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Crystal-field spectra of trivalent holmium in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $Y(OH)_3$ in the infrared region

H Bischoff, B Pilawa, A Kasten† and H G Kahle

Physikalisches Institut, Universität Karlsruhe (TH), POB 6980, D-7500 Karlsruhe 1, Federal Republic of Germany

Abstract. The polarized absorption spectra of Ho^{3+} in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $(Ho_{0.1}, Y_{0.9})(OH)_3$ were studied in the range from 5000 to $12\,000\ cm^{-1}$. Nearly all crystal-field components were found and their crystal quantum numbers $\bar{\mu}$, ν and S could be assigned.

1. Introduction

The trivalent holmium ion incorporated in the crystalline rare-earth compounds has proved to be a very suitable probe for studying the influence of electron correlation in crystal-field interactions. This was the motive for a series of articles in which we have investigated the visible spectra $(15\,000–28\,000\ cm^{-1})$ of Ho^{3+} in $HoVO_4$, $HoAsO_4$, $HoPO_4$ and $(Ho_{0.1}, Y_{0.9})(OH)_3$ in order to determine the contribution of electron correlation to the crystal-field splittings of Ho^{3+} (Enderle et al 1990b,c,a, Pilawa 1990, 1991a,b). In the course of this programme we have also studied the absorption spectra of Ho^{3+} in the near infrared region. Hence, in this article we report our data on the crystal-field components of the terms $^5I_{7,6}$ for Ho^{3+} in $HoVO_4$ and $HoAsO_4$, of the terms $^5I_{7,6,5}$ for Ho^{3+} in $HoPO_4$ and of the terms $^5I_{8,7,6,5}$ in $(Ho_{0.1}, Y_{0.9})(OH)_3$.

2. Experimental details

The spectra were taken with a Fourier spectrometer (Bruker IFS 88). Its resolution was $0.5\ cm^{-1}$. A parabola was fitted to the tips of the absorption lines, so that the corresponding wavenumbers could be determined to within $0.1\ cm^{-1}$, although the width of the observed absorption lines was normally bigger than approximately $4\ cm^{-1}$. The spectrometer was calibrated by means of the known spectra of water with an error smaller than $0.1\ cm^{-1}$. Therefore, the total error of the obtained wavenumbers should not exceed $0.2\ cm^{-1}$.

The host lattices of Ho^{3+} in $HoVO_4$, $HoAsO_4$ and $HoPO_4$ are tetragonal whereas that of $(Ho_{0.1}, Y_{0.9})(OH)_3$ is hexagonal. For details about the various host crystals, the crystal-field states of the Ho^{3+} ion and the selection rules for electric and magnetic dipole transitions see, for example, Enderle et al (1990b) and Pilawa (1990). Some of

† Present address: Bruker Analyt. Messtechnik, D-7512 Rheinstetten, Federal Republic of Germany.

the crystals were cut and polished perpendicular to the optical c-axis so that spectra could be taken with the incident light directed both parallel and perpendicular to c. For the vanadates and arsenates these crystals contained 10% Ho^{3+}. No remarkable differences were observed between the crystal-field energies of the pure and diluted samples. All spectra were polarized and taken at temperatures between 30 and 70 K.

3. Experimental results

3.1. Analysis of the spectra

In the observed spectra, characteristic energy differences between the absorption lines that are caused by two different patterns were observed, namely the differences in the crystal-field components of the ground term $^5I_8$ and those in the components of the excited terms. The analysis of these patterns showed that in the temperature range used the spectra consist of transitions out of the ground-term components up to about 150 cm^{-1}. The energy of the components could be ascertained with an error of less than 1 cm^{-1}. The crystal quantum numbers, $\bar{\mu}, \nu, S$, of the individual components were determined by the polarization of the absorption lines using the selection rules.

In some cases a definite assignment of the individual absorption line was not possible from the energy differences and polarization alone. One reason was that some allowed transitions were too weak to be observed. Another important reason was that if different absorption lines or even different crystal-field components were close together, energy differences became uncertain and polarization indistinct. Crystal-field calculations were therefore a helpful tool to support the analysis of the absorption spectra. It is known that in the case of Ho^{3+} such calculations allow very accurate predictions of crystal-field components for the terms of the multiplets ^5I and ^5F. Thus the spectra were compared with calculations. The assignments made from energy differences and polarization were checked and ambiguous absorption lines were ascertained according to the crystal-field predictions. The crystal-field parameters were obtained from a fit of the terms ^5F and those crystal-field components of the terms ^5I which could be definitely determined from the absorption spectra. The following crystal-field Hamiltonian was used

$$H_{CF} = \sum_{i=1}^{10} \sum_k \sum_q B_q^{(k)} t_q^{(k)}(i)$$

where i denotes the valence electrons of the Ho^{3+} ion, k can take the values 2, 4 and 6 for electrons of the 4f configuration and q can take the values 0, ± 4 and 0, ± 6 for the tetragonal and hexagonal host lattices, respectively. $B_q^{(k)}$ are the crystal-field parameters and $t_q^{(k)}(i)$ tensor operators which act on the electron i. The matrix elements of H_{CF} for the lowest terms of the $4f^{10}$ configuration of Ho^{3+} can be calculated within the approximation of pure 4f electrons. The values of the reduced matrix elements of $t^{(k)}(i)$ were taken to be

$$\langle l \| t^{(k)} \| l \rangle = (-1)^l \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}$$

with $l = 3$. Since electron correlation is included in the crystal-field parameters $B_q^{(k)}$ of the considered terms, no two-electron operators were introduced into the crystal-field description.

