Electron correlation and crystal-field splittings of Ho^{3+}. I. Ho^{3+} in YVO$_4$, YAsO$_4$ and HoPO$_4$

Electron correlation and crystal-field splittings of Ho^{3+}: I. Ho^{3+} in YVO_4, $YAsO_4$ and $HoPO_4$

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Abstract. The influence of electron correlation on the crystal-field splittings of Ho^{3+} in YVO_4, $YAsO_4$ and $HoPO_4$ is studied. Because the essential parts of the correlation effects cannot be attributed to spin correlation alone, the general correlated crystal field is used. Although this approach offers many parameters, the significant experimental results allow the determination of those parts of the electron correlation that are important for a description of crystal-field splittings.

1. Introduction

It is well known that the usual approach to calculating the crystal-field splittings of Ho^{3+} yields satisfactory results only for the terms of the multiplets ^5I and ^5F. For terms of other multiplets, significant deviations between experiment and calculation occur (Rajnak and Krupke 1967). No appreciable improvement can be achieved even with an extended Hamiltonian of the free Ho^{3+} ion with up to 20 parameters and diagonalizing all interactions simultaneously (Crosswhite *et al* 1977). The reason for the breakdown of the theory can already be understood within the electrostatic model of the crystal field. Rajnak and Wybourne (1964) showed that admixtures of excited configurations to the ground configuration, which are mainly caused by the Coulomb interaction, make the crystal-field parameters dependent on the L and S values of the Russell–Saunders multiplets. For Ho^{3+} the excited LS multiplets are strongly mixed (Rajnak and Krupke 1967), so that the crystal-field parameters become 'term-dependent'. Bishton and Newman (1970) included the contribution of the ligands to the wavefunctions of the rare-earth ion and proposed the application of the correlated crystal field (CCF), which allows the influence of the correlation to be described by means of an effective two-electron crystal-field operator whose matrix elements can be calculated within the ground configuration.

Since the general treatment of the correlation effects introduces many parameters in the crystal-field Hamiltonian, Judd (1977) proposed to restrict the phenomenological description to the so-called spin correlation. Judd showed that this can be done with the spin-correlated crystal-field (SCCF) operator, which is easy to handle. In the case of Ho^{3+} the SCCF greatly improves the description of the term $^3K_8$ but no progress is made in the case of the terms of ^5G (Yeung and Newman 1986, Moran *et al* 1990).

The main problem in making any progress in the investigation of the CCF for Ho^{3+} is that most of the theoretical work is concentrated on the spectra of Ho^{3+} in $LaCl_3$ (Reid 1987). The spectra of Ho^{3+} in other host lattices could not be used because of uncertainties caused by experimental problems. Therefore in three preceding papers (Enderle *et al* 1990b, c, a) we carried out a careful analysis of the crystal-field splittings of Ho^{3+} in YVO_4, $YAsO_4$ and $HoPO_4$ in the energy range 11 000 to 27 600 cm^{-1}. In this paper a description of the crystal-field splittings is presented, which includes the effect of electron correlation.

2. Crystal-field operators

To describe the crystal-field (CF) splittings of a rare-earth ion, the perturbation operator, which must be added to the Hamiltonian of the free ion, is usually expanded in spherical harmonics $Y_q^{(k)}(\theta_i, \varphi_i)$ or tensor operators $t_q^{(k)}(i)$, which act on the angles of the 4f electrons i.

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

The number of tensor operators is restricted by the angular momentum of the electrons and the symmetry of the rare-earth lattice site. For the 4f electrons of a rare-earth ion, k can take the values 2, 4 and 6. In the case of the zircon structures of YVO_4, $YAsO_4$ and $HoPO_4$, the tetragonal site symmetry of the Ho^{3+} ions is $\bar{4}2m$ so that q can take the values 0 (mod 4) and the crystal-field parameters $A_q^{(k)}$ are real. This is also true for the parameters of the correlated operators (equations (2) and (4) later).

Within the frame of the electrostatic crystal-field model Rajnak and Wybourne (1964) showed that the crystal-field parameters become dependent on the L and S values of a term because of the configuration interaction. Two-electron interactions therefore have to be included into the crystal-field description. Bishton and Newman (1970) proposed a phenomenological parametrization scheme to include most general correlation effects into a fitting procedure of the crystal-field components. They called it the correlated crystal-field (CCF) operator. It has to be added to operator (1), and in contrast to H_{CF} it acts simultaneously on the angles of two electrons,

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

Here $t_q^{(k)}(k_1, k_2; ij)$ is a tensor operator that can be written as a sum of products of two one-electron tensor operators by means of the Clebsch–Gordan expansion

$$t_q^{(k)}(k_1, k_2; ij) = \sum_{q_1,q_2} \langle k_1 q_1 k_2 q_2 | k_1 k_2 k q \rangle \, t_{q_1}^{(k_1)}(i) \, t_{q_2}^{(k_2)}(j) \tag{3}$$

where $\langle k_1 q_1 k_2 q_2 | k_1 k_2 k q \rangle$ is the Clebsch–Gordan coefficient. In the above, k_1 and k_2 can take all values between 0 and 6. The possible (k_1, k_2) pairs are listed in table 1; k_1 and k_2 can be exchanged. If k_1 or k_2 equals zero, operator (2) takes the same form as the crystal-field operator (1). Therefore such (k_1, k_2) pairs are omitted in table 1. The q_t ($t = 1, 2$) are restricted because of the Clebsch–Gordan expansion; k can take all values between 0 and 12. But there is no experimental evidence that k values bigger than 6 are necessary to describe the experiment. If the interaction between different terms can be neglected, the k values are all even. As for H_{CF}, q can take the values 0(mod 4). Within

