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Absorption spectra and Zeeman effect of the trivalent holmium ion in $Y(OH)_3$

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Abstract. The optical absorption spectrum of Ho^{3+} in hexagonal $(Ho_{0.1}, Y_{0.9})(OH)_3$ was studied in the range from 15 000 to 28 000 cm^{-1} at temperatures between 1.4 and 50 K in magnetic fields up to 4 T. Fields along the crystal c axis were used to determine the splitting factors of the doublets. Fields perpendicular to c were applied to induce transitions from the lowest component of the ground term which are forbidden without field. The energies and the symmetry types of almost all crystal-field components could be established with great certainty.

1. Introduction

Comparing the optical spectra of the trivalent holmium ion in different host crystals, one observes important similarities but also great differences arising from the particular surroundings of the ion. In three preceding papers (Enderle *et al* 1990b, c, a) we presented the results of our investigations on the spectra of Ho^{3+} in YVO_4 , $YAsO_4$ and $HoPO_4$. The present paper deals with the spectra of the Ho^{3+} ion in $Y(OH)_3$. They are related to those of Ho^{3+} in ethylsulphate and in $LaCl_3$, since the point symmetry of the Ho^{3+} site in the three lattices is the same (Grohmann *et al* 1961, Dieke and Pandey 1964, Scott 1970). Scott (1970) was the first to study the spectra and the crystal-field splittings of the terms 5I_8 , 5I_5 , 5I_4 and the terms of the multiplet 5F of Ho^{3+} in $Y(OH)_3$ and $Ho(OH)_3$. He also determined the crystal-field parameters which describe the splittings.

As is known from $HoPO_4$ (Becker 1970) and Ho^{3+} in $LaCl_3$ (Rajnak and Krupke 1967) crystal-field parameters which give a satisfactory description of terms belonging to the multiplets 5I and 5F often badly fail to reproduce the crystal-field splittings of other terms. A better agreement between the measured and the calculated crystal-field splittings can be reached by fitting the terms of different multiplets with different sets of crystal-field parameters. These differences, which are mainly induced by the Coulomb interaction (Rajnak and Wybourne 1964), led Bishton and Newman (1970) to develop the concept of the correlated crystal field. In order to study the correlation effects we re-examined the spectra and extended the analysis to the terms of the multiplets 3K , 5G and 3H . In this paper we report our data of the crystal-field components within the range from 15 000 cm^{-1} to 28 000 cm^{-1} .

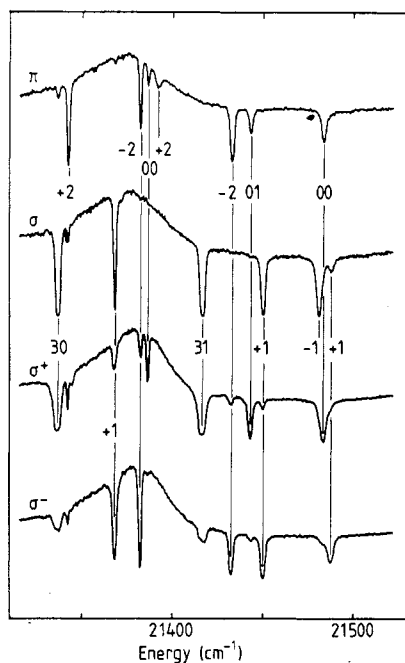


Figure 1. Transitions to the term 3K_8 at $T = 1.4$ K, $B = 1$ T. The labels are the crystal quantum numbers $\bar{\mu}$ and S of the components of 3K_8 .

