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Electron correlation and crystal-field splittings of Ho^{3+} : II. Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$

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Abstract. The influence of correlation effects on the crystal spectra of Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$ is investigated. It turns out that the variation of the crystal-field parameters from term to term is very similar to that found for the spectra of Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 . So the properties of the electron correlation in Ho^{3+} discovered for the zircon structure compounds are of more general validity and also apply for Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$.

1. Introduction

The obvious deficiencies of the well established procedure for calculating the energy levels of lanthanide ions in crystal lattices caused us to investigate the crystal-field splittings of Ho^{3+} in different host crystals. In four preceding papers the experimental results of our spectroscopic studies on Ho^{3+} in YVO_4 , YAsO_4 , HoPO_4 (Enderle *et al* 1990b, c, a) and on Ho^{3+} in $\text{Y}(\text{OH})_3$ (Pilawa 1990) were reported. The normal crystal-field description using single-electron tensor operators leads to striking differences. In order to reduce the differences between experiment and theory, one has to extend the crystal-field Hamiltonian by including two-electron crystal-field operators that can account for the correlation effects of the electrons. In the preceding paper (Pilawa 1991, henceforth to be referred to as I) the so-called spin-correlated crystal-field H_{SCCF} (Judd 1977) and the more general correlated crystal-field H_{CCF} (Bishton and Newman 1970) were applied to Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 . It was possible to characterize the essential parts of the crystal-field Hamiltonian that take the influence of the electron correlation into account. In this paper the investigation is extended to the spectra of Ho^{3+} in the hexagonal lattices of LaCl_3 (Crosswhite *et al* 1977) and $\text{Y}(\text{OH})_3$ (Pilawa 1990).

2. Crystal-field parameter

The site symmetry of the nearest surroundings of Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$ is $\bar{6}m2$. Therefore only four crystal-field parameters $A_q^{(k)}$ are necessary to describe the crystal-field splitting of the terms (Wybourne 1965), using the operator

$$H_{\text{CF}} = \sum_i \sum_{k,q} A_q^{(k)} t_q^{(k)}(i) \quad (1)$$

Table 1. 'Term-dependent' parameters $a_q^{(k)}(\gamma J)$ of Ho^{3+} in LaCl_3 . In this and table 2, σ denotes the RMS deviation that can be achieved by a fit of the calculated crystal-field energies to the measured ones. The terms of the multiplet ^5I were simultaneously fitted, and also the terms of the multiplet ^5F . The influence of the term $^3\text{S}_2$ on the neighbouring term $^3\text{F}_4$ was taken into account. All figures have the units cm^{-1} .

Term	$^5\text{I}_{8-4}$	$^5\text{F}_{5,4,3,2}$	$^3\text{K}_8$	$^4\text{G}_6$	$^4\text{G}_5$	$^5\text{G}_4$
σ	1.3	1.0	2.7	2.3	0.7	0.7
$a_0^{(2)}$	-305	-318	-198	-2678	-246	-174
$a_0^{(4)}$	-295	-298	-199	-343	-569	-8
$a_0^{(6)}$	569	553	986	488	482	514
$a_0^{(8)}$	-370	-380	-665	-309	-231	-336

with $k = 2, 4, 6$ and $q = 0 \pmod{6}$, where i denotes the 4f electrons. If the matrix elements of the tensor operators were evaluated for pure 4f electrons, one could not expect that four parameters would be sufficient to fit the crystal-field splitting of all terms within the investigated range from 0 to $28\,000\text{ cm}^{-1}$ simultaneously. Rajnak and Wybourne (1964) showed that even in the electrostatic crystal-field model the mixing of excited configurations into the $4f^n$ ground configuration can induce variations of the parameters $A_q^{(k)}$ from term to term. It is therefore justified to introduce 'term-dependent' crystal-field parameters, say $a_q^{(k)}(\gamma J)$, in order to fit the observed splittings. Estimates carried out with the crystal-field Hamiltonian (1) show that in the case of the Ho^{3+} ion the influence of J -mixing is small compared with the crystal-field splittings for most of the terms in the investigated energy range. It therefore makes sense to fit the crystal-field splittings of the individual terms in order to get values of $a_q^{(k)}(\gamma J)$. According to Rajnak and Wybourne (1964) one can expect to get the same values of the crystal-field parameters for the terms of a pure Russell-Saunders multiplet. This is almost true for the ^5I and the first excited multiplet ^5F . But the free-ion wavefunctions of the terms $^5\text{G}_{6,5,4}$ and $^3\text{K}_{8,7}$ form mixtures of different LS wavefunctions. Thus intermediate wavefunctions have to be used, and the $a_q^{(k)}(\gamma J)$ will be different. The terms $^3\text{H}_{5,6}$ were not considered, since no reliable parameter values can be obtained (see paper I).