Table 1. List of the (k_1, k_2) pairs of the correlated crystal-field operators (see text for details).

k	Even pairs	Odd pairs
2	(6,6); (6,4); (4,4); – (4,2); (2,2)	(5,5); (5,3); – (3,3); (3,1); (1,1)
4	(6,6); (6,4); (4,4); (6,2); (4,2); (2,2)	(5,5); (5,3); (5,1); (3,3); (3,1)
6	(6,6); (6,4); (4,4); (6,2); (4,2)	(5,5); (5,3); (5,1); (3,3)
8	(6,6); (6,4); (4,4); (6,2)	(5,5); (5,3)
10	(6,6); (6,4)	(5,5)
12	(6,6)	

the electrostatic crystal-field model only even (k_1, k_2) pairs should contribute to H_{CCF}. The influence of the neighbouring ions does not seriously affect this result (Newman 1977), although odd (k_1, k_2) pairs become possible. So the investigation of the CCF is restricted to operators with even (k_1, k_2) pairs.

In addition to the CCF, the spin-correlated crystal-field (Judd 1977) was applied to describe the correlation effects. The spin-correlated crystal-field (SCCF) operator is

$$H_{SCCF} = \sum_{i<j} \sum_{k,q} C_q^{(k)}(s_i \cdot s_j)\, t_q^{(k)}(i). \tag{4}$$

Here s_i and s_j are the spin operators of the electrons i and j; k and q have the same values as for H_{CF}. The calculation of the matrix elements of the crystal-field operators is outlined in the appendix.

3. Crystal-field parameters

The usual way of finding the crystal-field parameters is to fit the eigenvalues of the Hamiltonian H_{CF} to the measured crystal-field energies of the various terms by varying the parameters $A_q^{(k)}$. Since H_{CF} does not include correlation effects of the electrons, this method is successful only if terms of the same LS multiplet are considered. If the terms have to be described by means of intermediate-coupling wavefunctions, it turns out that each individual term needs its own parameter values. Thus one has to introduce 'term-dependent' crystal-field parameters $a_q^{(k)}(\gamma J)$. A most essential supposition for a determination of meaningful 'term-dependent' crystal-field parameters is that the J-mixing contribution to the energy of the crystal-field components is small compared with the total splitting of the terms. For the configuration $4f^{10}$ of the Ho^{3+} ion, this assumption is valid for most of the terms within the energy region of interest for this paper (15 000 to 27 600 cm^{-1}). The only exceptions are the terms $^3H_5$ and $^3H_6$, which are very close together. Therefore J-mixing will be important, with the consequence that these terms have to be fitted simultaneously. Additionally, the intermediate wavefunctions of these terms differ badly (Rajnak and Krupke 1967), so that similar parameter values cannot be expected.

The 'term-dependent' crystal-field parameters $a_q^{(k)}(\gamma J)$ that describe the crystal-field splittings of Ho^{3+} in YVO_4, $YAsO_4$ and $HoPO_4$ for each individual term are presented in tables 2, 3 and 4. These tables also contain the root-mean-square (RMS) deviation σ, which can be obtained in a five-parameter fit. The RMS deviations have the order of the J-mixing contributions, so that the parameters with k values up to 6 certainly give the

Table 2. 'Term-dependent' parameters $a_q^{(k)}(\gamma J)$ of 10% Ho^{3+} in YVO_4. In this and tables 3 and 4, σ denotes the RMS deviation that can be achieved by a fit of the calculated crystal-field energies to the measured ones. To fit the term $^5F_4$ the influence of the neighbouring term $^5S_2$ was taken into account. All figures have the units cm^{-1}.

Term σ	$^5F_5$ 0.3	$^5F_4$ 1.5	$^5F_3$ 0.0	$^5F_2$ 0.0	$^3K_8$ 2.4	$^5G_6$ 5.2	$^5G_5$ 0.7	$^5G_4$ 0.4	$^3K_7$ 2.3
$a_0^{(2)}$	246	220	416	248	423	−408	322	282	498
$a_0^{(4)}$	400	254	348	363	503	547	823	129	220
$a_4^{(4)}$	−805	−728	−783	−799	−424	−1006	−1705	−205	42
$a_0^{(6)}$	1140	913	845	—	1210	887	844	872	1392
$a_4^{(6)}$	−159	−142	−157	—	−197	−241	−85	−133	−403

Table 3. 'Term-dependent' parameters $a_q^{(k)}(\gamma J)$ of 10% Ho^{3+} in $YAsO_4$.