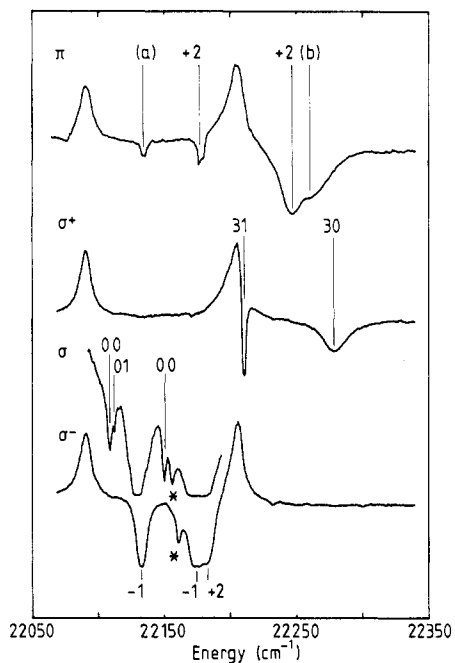


Figure 2. Transitions to the term 5G_6 . All spectra show two emission lines of the used Xe lamp. π -polarisation: $T = 40$ K, $B = 0$, $x = 0.05$. Lines (a) and (b) correspond to the transitions from the singlets $|01\rangle$ and $|00\rangle$ of the ground term to the singlets $|31\rangle$ and $|30\rangle$ of 5G_6 , respectively. σ^+/σ^- -polarisation: $T = 1.4$ K, $B = 1$ T, $x = 0.05$. A part of the σ -spectrum $k \parallel c$, $B \perp c$, $T = 1.4$ K, $B = 1$ T, $x = 0.1$ is included. It shows the transitions to the singlets $\bar{\mu} = 0$. Since the shift of the ground doublet depends on the direction of the applied magnetic field, the energies of the transitions of the doublets $\bar{\mu} = \pm 1$ and to the marked line in the σ -spectrum are somewhat smaller, as in the σ^- -spectrum.

2. Experimental details

The crystals were grown by a hydrothermal technique at Yale University (Mroczkowski *et al* 1970). They crystallise in the hexagonal space group $C6_3/m$ with lattice constants $a = (0.6241 \pm 0.0005)$ nm, $c = (0.3539 \pm 0.0005)$ nm at room temperature (Beall *et al* 1977). There are two equivalent Ho^{3+} sites with point symmetry $\bar{6}$ in the unit cell. The needle-shaped crystals were typically 5 mm long in the direction of the c axis and had diameters of about 0.2 mm. Besides the pure $Ho(OH)_3$, diluted $(Ho_x, Y_{1-x})(OH)_3$ crystals with Ho^{3+} concentrations $x = 0.01$, 0.05 and 0.1 were used to avoid over-absorption by intense lines. Some of the needles were cut and polished perpendicular to c . Thus spectra could be taken with the incident light directed both parallel and perpendicular to c . The absorption spectrum and its Zeeman effect in fields up to 4 T along the crystal c axis were investigated with linear and circular polarisation at

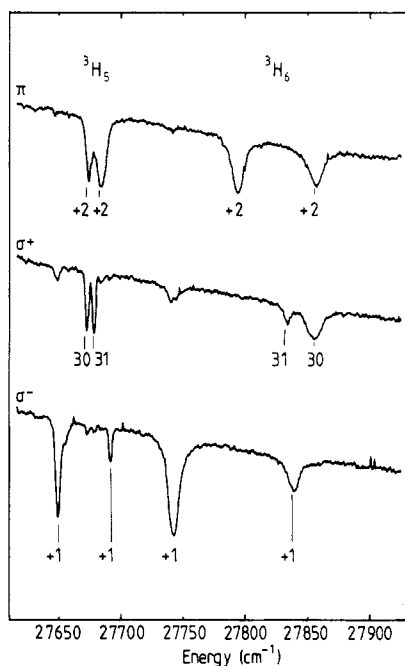


Figure 3. Transitions to the terms ${}^3\text{H}_5$ and ${}^3\text{H}_6$. π -polarisation: $T = 1.4$ K, $B = 1$ T, $x = 0.1$; σ^+/σ^- -polarisation: $T = 1.4$ K, $B = 1$ T, $x = 0.05$.

temperatures between 1.4 K and 50 K. The used experimental equipment is described in detail by Enderle *et al* (1990b).

