contributions show a strong dependence not only on the orbital energy difference but also on the Madelung potential, which represents the interaction of the rest of the crystal with the ion pair. Scaling of the Madelung potential by the distance between the metal and ligand ions is one of the major differences in the present work with respect to the previous calculation [7]. It seems reasonable to assume that the Madelung potential varies inversely proportional with the interionic distance. The previous distance dependences [7] for the overlap and covalency contributions at different internuclear distances are reproduced, if a constant Madelung potential is used. Thus it might be assumed that a constant Madelung term was used by Newman and Ng [7] and this assumption seems not to be reasonable for the evaluation of crystal-field parameters under pressure.

The covalency parameters γ and λ are given in table 3. These parameters are coefficients

Table 3. Calculated covalency parameters γ and λ ($\times 10^2$) for different internuclear distances R (au).

			R			
	5.5812	5.2812	4.9812	4.6812	4.3812	4.0812
γ_s	0.586	0.816	1.128	1.550	2.113	2.858
γ_σ	2.632	2.990	3.411	3.891	4.447	5.099
γ_π	1.070	1.229	1.359	1.617	1.896	2.126
λ_s	1.592	2.140	2.848	3.752	4.888	6.290
λ_σ	4.121	4.764	5.497	6.310	7.200	8.160
λ_π	2.041	2.482	2.971	3.686	4.541	5.489

for mixing of 4f electrons with ligand orbitals. The present values for γ at R_0 are close to the literature values [5]. One can notice that the variation of the s contribution is twice that of the σ and π contributions. It is also of particular interest to compare the present results with the early *ab initio* MO calculation of the Pr^{3+}–F^- ion-pair system [16]. Though the two systems are different, the corresponding parameters have approximately similar distance dependences. The results for the Pr^{3+}–Cl^- and Pr^{3+}–F^- calculations are:

$$Pr^{3+} - Cl^- : t_4 = 6.0 \qquad t_6 = 6.9$$

$$Pr^{3+} - F^- : t_4 = 5.7 \qquad t_6 = 5.6.$$

Therefore the MO calculations predict similar distance dependences of the crystal-field parameters for these two ion pairs. Yeung and Reid [17] have recently analysed the experimental data of Pr^{3+} in LaF_3 with the superposition model and obtained the power-law exponents $t_4 = 6.1(1.3)$ and $t_6 = 8.7(1.1)$ for the Pr^{3+}–F^- ion pair, which shows also reasonable agreement with the previous theoretical values in this case.

The five mechanisms considered in the present work describe successfully the experimental results. This means that these mechanisms together already represent the most important contributions to the crystal field. Ng and Newman [13] have further considered a complete set of possible mechanisms in the second-order perturbation theory and in fact the absolute value for $\overline{B}_4$ was found to be 240 cm^{-1} at R_0 which compared more favourably with the experimental value of 224 cm^{-1}. In the other cases, where all three-centre integrals are automatically eliminated by the basic assumptions of the superposition model, Curtis and Newman [14] checked the contribution from the ligand–ligand interactions (only overlap effects) to the lanthanide crystal field. To describe the experimental values [3] more accurately one has to take into account also the ligand–ligand interaction, which amounts to a contribution of $\Delta\overline{B}_6 = 56$ cm^{-1} and thus for the corrected theoretical value one obtains the effective intrinsic parameter $\overline{B}_6(R_0) = 249$ cm^{-1} and similarly $\overline{B}_4(R_0) = 208$ cm^{-1}. In particular, it is assumed that the ligand–ligand interaction becomes stronger under pressure, so that the power-law exponents t_k could be further reduced.

In the case of $\overline{B}_2$, the electrostatic contributions appear to be dominant. It is well known that the shielding of the electrostatic field by the filled outer $5s^2 5p^6$ shell of the lanthanide ion considerably reduces the electrostatic field seen by the 4f electrons. The effect of the configuration interaction on the crystal-field parameters must also be taken into account in the more general cases [13]. It is interesting that the electrostatic contribution to $\overline{B}_2$, including point charge and charge penetration, shows a maximum with decreasing distance in the present calculation (table 2), which could help to understand the minimum in

the pressure-induced variation of B_{20} observed experimentally [3]. On the other hand, the contact contributions are not shielded and must therefore be subtracted from the observed parameters before the true electrostatic contribution can be obtained. An attempt has been made by Newman and Price [15] to separate the electrostatic and contact contributions to $\overline{B}_2$. However, due to the uncertainties in these procedures, the pressure dependence of the $\overline{B}_2$ parameter of Ln^{3+}:$LaCl_3$ [3] is not further studied in the present work.

In order to test the accuracy of the present calculation, the more accurate Hartree–Fock wave functions for Pr^{3+} with six Slater-type orbitals [12] could be used. This type of wave function would increase the contributions to the intrinsic parameters $\overline{B}_4$ and $\overline{B}_6$ by 9% and 6%, respectively. However, the comparison between the theoretical and experimental distance dependences of the intrinsic parameters indicates much larger systematic differences (see figures 1 and 2). Probably, the real wave function of the 4f electrons in solids should be expanded with respect to the free 4f electron wave function, and these differences could probably explain an apparent shift in the distance dependences of the experimental results with respect to the present restricted *a priori* calculations.

4. Conclusion

The distance dependences of the crystal-field parameters for Pr^{3+}:$LnCl_3$ have been studied in the framework of an LCAO–MO calculation. The present results can describe reasonably the pressure dependences of the intrinsic crystal-field parameters $\overline{B}_4$ and $\overline{B}_6$. In comparison with the earlier theoretical work on the Pr^{3+}–Cl^- ion pair system, the distance dependent scaling of the Madelung term in the present calculation appears to be the most significant change, which leads to a closer agreement with the experimental results. The remaining differences between the absolute values found from the present calculation and the recent experimental studies [3] seem to point out the necessity of some other type of orbital expansion for a perfect theoretical modelling of the experimental results.

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