Term σ	$^5F_5$ 0.2	$^5F_4$ 0.8	$^5F_3$ 0.0	$^5F_2$ 0.0	$^3K_8$ 1.8	$^5G_6$ 2.6	$^5G_5$ 0.8	$^5G_4$ 0.3	$^3K_7$ 0.9
$a_0^{(2)}$	52	62	103	−43	183	−901	203	308	525
$a_0^{(4)}$	60	−23	53	121	−36	146	325	−92	30
$a_4^{(4)}$	−731	−738	−732	−793	35	−905	−1533	−45	83
$a_0^{(6)}$	924	819	876	—	1064	781	820	808	1062
$a_4^{(6)}$	32	−29	21	—	−190	27	−232	81	−117

Table 4. 'Term-dependent' parameters $a_q^{(k)}(\gamma J)$ of $HoPO_4$.

Term σ	$^5F_5$ 0.3	$^5F_4$ 0.7	$^5F_3$ 0.0	$^5F_2$ 0.0	$^3K_8$ 1.6	$^5G_6$ 3.0	$^5G_5$ 1.9	$^5G_4$ 0.9	$^3K_7$ 1.2
$a_0^{(2)}$	−593	−514	−559	−356	−191	−3444	−352	−238	1023
$a_0^{(4)}$	−7	30	59	−22	67	144	215	−118	−17
$a_4^{(4)}$	−680	−771	−641	−765	−253	−908	−1580	2	232
$a_0^{(6)}$	1039	944	990	—	1189	936	942	905	1194
$a_4^{(6)}$	28	−14	−12	—	127	75	227	91	−183

leading contribution to the crystal-field splittings. For all terms the parameter values are clear in principle if the energies of all crystal-field components and their Zeeman shifts are known. But in spite of this the values of the crystal-field parameters obtained are often not well defined if each individual term is fitted separately.

The comparison of the parameter values obtained for the terms of ^5F allows one to estimate the errors that may occur in such fits. These parameter values should be nearly the same for all terms, because ^5F is a rather pure Russell–Saunders multiplet. The quoted values in tables 2, 3 and 4 show that deviations from the mean values $\bar{a}_q^{(k)}(^5F)$ of more than $100\ cm^{-1}$ can occur. Another indicator for the reliability of the parameter values is their stability during the fitting procedure. Some of the parameters, especially $a_4^{(4)}(\gamma J)$ and $a_0^{(6)}(\gamma J)$, quickly obtain their final values although the RMS deviation is far

away from the best value, whereas others can change their values without changing the RMS deviation significantly. The discussion of the correlation effects is therefore restricted to those crystal-field parameters whose values or whose variations from term to term are much bigger than 100 cm^{-1}, so that a possible change of the parameter value of up to 100 cm^{-1} cannot seriously affect the investigation of the large correlation effects. Thus the parameters included in the following discussion are $a_0^{(2)}(\gamma J)$, $a_4^{(4)}(\gamma J)$ and $a_0^{(6)}(\gamma J)$.

The term dependence of these parameters is shown in figures 1, 2 and 3. The parameters $a_0^{(6)}(\gamma J)$ are only slightly influenced by electron correlation. Their values are nearly constant ($\sim 900 \pm 100 \text{ cm}^{-1}$); see figure 3. Only the parameter values $a_0^{(6)}(^3K_{8,7})$ are somewhat higher. But in the case of $a_0^{(2)}(\gamma J)$ and $a_4^{(4)}(\gamma J)$ significant variations of the parameter values occur. This clearly shows that the influence of electron correlation cannot be neglected. If the Russell–Saunders wavefunctions were not mixed because of the spin–orbit interaction, the $a_q^{(k)}(\gamma J)$ values should be different for the multiplets ^5F, ^3K and ^5G, but nevertheless they should be the same within each multiplet. Figures 1 and 2 show that this only holds for the multiplet ^5F. The big variations of the $a_0^{(2)}(\gamma J)$ and $a_4^{(4)}(\gamma J)$ values within the multiplet ^5G indicate the breakdown of the *LS* approximation. The similarity of the results obtained for Ho³⁺ in YVO₄, YAsO₄ and HoPO₄ (see figures 1, 2 and 3) supports the assumption that the variations of these crystal-field parameters are reliable.

4. Investigation of the correlation effects

In order to explain the variations of the $a_q^{(k)}(\gamma J)$, the influence of electron correlation must be introduced into the crystal-field description. *J*-mixing will be neglected for the terms taken into consideration. Then using the Wigner–Eckart theorem, the following sets of linear equations are obtained, which allow the study of the combined contributions of the crystal-field operators (1) and (2),

$$b_q^{(k)}(\gamma J) = A_q^{(k)} \left\langle \gamma J \left\| \sum_{i=1}^{10} t^{(k)}(i) \right\| \gamma J \right\rangle$$

$$+ \sum_{(k_1, k_2)} B_q^{(k)}(k_1, k_2) \left\langle \gamma J \left\| \sum_{i<j}^{10} t^{(k)}(k_1, k_2; ij) \right\| \gamma J \right\rangle \tag{5}$$

and those of the operators (1) and (4),

$$b_q^{(k)}(\gamma J) = A_q^{(k)} \left\langle \gamma J \left\| \sum_{i=1}^{10} t^{(k)}(i) \right\| \gamma J \right\rangle + C_q^{(k)} \left\langle \gamma J \left\| \sum_{i<j}^{10} (s_i \cdot s_j) t^{(k)}(i) \right\| \gamma J \right\rangle \tag{6}$$

respectively. $A_q^{(k)}$, $B_q^{(k)}(k_1, k_2)$ and $C_q^{(k)}$ are 'term-independent' parameters and $b_q^{(k)}(\gamma J)$ abbreviates the product of the reduced matrix element $\langle \gamma J \| \Sigma t^{(k)}(i) \| \gamma J \rangle$ with the fitted crystal-field parameter $a_q^{(k)}(\gamma J)$.