3. Selection rules

The observed absorptions result from transitions between states of the $4f^{10}$ configuration of the Ho^{3+} ion. Due to crystal-field interactions, these states are not pure $4f^{10}$ but contain admixtures of excited configurations. The odd-parity contributions of these admixtures induce the observed electric dipole transitions. The eigenstates of the ion in the lattice are linear combinations of the free-ion states $|\gamma JM\rangle$. The free-ion states are characterised by the quantum numbers of the total angular momentum, J and M , and by γ which distinguishes the states with the same J .

Although the strict symmetry of the Ho^{3+} site in the $\text{Y}(\text{OH})_3$ lattice is $\bar{6}$ (C_{3h}), the effective crystal field shows $\bar{6}m2$ (D_{3h}) symmetry without discernible deviations. The same is true for the effective crystal field in ethylsulphate and in LaCl_3 . The eigenstates in the lattice are characterised by their transformation behaviour with respect to the operations of $\bar{6}m2$. With regard to the $\bar{6}$ axis all crystal-field states are symmetry singlets and can be labelled by the crystal quantum number $\bar{\mu}$ with

$$\bar{6}|j\bar{\mu}\rangle = e^{i(2\pi/6)\bar{\mu}}|j\bar{\mu}\rangle$$

where j is a running index. $\bar{\mu}$ is limited to the values 0, ± 1 , ± 2 and 3. The connection between the values of $\bar{\mu}$ and those of M for the participating free-ion states is given by

$$\begin{aligned} M &= \bar{\mu} \pmod{6} && \text{for even parity and} \\ M &= \bar{\mu} \pmod{6} + 3 && \text{for odd parity states.} \end{aligned}$$

Table 1. Selection rules for optical transitions in a crystal field of point symmetry $\bar{6}m2$. E and H are the electric and magnetic vector, respectively, of the incident light.

Direction of incident light	Polarisation	Electric dipole transitions	Magnetic dipole transitions
$k \perp c$	$\sigma: E \perp c, H \parallel c$	$\Delta\bar{\mu} = \pm 2(\text{mod } 6)$	$\Delta\bar{\mu} = 0$ and $\Delta S = \pm 1$
	$\pi: E \parallel c, H \perp c$	$\Delta\bar{\mu} = 3(\text{mod } 6)$ and $\Delta S = 0$	$\Delta\bar{\mu} = \pm 1(\text{mod } 6)$
$k \parallel c^\dagger$	$\sigma^+: E^+, H^+$	$\Delta\bar{\mu} = -2(\text{mod } 6)$	$\Delta\bar{\mu} = +1(\text{mod } 6)$
	$\sigma^-: E^-, H^-$	$\Delta\bar{\mu} = +2(\text{mod } 6)$	$\Delta\bar{\mu} = -1(\text{mod } 6)$

† The indices + and – refer to right- or left-handed circular polarisation, respectively.

The selection rules (which result from those in M) for electric and magnetic dipole transitions are given in table 1. In addition to these selection rules $|\Delta J| \leq 1$ holds for magnetic dipole transitions and $|\Delta J| \leq 6$ for electric dipole transitions (Judd 1962, Ofelt 1962). Because of time-reversal symmetry the states $\bar{\mu} = \pm 1$ and $\bar{\mu} = \pm 2$ are Kramers degenerate doublets. Thus only the states $\bar{\mu} = 0$ and $\bar{\mu} = 3$ are real singlets. These singlets can be labelled by a second quantum number S , which indicates the transformation behaviour with regard to the mirror plane $m\bar{\sigma}$

$$m|j\bar{\mu}S\rangle = (-1)^S|j\bar{\mu}S\rangle \quad \text{with } S = 0, 1.$$

The selection rules in S are included in table 1. Alternatively, the quantum number ν can be used, which indicates the transformation behaviour with regard to the two-fold axis 2

$$2|j\bar{\mu}\nu\rangle = e^{i\pi\nu}|j\bar{\mu}\nu\rangle \quad \text{with } \nu = 0, 1.$$

Since the symmetry transformations of $\bar{6}m2$ can be generated by each pair of symmetry elements, the crystal quantum numbers $\bar{\mu}$ and S are sufficient to specify the singlet states. The quantum number ν can be calculated from the relation $\bar{\mu}(\text{mod } 6) = 3(S + \nu)$.