For Ho^{3+} in LaCl_3 the data of Crosswhite *et al* (1977) in the range 0 to $25\,900\text{ cm}^{-1}$ were used to determine the values of the parameters $a_q^{(k)}(\gamma J)$. This energy interval includes the terms of the multiplets ^5I , ^5F , ^5G and the term $^3\text{K}_8$. The term $^3\text{K}_7$ is omitted, since the analysis is incomplete. In the case of Ho^{3+} in $\text{Y}(\text{OH})_3$, most of the terms of ^5I are not investigated. The study of the crystal-field Hamiltonian therefore includes the terms of the multiplets ^5F , ^5G and the terms $^3\text{K}_{8,7}$ ($15\,400$ to $27\,900\text{ cm}^{-1}$). In tables 1 and 2 the values of the parameters $a_q^{(k)}(\gamma J)$ are listed together with the root-mean-square (RMS) deviation σ of the fit for Ho^{3+} in LaCl_3 and in $\text{Y}(\text{OH})_3$, respectively.

3. Correlated crystal-field operators

In order to describe the variations of the 'term-dependent' crystal-field parameters $a_q^{(k)}(\gamma J)$, the correlated crystal field (CCF)

$$H_{\text{CCF}} = \sum_{i < j} \sum_{k, q} \sum_{(k_1, k_2)} B_q^{(k)}(k_1, k_2) t_q^{(k)}(k_1, k_2; ij) \quad (2)$$

or the spin-correlated crystal field (SCCF)

$$H_{\text{SCCF}} = \sum_{i < j} \sum_{k, q} C_q^{(k)}(s_i \cdot s_j) t_q^{(k)}(i) \quad (3)$$

Table 2. 'Term-dependent' parameters $a_0^{(k)}(\gamma J)$ of 10% Ho^{3+} in $\text{Y}(\text{OH})_3$.

Term	${}^5\text{F}_{5,4,3,2}$	${}^3\text{K}_8$	${}^3\text{K}_7$	${}^5\text{G}_6$	${}^5\text{G}_5$	${}^5\text{G}_4$
σ	2.0	4.7	2.4	2.3	1.8	0.4
$a_0^{(2)}$	-615	-628	1300	-6350	-560	-450
$a_0^{(4)}$	-544	-437	328	-485	-966	230
$a_0^{(6)}$	908	986	1216	850	764	769
$a_6^{(6)}$	-796	-870	-923	-697	-432	-682

have to be added to the one-electron crystal-field Hamiltonian (1). Both the SCCF and the CCF were applied on the crystal-field splittings of Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 in paper I, and it turned out that only a small selection of the operators of equations (2) and (3) are actually necessary. Now it is supposed that for the hexagonal host lattices the same correlated operators of equations (2) and (3) are effective. In order to make possible a comparison of the results obtained for the zircons and those for the hexagonal structures, exactly the same linear combinations of operators are used to investigate the crystal-field splittings of Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$ (table 5 of paper I). The reduced matrix elements of the operators are also the same as in paper I. Table 3 contains the 'term-independent' crystal-field parameters $e_q^{(k)}$ (see also table 6 in paper I).

4. Discussion of the results

4.1. Contribution to the crystal field connected with $t_0^{(2)}$

Figure 1 shows the values of the parameter $a_0^{(2)}(\gamma J)$. The big negative value of the parameter $a_0^{(2)}({}^5\text{G}_6)$ and the positive value of the parameter $a_0^{(2)}({}^3\text{K}_7)$ in $\text{Y}(\text{OH})_3$ indicate that similarly to the zircon-structure compounds the correlated crystal-field operator with $(k_1, k_2) = (2, 2)$ is effective (see table 3).