Equations (5) and (6) are applied to the terms $^5F_{5,4,3,2}$, $^3K_{8,7}$ and $^5G_{6,5,4}$ of Ho³⁺. The parameters $b_q^{(k)}(\gamma J)$ are contracted to a vector $b_q^{(k)}$ and the reduced matrix elements of

the various crystal-field operators (abbreviated $X^{(k)}{}_{,t}$) likewise. So equations (5) and (6) can be written for each investigated (k, q) combination as

$$b_q^{(k)} = \sum_t X^{(k)}{}_{,t} \cdot c_q^{(k)}{}_{,t}. \tag{7}$$

Here $c_q^{(k)}{}_{,t}$ represents the crystal-field parameters $A_q^{(k)}$, $B_q^{(k)}(k_1, k_2)$ and $C_q^{(k)}$. Instead of solving equation (7) directly it is reasonable to construct the orthonormal basis $O^{(k)}{}_{,t}$, which stretches the space of the vectors $X^{(k)}{}_{,t}$,

$$b_q^{(k)} = \sum_t O^{(k)}{}_{,t} \cdot e_q^{(k)}{}_{,t}. \tag{8}$$

The advantage of calculating parameter values $e_q^{(k)}{}_{,t}$ with respect to an orthonormal basis of operators is that the number of operators in equation (8) can be increased without thereby changing the parameter values already determined.

The vector components of the orthonormal operators are linear combinations of the reduced matrix elements of the different crystal-field operators. These are listed in table 5. This table shows how the $O^{(k)}{}_{,t}$ are constructed from the operators of equations (1), (2) and (4). For example the components of $O^{(k)}{}_{,1}$ are simply proportional to the reduced matrix elements of $\sum t^{(k)}(i)$ and the $O^{(k)}{}_{,2}$ are a combination of the reduced matrix elements of $\sum t^{(k)}(i)$ and $\sum (s_i \cdot s_j) t^{(k)}(i)$. The 'term-independent' parameters $e_q^{(k)}{}_{,t}$ calculated with the operators $O^{(k)}{}_{,t}$ of table 5 are quoted in table 6. This table also includes the RMS deviations $\Delta_q^{(k)}$ between the fitted and calculated 'term-dependent' parameters $a_q^{(k)}(\alpha J)$.

5. Discussion

The comparison between the fitted values of the term-dependent parameters $a_q^{(k)}(\gamma J)$ and the values calculated by means of equation (8) using 'term-independent' parameters is shown in figures 1, 2 and 3.

5.1. The contribution connected with $t_0^{(2)}$

Figure 1 shows that the variation of the parameters $a_0^{(2)}(\gamma J)$ is roughly the same for all three host lattices. Nearly all parameters have a positive value in the case of Ho^{3+} in YVO_4, a value near zero in the case of $YAsO_4$ and a negative value in the case of $HoPO_4$. Only the parameter values of the term $^5G_6$ and to a lesser extent of the term $^3K_7$ show significant deviations. Especially in the case of $HoPO_4$ this can be well explained by the influence of the correlated crystal-field operator $(2,2)$ whose orthonormal components are represented by $O^{(2)}{}_{,3}$. Table 6 shows that $\Delta_0^{(2)}$ can be reduced drastically through the introduction of the parameter $e_0^{(2)}{}_{,3}$.

5.2. The contribution connected with $t_4^{(4)} + t_{-4}^{(4)}$

Neither the crystal-field operator H_{CF} (parameter $e_4^{(4)}{}_{,1}$) alone nor a combination of H_{CF} and H_{SCCF} ($e_4^{(4)}{}_{,1}$ and $e_4^{(4)}{}_{,2}$) is able to remove the large differences between the observed and calculated parameter values $a_4^{(4)}(\gamma J)$. The values of $\Delta_4^{(4)}$ in table 6 show that a selection of CCF operators that is able to reduce the deviations distinctly is that with the (k_1, k_2) pairs $(2,2)$, $(4,2)$ and $(6,2)$. These are combined to the orthonormal operators $O^{(4)}{}_{,3,4,5}$. No improvement can be achieved if that selection of operators is extended or

Table 5. List of the orthonormal operators $O^{(k)}_{,t}$ that are necessary to describe the correlation effects. The operators $O^{(k)}_{,t}$ can be found by summing the products of the crystal-field operators, listed in the column heading, and the factors given in the respective line.