4. Experimental results

4.1. Analysis of the spectra

Similar to Ho^{3+} in $(\text{Ho}, \text{Y})\text{AsO}_4$ and $(\text{Ho}, \text{Y})\text{PO}_4$ the lowest crystal field component of the ground term 5I_8 is a doublet with $\bar{\mu} = \pm 1$ (mainly $M = \pm 7$). From this doublet electric dipole transitions to excited doublets are allowed with $\bar{\mu} = \pm 2$ in π -polarisation and to both doublets with $\bar{\mu} = \pm 1$ and singlets with $\bar{\mu} = 3$ in σ -polarisation. If magnetic dipole transitions are also possible (to terms with $J = 7, 8, 9$), singlets with $\bar{\mu} = 0$ can be observed in π -polarisation and doublets with $\bar{\mu} = \pm 1$ in σ -polarisation just as for electric dipole transitions. Much information is gained if the time-reversal symmetry is broken by a magnetic field applied along c . Now the lowest crystal-field component is a singlet with $\bar{\mu} = -1$ and circularly polarised transitions to excited states with $\bar{\mu} = -2, 0, +1$ and 3 can be observed. Magnetic dipole transitions to $\bar{\mu} = 0$ show right-handed polarisation,

‡ In the paper of Hellwege *et al* (1957), the quantum number S has been called $\bar{\nu}$. In the paper of Grohmann *et al* (1961), it has been called ν which is not identical to the quantum number introduced in the following for the two-fold axis.

those to $\bar{\mu} = -2$ left-handed polarisation, electric dipole transitions to $\bar{\mu} = 3$ are right-handed, those to $\bar{\mu} = +1$ left-handed.

The observed singlet-singlet transitions in electric dipole radiation indicate that the quantum number S is well defined. If all singlets with $\bar{\mu} = 0$ for a term are found, their S values are plain without experimental verification. A term with $J < 6$ contains only one singlet $\bar{\mu} = 0$, with $S = 0$ for even J and $S = 1$ for odd J . Terms with $J = 6$ to 11 contain three singlets $\bar{\mu} = 0$. As a consequence of the $\bar{6}m2$ symmetry, these singlets follow in a special sequence: for even J the singlet with the lowest energy has $S = 0$, the next one $S = 1$ and that with the highest energy $S = 0$; for odd J the S values are 1, 0, 1. This rule holds as long as the J -mixing contribution to the energy of the crystal-field components is small compared with the distance of the singlets. The quantum number S of the singlets $\bar{\mu} = 3$ can be determined by means of the selection rules of table 1.

The spectra taken at low and medium temperatures allow a complete analysis for terms with $J = 7, 8$ or 9 only. The reason is that transitions from the lowest components of the ground term to singlets with $\bar{\mu} = 0$ are allowed in magnetic dipole radiation only. In order to find the energy of the singlets with $\bar{\mu} = 0$ in terms with $J < 7$ a magnetic field was applied perpendicular to c . This induces a mixing between the doublets $\bar{\mu} = \pm 1$ and the singlets $\bar{\mu} = 0$. A magnetic field of up to 4 T, however, was not always sufficient to detect the singlet $\bar{\mu} = 0$.

The results of the investigation are presented in table 2. They were obtained from $(\text{Ho}_x, \text{Y}_{1-x})(\text{OH})_3$ crystals with $x = 0.1$. Only the analysis of the terms ${}^5\text{F}_2$ and ${}^3\text{K}_7$ required pure $\text{Ho}(\text{OH})_3$ samples. The energies $E_{j\bar{\mu}}$ are related to the lowest component of the ground term ${}^5\text{I}_8$. Their errors amount to $\pm 0.4 \text{ cm}^{-1}$. The splitting factors $s_{j\bar{\mu}}$ of the doublets, which are defined by $s_{j\bar{\mu}} = \partial E_{j\bar{\mu}}(B) / \partial (\mu_B B)$ ($\mu_B = \text{Bohr magneton}$) are given in the limit of small magnetic fields B .