3.2. Discussion of the individual terms

The results of our investigation are presented in tables 1 to 4 for Ho^{3+} in HoVO$_4$, HoAsO$_4$, HoPO$_4$ and (Ho$_{0.1}$, Y$_{0.9}$)(OH)$_3$, respectively. The measured energies of the crystal-field components are related to the lowest component of the ground term $^5I_8$. These energies are compared with the calculated crystal-field energies. The corresponding crystal-field parameters are given in table 5.

Table 1. Energies and quantum numbers of the crystal-field components of Ho^{3+} in HoVO$_4$.

J term	Centre of gravity (cm^{-1})	Crystal quantum numbers $\bar{\mu}$	ν	Energy of the component (cm^{-1})	Calculated energy (cm^{-1})
$^5I_7$	5193.6	0	1	5125.2	5127.7
		±1		5130.1	5133.4
		2	0	5136.4	5139.8
		2	1	5183.5	5187.3
		2	0	5199.4	5197.9
		±1		5201.7	5202.0
		±1		5211.7	5210.5
		0	0	5213.9	5216.0
		2	1	5231.4	5229.5
		±1		5240.1	5236.1
		0	1	5247.4	5241.8
$^5I_6$		2	1	8638.9	8635.1
		±1		8644.4	8643.6
		0	0	8648.8	8653.2
		2	0	8674.6	8673.1
		2	1	8690.0	8687.9
		0	1	8691.6	8696.9
		±1		8691.7	8693.0
		2	0	—	8705.3
		0	0	8728.8	8727.1
		±1		8740.1	8738.8

3.2.1. Ho^{3+} in HoVO$_4$. At 30 K, transitions from the five lowest crystal-field components of the ground term $^5I_8$ could be observed. For a discussion of this term see, for example, Battison *et al* (1977). It is remarkable that in concentrated HoVO$_4$ the lowest doublet at 20.7 cm^{-1} is split into two components (2.3 cm^{-1}) in spite of the tetragonal symmetry of the host lattice. Therefore absorption lines corresponding to transitions out of this doublet showed a doublet structure. So it was easy to identify such transitions within the absorption spectra.

$^5I_7$: All crystal-field components could be assigned. From the lowest crystal-field component of $^5I_8$ electric and magnetic dipole transitions were observed to all doublets of the term, magnetic transitions were found to the singlets $\bar{\mu} = 0$, $\nu = 1$ and electric transitions to the singlets $\bar{\mu} = 2$, $\nu = 1$. The remaining singlets $\bar{\mu} = 2$, $\nu = 0$ and $\bar{\mu} = 0$, $\nu = 0$ were fixed by means of transitions from the first excited doublet of the ground term. Their quantum numbers were assigned according to the calculated energies. All absorption lines of the spectrum could be addressed to transitions between crystal-field components of the ground term $^5I_8$ and those of the term $^5I_7$.

Table 2. Energies and quantum numbers of the crystal-field components of Ho^{3+} in $HoAsO_4$.

J term	Centre of gravity (cm^{-1})	Crystal quantum numbers $\bar{\mu}$	ν	Energy of the component (cm^{-1})	Calculated energy (cm^{-1})
$^5I_7$	5164.1	0	1	5111.3	5114.9
		± 1		5114.4	5118.0
		2	0	5117.2	5120.4
		2	1	5142.0	5144.6
		2	0	5161.9	5159.5
		± 1		5164.5	5165.7
		0	0	5176.7	5176.1
		± 1		5177.9	5176.8
		2	1	5207.3	5204.9
		± 1		5209.9	5206.4
		0	1	5211.8	5207.1
$^5I_6$		2	1	8620.7	8618.8
		± 1		8623.5	8624.1
		0	0	8629.4	8634.3
		2	0	8652.7	8651.4
		2	1	8657.7	8657.5
		0	1	—	8658.9
		± 1		8671.2	8671.5
		2	0	8681.0	8682.4
		0	0	8701.6	8700.0
		± 1		8701.6	8700.7

$^5I_6$: All but one crystal-field component could be assigned. By means of transitions from the lowest component of the term $^5I_8$, all doublets and the singlets $\bar{\mu} = 2$, $\nu = 1$ could be determined. Transitions from the first excited ground-term doublet revealed the positions of four of the remaining singlets. Their quantum numbers $\bar{\mu} = 0, 2$ were assigned according to the calculated positions. All the other transitions of the spectrum could be attached to transitions between more excited components of the term $^5I_8$ and those of the term $^5I_6$. However, no hint on the missing singlet $\bar{\mu} = 2$, $\nu = 0$ could be found.