	$\Sigma t^{(k)}(i)$	$\Sigma t^{(k)}(2,2;ij)$	$\Sigma t^{(k)}(4,2;ij)$	$\Sigma t^{(k)}(6,2;ij)$	$\Sigma s_i \cdot s_j t^{(k)}(i)$
$O^{(2)}_{,1}$	1.78	0.0	0.0	0.0	0.0
$O^{(2)}_{,2}$	−1.77	0.0	0.0	0.0	3.2
$O^{(2)}_{,3}$	−0.36	3.14	0.0	0.0	0.0
$O^{(4)}_{,1}$	1.06	0.0	0.0	0.0	0.0
$O^{(4)}_{,2}$	−2.51	0.0	0.0	0.0	4.11
$O^{(4)}_{,3}$	0.48	7.09	0.0	0.0	0.0
$O^{(4)}_{,4}$	1.08	−1.36	7.21	0.0	0.0
$O^{(4)}_{,5}$	0.15	6.3	−2.32	9.73	0.0
$O^{(6)}_{,1}$	1.20	0.0	0.0	0.0	0.0
$O^{(6)}_{,2}$	−0.65	0.0	0.0	0.0	2.15

Table 6. 'Term-independent' parameters $e^{(k)}_{q,t}$ of the crystal-field operators. There are three columns for each of the three different host lattices. The first column includes the parameter values if only the operator H_{CF} is applied. The second and the third columns include the parameter values if combinations of the operators H_{CF} with H_{SCCF} or of H_{CF} with H_{CCF} are used. The RMS deviations $\Delta^{(k)}_q$ are given in the lines below the parameters $e^{(k)}_{q,t}$ of each (k, q) combination. All figures have the units cm⁻¹.

	Ho³⁺ in YVO₄			Ho³⁺ in YAsO₄			Ho³⁺ in HoPO₄		
$e^{(2)}_{0,1}$	162	162	162	60	60	60	−264	−264	−264
$e^{(2)}_{0,2}$	—	12	—	—	23	—	—	42	—
$e^{(2)}_{0,3}$	—	—	−31	—	—	−45	—	—	−116
$\Delta^{(2)}_0$	256	235	81	381	346	76	1119	1036	81
$e^{(4)}_{4,1}$	−851	−851	−851	−745	−745	−745	−745	−745	−745
$e^{(4)}_{4,2}$	—	−122	—	—	−181	—	—	−137	—
$e^{(4)}_{4,3}$	—	—	110	—	—	96	—	—	112
$e^{(4)}_{4,4}$	—	—	−216	—	—	−266	—	—	−232
$e^{(4)}_{4,5}$	—	—	−167	—	—	−138	—	—	−167
$\Delta^{(4)}_4$	510	469	31	533	461	90	538	490	76
$e^{(6)}_{0,1}$	823	823	—	738	738	—	840	840	—
$e^{(6)}_{0,2}$	—	−132	—	—	−91	—	—	−95	—
$\Delta^{(6)}_0$	195	104	—	104	90	—	111	79	—

if odd pairs were preferred instead of even (k_1, k_2) pairs. These only increase the number of operators necessary without diminishing the differences. Figure 2 shows the parameters $a^{(4)}_4(\gamma J)$.

5.3. The contribution connected with $t^{(6)}_0$

The values of the parameters $a^{(6)}_0(^5F)$ and $a^{(6)}_0(^5G)$ are nearly the same in all three host lattices. The scattering of the values is caused by the uncertainties in fitting single terms
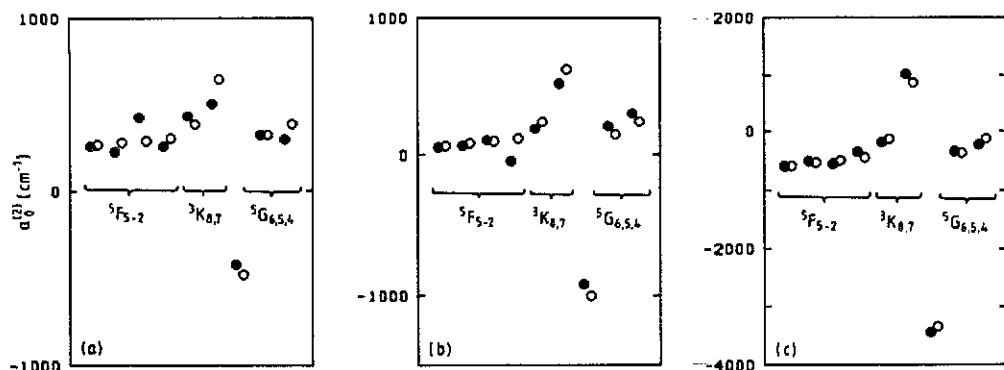
Figure 1. 'Term-dependent' crystal-field parameters $a_0^{(2)}(\gamma J)$. In this and figures 2 and 3 the full circles denote the values obtained by fitting the experimental crystal-field splittings of each term: (a) Ho^{3+} in YVO_4, (b) Ho^{3+} in $YAsO_4$, (c) Ho^{3+} in $HoPO_4$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the third column in table 6.
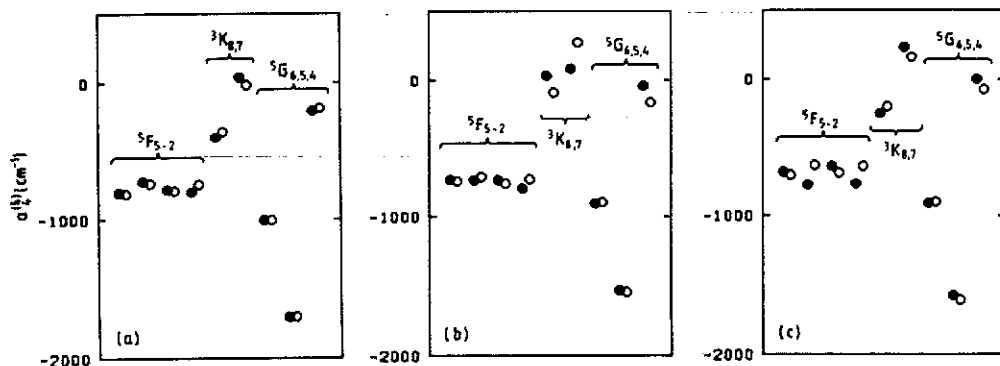