4.2. Discussion of the individual terms

${}^5\text{I}_8$: Only 4 of the 11 crystal-field components could be determined. The three lower ones were all used for the analysis of the excited terms. From the splitting factor +8.05 of the lowest doublet it follows that it mainly consists of $M = \pm 7$.

${}^5\text{F}_{5,4,3,2}$ and ${}^5\text{S}_2$: Apart from the singlets $\bar{\mu} = 0$ all crystal-field components were found. Since the transitions to the term ${}^5\text{F}_2$ are very weak a pure $\text{Ho}(\text{OH})_3$ crystal was used to determine its crystal-field components.

${}^3\text{K}_8$: The 11 crystal-field components of the term could be determined at low temperatures. Figure 1 shows the absorption spectra for this term at $T = 1.4 \text{ K}$, $B = 1 \text{ T}$. The measurement of the polarisation allows a unique assignment of the crystal quantum numbers. Magnetic dipole transitions occur not only to the singlets $\bar{\mu} = 0$ but also to the highest doublet with $\bar{\mu} = \pm 1$ and the two upper doublets with $\bar{\mu} = \pm 2$.

${}^5\text{G}_6$: All crystal-field components of the term were measured at low temperatures. Figure 2 shows the spectra. The crystal quantum numbers follow definitely from the polarisation of the absorption lines. The lower doublet with $\bar{\mu} = \pm 2$ which should only appear in π -polarisation is depolarised probably due to the nearby doublet with $\bar{\mu} = \pm 1$. The π -transition to this doublet shows a double-line structure, which does not change in magnetic fields. The origin of the marked line between the two doublets with $\bar{\mu} = \pm 1$ in the σ^- -spectrum is unknown. Its position does not shift when a magnetic field is applied along c . Transitions to the singlets $\bar{\mu} = 0$ could be induced by a magnetic field perpendicular to c . Three additional lines with growing intensity for increasing field

Table 2. Energies, crystal quantum numbers and Zeeman splitting factors.

<i>J</i> -term	Energy of the component (cm ⁻¹)	Crystal quantum numbers		Splitting factor
		μ	<i>S</i>	
⁵ I ₈	0.0	±1		+8.05
	11.32	0	0	
	72.76	0	1	
	102.14	±1		
⁵ F ₅	15 491.3	3	1	+2.7
	15 504.7	±2		
	15 508.5	3	0	
	15 526.8	±1		
	15 535.5	±2		
	15 602.6	±1		
⁵ S ₂	18 478.5	±2		+3.8
	18 480.9	±1		+2.2
⁵ F ₄	18 553.8	3	1	+1.3
	18 573.1	±1		
	18 605.2	±2		
	18 634.1	3	0	
	18 672.8	±2		
⁵ F ₃	20 618.6	±1		+1.2
	20 640.9	3	1	+2.5
	20 690.5	±2		
	20 713.6	3	0	
⁵ F ₂	21 123.9	±1		
	21 126.6	±2		+4.7
³ K ₈	21 333.3	3	0	+8.1
	21 340.0	±2		
	21 366.3	±1		
	21 383.1	±2		
	21 384.1	0	0	
	21 413.2	3	1	
	21 429.4	±2		
	21 440.2	0	1	
	21 446.9	±1		
	21 480.1	0	0	
	21 480.5	±1		
⁵ G ₆	22 108.9	0	0	-5.5†
	22 112.6	0	1	-0.7
	22 129.7	±1		
	22 150.7	0	0	
	22 176.5	±1		
	22 178.1	±2		
	22 207.6	3	1	
	22 248.4	±2		
	22 276.8	3	0	

appeared, a pair of lines below the lowest doublet and one line between the doublets with $\bar{\mu} = \pm 1$. The lowest one of these additional lines could also be observed with a magnetic field along *c*. It experienced a linear shift for not too low fields with a splitting

Table 2. Continued.