4.2. Contribution connected with $t_0^{(4)}$

The experimentally observed variation of the parameter $a_0^{(4)}(\gamma J)$ (figure 2) shows the same trend not only in both substances but also in comparison with the parameter $a_0^{(4)}(\gamma J)$ found in the compounds with the zircon structure (paper I). The term dependence of the parameters can be reproduced with operators of the CCF but not with the SCCF (see table 3).

4.3. Contributions connected with $t_0^{(6)}$ and $t_0^{(6)} + t_{-6}^{(6)}$

Figures 3 and 4 show that the term dependence of both parameters $a_0^{(6)}(\gamma J)$ and $a_6^{(6)}(\gamma J)$ can be approximated through the SCCF. Since the variation of the parameter values is small, no attempt was made to apply operators of the CCF.

4.4. Comparison of different host crystals

Although the particulars of the crystal-field splittings of Ho^{3+} differ for the various host crystals, the investigation of the 'term-dependent' crystal-field parameters shows that the variation in the parameter values that is induced by the correlation of the electrons

Table 3. 'Term-independent' parameters $e_q^{(k)}$, of the crystal-field operators. There are three columns for each of the two different host lattices. The first column includes the parameter values if only the operator H_{CF} is used. The second and the third columns include the parameter values if combinations of the operator H_{CF} with H_{SECF} or of H_{CF} with H_{CCF} are used. The RMS deviations $\Delta_q^{(k)}$ between the fitted and the calculated 'term-dependent' parameters $a_q^{(k)}(\gamma J)$ are given in the lines below the parameters $e_q^{(k)}$, of each (k, q) combination. All figures have the units cm^{-1} .

	Ho ³⁺ in LaCl ₃			Ho ³⁺ in Y(OH) ₃		
$e_0^{(2)}_{.1}$	-170	-150	-153	-339	-339	-339
$e_0^{(2)}_{.2}$	-	47	-	-	118	-
$e_0^{(2)}_{.3}$	-	-	-62	-	-	-132
$\Delta_0^{(2)}$	661	428	245	2019	1191	856
$e_4^{(4)}_{.1}$	-297	-303	-296	-465	-465	-465
$e_4^{(4)}_{.2}$	-	-6	-	-	-40	-
$e_4^{(4)}_{.3}$	-	-	21	-	-	-20
$e_4^{(4)}_{.4}$	-	-	-54	-	-	-133
$e_4^{(4)}_{.5}$	-	-	-60	-	-	-124
$\Delta_0^{(4)}$	116	117	13	398	388	131
$e_6^{(6)}_{.1}$	491	583	—	734	734	—
$e_6^{(6)}_{.2}$	—	-180	—	—	-74	—
$\Delta_0^{(6)}$	126	34	—	184	65	—
$e_8^{(8)}_{.1}$	-321	-386	—	-629	-629	—
$e_8^{(8)}_{.2}$	—	129	—	—	70	—
$\Delta_0^{(8)}$	96	27	—	141	104	—

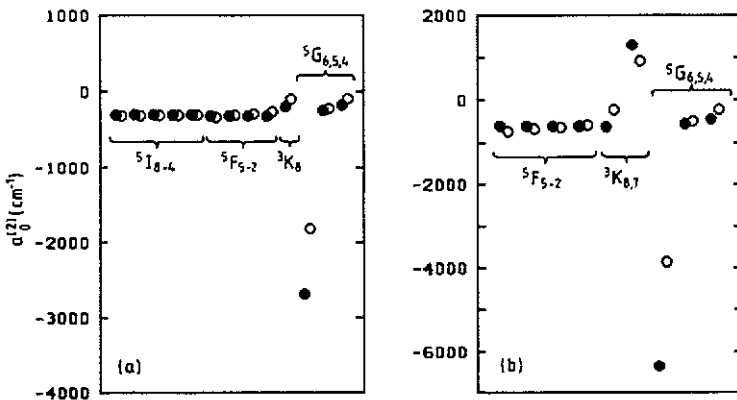


Figure 1. 'Term-dependent' crystal-field parameters $a_0^{(2)}(\gamma J)$. In this figure and figures 2, 3 and 4 the full circles denote the values obtained by fitting the experimental crystal-field splittings of each term: (a) Ho³⁺ in LaCl₃, (b) 10% Ho³⁺ in Y(OH)₃. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the third column of table 3.