Figure 2. 'Term-dependent' crystal-field parameters $a_4^{(4)}(\gamma J)$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the third column in table 6.

only. This is particularly true for $a_0^{(6)}(^5F_5)$ of Ho^{3+} in YVO_4. This term can be fitted with an extremely small σ. If $a_0^{(6)}(^5F_5)$ is reduced from 1140 to ~600 cm^{-1}, σ increases from 0.3 to 2.8 cm^{-1}. This shows that $a_0^{(6)}(^5F_5)$ is not very well defined since every σ value in the mentioned interval is possible. In contrast to the behaviour of $a_0^{(6)}(^5F_5)$, the parameters of the terms ^3K systematically have larger values. This indicates the influence of the SCCF. Table 6 shows that the introduction of the additional parameter $e_0^{(6)}{}_{,2}$ reduces the $\Delta_0^{(6)}$ values. Figure 3 contains the comparison between the experiment and the calculation.

6. Conclusions

The crystal spectra of Ho^{3+} are particularly suitable for a discussion of correlation effects. Firstly, they allow an accurate determination of almost all crystal-field
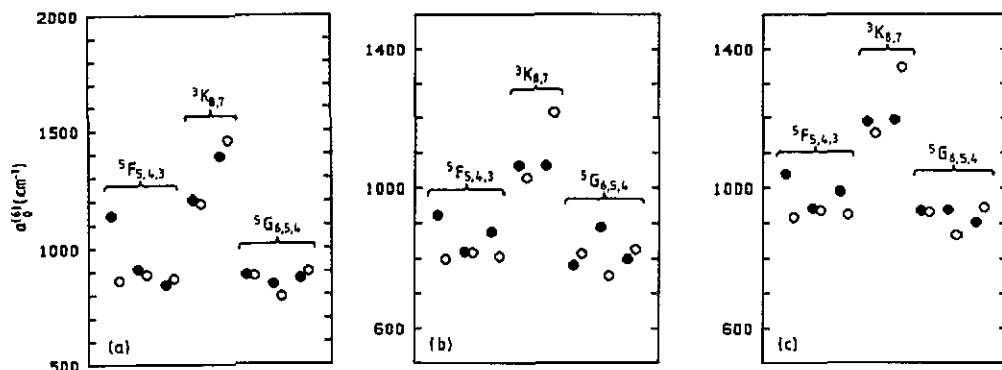
Figure 3. 'Term-dependent' crystal-field parameters $a_0^{(6)}(\gamma J)$. The values of the open circles were calculated with the corresponding 'term-independent' parameters of the second column in table 6.

components; and secondly, the crystal-field splittings of many terms can be well described by means of first-order perturbation theory neglecting the influence of J-mixing. So it is possible to determine the several multipole contributions of the crystal field for each term separately. For all three host crystals YVO$_4$, YAsO$_4$ and HoPO$_4$, those parts of the crystal field are important that are connected with the tensor operators $t_4^{(4)} + t_{-4}^{(4)}$ and $t_0^{(6)}$. In contrast to many of the other parts that may contribute to the crystal-field interaction, the contributions of these multipoles are defined rather well. The parameter values $a_4^{(4)}(\gamma J)$ and $a_0^{(6)}(\gamma J)$ vary in the same way for all three host lattices. The comparison of the parameter values shows that this is also true for the parameter $a_0^{(2)}(\gamma J)$.

In order to describe the variations of the contributions of the tensor operators for the different terms, the spin-correlated and correlated crystal fields are used. In the case of $t_0^{(6)}$ the spin-correlated crystal field is already a reasonable completion; in the other cases no improvement of the description can be achieved with the SCCF. In these cases the correlated crystal field is introduced. For $t_4^{(4)} + t_{-4}^{(4)}$ there are at least three operators of the correlated crystal field necessary to describe the variation. In agreement with theoretical considerations the (k_1, k_2) pairs of these operators are even. For $t_0^{(2)}$ it turns out that only one operator of the correlated crystal field is effective.

Acknowledgments

Appendix. Evaluation of the matrix elements

The method of calculating the matrix elements of tensor operators is well known. The formulae for one-particle tensor operators within the LS scheme can be found in textbooks, for instance in Judd (1963). The corresponding formulae for two-particle

operators are known to a lesser extent. Therefore in this appendix all formulae necessary to calculate the matrix elements are listed so that the results quoted in the text can most easily be reproduced.