J -term	Energy of the component (cm^{-1})	Crystal quantum numbers		Splitting factor
		μ	S	
$^5\text{F}_1$	22 358.6	± 1		0.0
$^5\text{G}_5$	23 964.1	0	1	
	23 968.4	± 1		+1.3
	23 982.7	± 2		+3.2
	24 003.6	3	1	
	24 006.2	± 1		-6.1
	24 026.2	3	0	
$^5\text{G}_4$	24 059.4	± 2		-5.9
	25 805.7	± 2		+0.2
	25 866.0	3	0	
	25 876.4	± 1		+1.1
	25 907.3	± 2		-3.0
$^3\text{K}_7$	25 982.6	3	1	
	26 167.1	3	1	
	26 169.7	± 2		-2.6
	26 181.1	± 1		-2.8
	26 185.5	± 1		+6.6
	26 194.1	0	1	
	26 196.6	3	0	
	26 202.8	± 2		+0.4
	26 206.5	0	0	
	26 218.5	± 1		-0.5
$^3\text{H}_5$	26 231.1	0	1	
	27 647.5	± 1		-6.1
	27 669.6	± 2		+1.8
	27 669.6	3	0	
	27 673.4	3	1	
	27 682.0	± 2		-3.4
$^3\text{H}_6$	27 687.4	± 1		+1.0
	27 740.6	± 1		-5.5
	27 792.4	± 2		-4.5
	27 832.0	3	1	
	27 832.7	± 1		+2.2
	27 851.0	± 2		+2.3
	27 852.4	3	0	

† Corresponding to the shift at $B = 3$ T.

factor $s = -5.5$ (determined at $B = 3$ T). This confirms that another singlet $\bar{\mu} = 0$ is nearby and that these two singlets mainly contain $M = \pm 6$.

$^5\text{G}_5$: Transitions to all crystal-field components could be observed at low temperatures. The polarisation allowed a clear assignment of the crystal quantum numbers. The position of the singlet $\bar{\mu} = 0$ could be determined by means of a magnetic field perpendicular to c .

$^5\text{G}_4$: Apart from the singlet $\bar{\mu} = 0$ all crystal-field components were found at low temperatures. Transitions to the singlet $\bar{\mu} = 0$ could not be induced although magnetic fields up to 4 T were applied perpendicular to c .

3K_7 : The transitions to this term are very weak, thus the spectrum of pure $\text{Ho}(\text{OH})_3$ had to be used. All crystal-field components were detected at low temperatures. The crystal quantum numbers could be assigned from the polarisation of the absorption lines.

3H_5 and 3H_6 : Apart from the singlets $\bar{\mu} = 0$ transitions to all crystal-field components were observed. Figure 3 shows the circularly and π -polarised spectra at $T = 1.4 \text{ K}$, $B = 1 \text{ T}$. Transitions to the singlets $\bar{\mu} = 0$ could not be induced, not even with a magnetic field of 4 T.

5. Conclusions

Nearly all crystal-field components of Ho^{3+} in $\text{Y}(\text{OH})_3$ in the energy range between $15\,000 \text{ cm}^{-1}$ and $28\,000 \text{ cm}^{-1}$ could be determined. The polarisation of the transitions from the three lowest components of the ground term 5I_8 allowed a decided assignment of the quantum numbers of the excited crystal-field components. In this paper only the experimental data are presented. A comparison of the experimental results with calculations using crystal-field theories including correlation effects will be given in two subsequent papers for Ho^{3+} in YVO_4 , YAsO_4 and HoPO_4 (Pilawa 1990a) and for Ho^{3+} in $\text{Y}(\text{OH})_3$ and LaCl_3 (Pilawa 1990b).

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