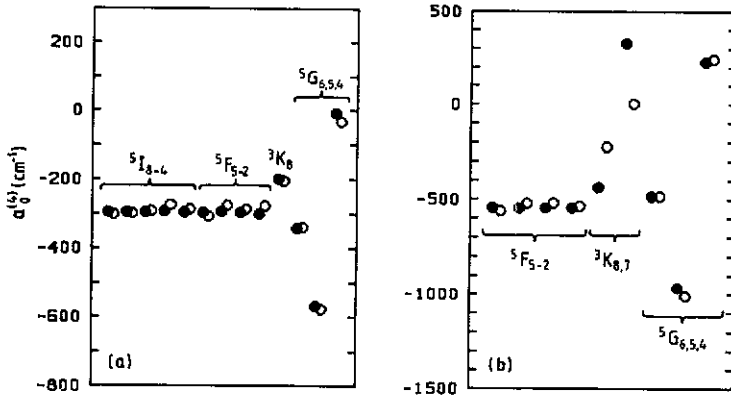


Figure 2. 'Term-dependent' crystal-field parameters $a_0^{(4)}(\gamma J)$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the third column of table 3.

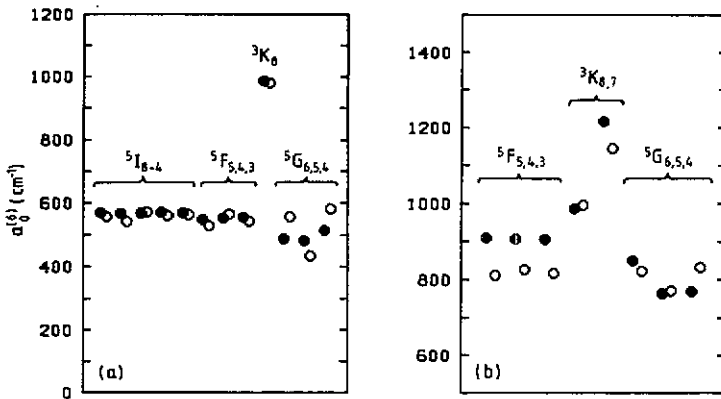


Figure 3. 'Term-dependent' crystal-field parameters $a_0^{(6)}(\gamma J)$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the second column of table 3.

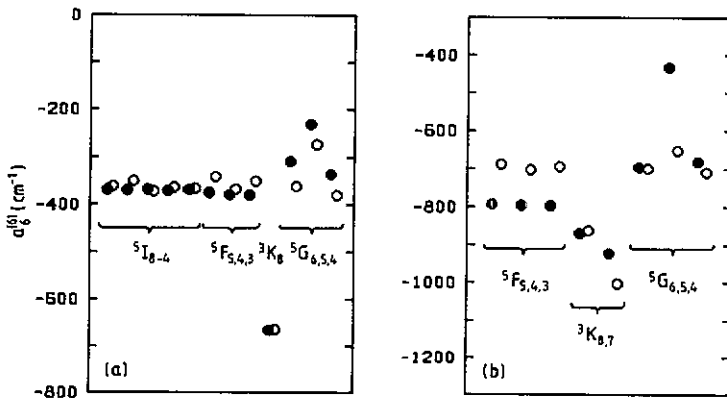


Figure 4. 'Term-dependent' crystal-field parameters $a_0^{(6)}(\gamma J)$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the second column of table 3.