The matrix elements of a tensor operator $t_q^{(k)}$ can be written, using the Wigner–Eckart theorem, as

$$\langle \gamma JM | t_q^{(k)} | \gamma' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \gamma J \| t^{(k)} \| \gamma' J' \rangle. \qquad (A1)$$

Here γ distinguishes different states with the same J-value. To obtain the reduced matrix elements $\langle \gamma J \| t^{(k)} \| \gamma' J' \rangle$ the wavefunctions $| \gamma JM \rangle$ of the free Ho^{3+} ion have to be calculated. Since the interaction between the valence electrons is dominated by their Coulomb repulsion, the Russell–Saunders states of the $4f^{10}$ configuration (Nielson and Koster 1963) can be used to get a matrix representation of the free–ion Hamiltonian. The Coulomb interaction (parameters E^1, E^2, E^3), the spin–orbit interaction (parameter ζ) and in addition three correction factors (parameters α, β and γ) that are necessary to describe the influence of configuration interaction were included. These parameters also include crystal-field effects that do not lead to a term splitting but to a shift of the centres of gravity of the terms. Thus the parameter values are somewhat different for different host crystals. Since variations of the used free-ion wavefunctions only produce small corrections to the calculated crystal-field splittings, the same set of free-ion parameters were used for Ho^{3+} in the three lattices (Domann 1974): $E^1 = 6698.4 \, cm^{-1}$, $E^2 = 28.79 \, cm^{-1}$, $E^3 = 630.2 \, cm^{-1}$, $\zeta = -2086.7 \, cm^{-1}$, $\alpha = 31.20 \, cm^{-1}$, $\beta = -992.6 \, cm^{-1}$ and $\gamma = 0$. These values were obtained by a fit of the centres of gravity of the investigated terms in $HoPO_4$. The eigenfunctions of the free-ion Hamiltonian are

$$| \bar{\gamma} J \rangle = \sum_{\gamma, S, L} a_{\gamma, S, L}^{(\gamma J)} | 4f^{10} \gamma SL \rangle. \qquad (A2)$$

The Clebsch–Gordan series which adds L and S to J is omitted. The step back from the $| JM \rangle$ scheme to the $| LM_L SM_S \rangle$ scheme is carried out with (Judd 1963, formula 3-35)

$$\langle l^n \gamma SLJ \| T^{(K)} \| l^n \gamma' S' L' J' \rangle = [J, K, J']^{1/2} \begin{Bmatrix} S & S' & \kappa \\ L & L' & k \\ J & J' & K \end{Bmatrix} \langle l^n \gamma SL \| s^{(\kappa)} t^{(k)} \| l^n \gamma' S' L' \rangle. \qquad (A3)$$

Here $[J, K, J']^{1/2}$ abbreviates $\{[J][K][J']\}^{1/2}$ with $[J] = 2J + 1$, and $T_Q^{(K)}$ is a tensor operator that acts on both spin ($s^{(\kappa)}$) and orbit ($t^{(k)}$) of the electrons,

$$T_Q^{(K)} = \sum_{\pi, q} \langle \kappa \pi k q | \kappa k K Q \rangle s_\pi^{(\kappa)} t_q^{(k)}. \qquad (A4)$$

If $s_\pi^{(\kappa)} t_q^{(k)}$ can be written as a sum of one-electron operators $F = \Sigma f(i)$ the reduced matrix elements of equation (A3) can be reduced directly to a sum of one-electron matrix elements (Judd 1963, formula 7-54)

$$\left\langle l^{n}\gamma SL \left| \left| \sum_{i=1}^{n} s^{(\kappa)}(i) t^{(k)}(i) \right| \right| l^{n}\gamma'S'L' \right\rangle$$

$$= n[S, S', L, L']^{1/2} \sum_{\bar{\gamma},\bar{S},\bar{L}} (-1)^{\bar{S}+s+S+\kappa}(-1)^{\bar{L}+l+L+k}$$

$$\times \begin{Bmatrix} S & \kappa & S' \\ s & \bar{S} & s \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ l & \bar{L} & l \end{Bmatrix} (l^{n-1}\bar{\gamma}\bar{S}\bar{L}|\}l^{n}\gamma SL)$$

$$\times (l^{n-1}\bar{\gamma}\bar{S}\bar{L}|\}l^{n}\gamma'S'L')\langle s||s^{(\kappa)}||s\rangle\langle l||t^{(k)}||l\rangle \tag{A5}$$

where $(l^{n-1}\bar{\gamma}\bar{S}\bar{L}|\}l^{n}\gamma'S'L')$ is a coefficient of fractional parentage (Nielson and Koster 1963). On the other hand, if $s_{\pi}^{(\kappa)}t_{q}^{(k)}$ can be written as a sum of two-electron operators $G = \Sigma g_{ij}$ the calculation is carried out in two steps (Judd 1963, formula 7-5)

$$\langle l^{n}\Omega | G | l^{n}\Omega' \rangle = \frac{n}{(n-2)} \sum_{\bar{\Omega},\bar{\Omega}',\omega} \left\langle l^{n-1}\bar{\Omega} \left| \sum_{i<j}^{n-1} g_{ij} \right| l^{n-1}\bar{\Omega}' \right\rangle \langle \bar{\Omega}\omega | \Omega \rangle \langle \bar{\Omega}'\omega | \Omega' \rangle. \tag{A6}$$