is very similar for all host crystals. The variation depends on the k values but not on the q values. This is confirmed by a comparison of the $a_0^{(6)}(\gamma J)$ and $a_0^{(6)}(\gamma J)$ in LaCl_3 and $\text{Y}(\text{OH})_3$ (figures 3 and 4), on the one hand, and a comparison of the $a_4^{(4)}(\gamma J)$ found for the zircons (paper I, figure 2) with the $a_4^{(4)}(\gamma J)$ found for the hexagonal structures (figures 2), on the other. The parameters $a_0^{(2)}(\gamma J)$ show remarkable variations, consistent for all substances in question, one to very big negative values for the term 5G_6 and one to positive values for the term 3K_7 . This corresponds to the characteristics of the correlated crystal-field operator $\Sigma t^{(2)}(2, 2; ij)$ of (2). The variation in the parameters $a_0^{(4)}(\gamma J)$ is decided by the influence of the three correlated operators $\Sigma t^{(4)}(2, 2; ij)$, $\Sigma t^{(4)}(4, 2; ij)$ and $\Sigma t^{(4)}(6, 2; ij)$ whose orthonormal operators (defined in paper I) cause contributions that have roughly the ratios (~ 0):0.3:0.2 relative to that of the one-electron operator. The variations in the parameters $a_0^{(6)}(\gamma J)$ can be fitted already with the spin-correlated operator. Its contribution is smaller by a factor of about -0.1 in relation to that of the one-electron operator.

A comparison of the crystal-field splittings of Ho^{3+} in different host crystals can conveniently be carried out with the help of the 'term-independent' parameters of the orthonormal operators given in table 3 of this paper and in table 6 of paper I. For the hexagonal structures the contribution to the crystal-field splitting of the parameters $e_0^{(6)}_{,1}$ and $e_0^{(6)}_{,1}$ is very important. This and the fact that for Ho^{3+} in LaCl_3 the influence of the one-electron operator, instead of -0.1 for the other substances) distinguish this host lattice from the others. For this reason Crosswhite and Newman (1984) had been able to realize an improved fit of the crystal-field splittings of Ho^{3+} in LaCl_3 by extending H_{CF} with the SCCF operator only. For the zircons the leading contributions are connected with the parameters $e_0^{(6)}_{,1}$ and $e_4^{(4)}_{,1}$. Although the influence of the spin-correlated crystal field on $e_0^{(6)}_{,1}$ is of minor importance, $e_4^{(4)}_{,1}$ nevertheless shows the strong influence of the correlated crystal field. Therefore in contrast to Ho^{3+} in LaCl_3 the spin-correlated crystal field alone is not able to give a convincing refinement to the calculation of the measured splittings for the zircon-structure compounds.

5. Conclusions

The investigation of the crystal-field splittings of Ho^{3+} in LaCl_3 and $\text{Y}(\text{OH})_3$ and of Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 shows that a uniform description is possible for all terms in the energy range from 0 to $\sim 28\,000\text{ cm}^{-1}$ if the correlation of the electrons is included by using five additional parameters. These parameters depend only on the k values but do not depend on the q values. There is one correlation parameter connected with $k = 2$, three connected with $k = 4$ and one connected with $k = 6$.

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References

- Bishton S S and Newman D J 1970 *J. Phys. C: Solid State Phys.* **3** 1753-61
 Crosswhite H M, Crosswhite H, Edelstein N and Rajnak K 1977 *J. Chem. Phys.* **67** 3002-10

- Crosswhite H and Newman D J 1984 *J. Chem. Phys.* **81** 4959–62
Enderle M, Pilawa B and Kahle H G 1990a *J. Phys.: Condens. Matter* **2** 4711–15
Enderle M, Pilawa B, Schlaphof W and Kahle H G 1990b *J. Phys.: Condens. Matter* **2** 4685–700
Enderle M, Pilawa B, Schwab M and Kahle H G 1990c *J. Phys.: Condens. Matter* **2** 4701–10
Judd B R 1977 *Phys. Rev. Lett.* **39** 242–4
Pilawa B 1990 *J. Phys.: Condens. Matter* **2** 5555–62
— 1991 *J. Phys.: Condens. Matter* **3** 655–66
Rajnak K and Krupke W F 1967 *J. Chem. Phys.* **46** 3532–41
Rajnak K and Wybourne B G 1964 *J. Chem. Phys.* **41** 565–9
Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: Wiley-Interscience) p 166