Within the *LS* coupling scheme this formula can be written as

$$\left\langle l^{n}\gamma SL \left| \left| \sum_{i<j}^{n} s^{(k)}(ij) t^{(k)}(ij) \right| \right| l^{n}\gamma'S'L' \right\rangle$$

$$= \frac{n}{(n-2)} \sum_{\substack{\bar{\gamma},\bar{L},\bar{S}, \\ \bar{\gamma}',\bar{L}',\bar{S}'}} (l^{n-1}\bar{\gamma}\bar{S}\bar{L}|\}l^{n}\gamma SL)(l^{n-1}\bar{\gamma}'\bar{S}'\bar{L}'|\}l^{n}\gamma'S'L')$$

$$\times (-1)^{\bar{S}+\kappa+S'+s} \begin{Bmatrix} S & \kappa & S' \\ \bar{S}' & s & \bar{S} \end{Bmatrix} [S, S']^{1/2}$$

$$\times (-1)^{\bar{L}+k+L'+l} \begin{Bmatrix} L & k & L' \\ \bar{L}' & l & \bar{L} \end{Bmatrix} [L, L']^{1/2}$$

$$\times \left\langle l^{n-1}\bar{\gamma}\bar{S}\bar{L} \left| \left| \sum_{i<j}^{n-1} s^{(k)}(ij) t^{(k)}(ij) \right| \right| l^{n-1}\bar{\gamma}'\bar{S}'\bar{L}' \right\rangle. \tag{A7}$$

At first the step $4f^{2} \to 4f^{3}$ and then the step $4f^{3} \to 4f^{4}$ is carried out. The reduced matrix elements of the $4f^{2}$ configuration are

$$\langle l^{2}SL|s^{(\kappa)}(\kappa_{1}, \kappa_{2}; 12)t^{(k)}(k_{1}, k_{2}; 12)|l^{2}S'L'\rangle$$

$$= [S, \kappa, S']^{1/2}[L, k, L']^{1/2} \begin{Bmatrix} s & s & \kappa_{1} \\ s & s & \kappa_{2} \\ S & S' & \kappa \end{Bmatrix} \begin{Bmatrix} l & l & k_{1} \\ l & l & k_{2} \\ L & L' & k \end{Bmatrix}$$

$$\times \langle s||s^{(\kappa_{1})}||s\rangle\langle s||s^{(\kappa_{2})}||s\rangle\langle l||t^{(k_{1})}||l\rangle\langle l||t^{(k_{2})}||l\rangle. \tag{A8}$$

In the case of Ho³⁺ the reduced matrix elements of the $4f^{4}$ configuration have to be transformed to the conjugate configuration $4f^{10}$. This is carried out for two-electron operators using a formula given by Donlan (1970):

$$\left\langle l^{4l+2-n}\gamma SL\left|\left|\sum_{i<j}^{4l+2-n} s^{(\kappa)}(\kappa_1,\kappa_2;ij)t^{(k)}(k_1,k_2;ij)\right|\right|l^{4l+2-n}\gamma'S'L'\right\rangle$$

$$= (-1)^{\kappa+k}\left\langle l^n\gamma SL\left|\left|\sum_{i<j}^n s^{(\kappa)}(\kappa_1,\kappa_2;ij)t^{(k)}(k_1,k_2;ij)\right|\right|l^n\gamma'S'L'\right\rangle$$

$$- \langle s||s^{(\kappa_1)}||s\rangle\langle s||s^{(\kappa_2)}||s\rangle\langle l||t^{(k_1)}||l\rangle\langle l||t^{(k_2)}||l\rangle$$

$$\times \begin{Bmatrix} \kappa_1 & \kappa_2 & \kappa \\ s & s & s \end{Bmatrix}\begin{Bmatrix} k_1 & k_2 & k \\ l & l & l \end{Bmatrix}\left\langle l^n\gamma SL\left|\left|\sum_{i=1}^n s^{(\kappa)}(i)t^{(k)}(i)\right|\right|l^n\gamma'S'L'\right\rangle$$

$$\times [\kappa,k]^{1/2}(\langle s||s^{(\kappa)}||s\rangle\langle l||t^{(k)}||l\rangle)^{-1}. \tag{A9}$$

The values of the reduced one-electron matrix elements are arbitrary. For performing the calculations they were taken as $\langle l||t^{(k)}||l\rangle = 1$ for $k \neq 0$ and $\langle s||s^{(1)}||s\rangle = \sqrt{(3/2)}$. With $\langle l||t^{(0)}||l\rangle = [l]^{1/2}$ and $\langle s||s^{(0)}||s\rangle = [s]^{1/2}$ for the values of the reduced matrix elements of the scalar operators, their one-electron matrix elements have the value 1. Therefore the matrix elements of pure orbital operators were calculated with these values using the quoted formulae.

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