3.2.2. Ho^{3+} in $HoAsO_4$. At 30 K, transitions originating from the six lowest crystal-field components of the ground term $^5I_8$ could be observed (Enderle *et al* 1990c).

$^5I_7$: All crystal-field components could be determined unambiguously from the absorption spectrum and all absorption lines of the spectrum could be assigned.

$^5I_6$: The two lowest doublets and the singlets $\bar{\mu} = 2$, $\nu = 1$ could be definitely determined from the absorption spectrum. According to the crystal-field calculation the upper doublet coincides with the upper singlet $\bar{\mu} = 0$, $\nu = 0$. This prediction was in agreement with the observed polarization of the absorption lines. The energies of three further singlets could be fixed through transitions from the ground doublet and the first excited doublet in σ-polarization. According to the crystal-field calculation these should correspond to the remaining singlets $\bar{\mu} = 2$, $\nu = 0$ and the singlet $\bar{\mu} = 0$, $\nu = 0$. No convincing hint on the singlet $\bar{\mu} = 0$, $\nu = 1$ was found.

3.2.3. Ho^{3+} in $HoPO_4$. The ground term was studied by Becker *et al* (1969). They

Table 3. Energies and quantum numbers of the crystal-field components of Ho^{3+} in $HoPO_4$.

J term	Centre of gravity (cm^{-1})	Crystal quantum numbers $\bar{\mu}$	ν	Energy of the component (cm^{-1})	Calculated energy (cm^{-1})
$^5I_7$	5204.2	2	0	5152.5	5153.0
		2	1	5158.5	5157.4
		±1		5164.7	5164.7
		0	1	5170.3	5174.7
		±1		5172.1	5174.5
		2	0	5203.5	5203.0
		±1		5211.4	5210.6
		0	0	5220.4	5220.8
		0	1	5264.2	5259.2
		2	1	5264.2	5263.6
		±1		5266.2	5261.8
$^5I_6$		2	1	8650.3	8648.5
		2	0	8650.3	8649.5
		0	0	8673.5	8679.4
		±1		8674.1	8674.8
		2	1	8681.9	8679.4
		0	1	8690.3	8692.0
		±1		8703.4	8703.2
		2	0	—	8737.2
		±1		8750.1	8749.3
		0	0	8759.0	8757.3
$^5I_5$	11257.1	±1		11215.9	11212.1
		±1		11234.5	11238.8
		2	0	11244.6	11234.7
		0	1	11253.0	11250.1
		0	0	11262.0	11259.6
		2	1	11279.6	11283.5
		±1		11290.7	11295.6
		0	1	11306.9	11307.4

found that the first excited crystal-field component is 66 cm^{-1} above the ground doublet. At 30 K, only transitions originating from the lowest crystal-field component could be observed. The spectra only show the energies of the doublets and singlets but do not reveal the crystal quantum numbers of the singlets. Therefore these were assigned according to the crystal-field calculation.

$^5I_{7,6}$: Transitions from the ground doublet to all but one crystal-field component ($^5I_6$ $\bar{\mu} = 2$, $\nu = 0$) could be observed. The predicted energies agree excellently with the observed energies of the crystal-field components.

$^5I_5$: All crystal-field components could be determined. The transitions from the ground doublet to the singlets $\bar{\mu} = 0$ caused very strong absorptions, whereas absorptions corresponding to the singlets $\bar{\mu} = 2$ were extremely weak. The difference between measurement and calculation is especially big for the singlet $\bar{\mu} = 2$, $\nu = 0$. Thus additional investigations are desirable, for example Zeeman effect measurements or application of circularly polarized light, to confirm the assignment of this singlet.

Table 4. Energies and quantum numbers of the crystal-field components of Ho^{3+} in $(Ho_{0.1}, Y_{0.9})(OH)_3$.

J term	Centre of gravity (cm^{-1})	Crystal quantum numbers $\bar{\mu}$	S	Energy of the component (cm^{-1})	Calculated energy (cm^{-1})
$^5I_8$		±1		0.0	−1.5
		0	0	11.3	13.5
		0	1	72.8	71.3
		±1		102.1	102.4
		±2		131.3	132.3
		3	1	152.1	153.0
		0	0	—	219.6
		±2		—	232.3
		±1		—	270.4
		±2		—	339.0
		3	0	—	361.4
$^5I_7$	5221.1	0	1	5160.3	5159.1
		0	0	5160.3	5161.8
		±1		5181.7	5183.0
		±1		5205.8	5203.6
		±2		5210.4	5212.4
		3	0	5223.3	5227.1
		3	1	5261.0	5258.1
		±2		5262.5	5262.1
		±1		5263.0	5263.2
		0	1	5265.0	5262.3
$^5I_6$		0	0	—	8678.7
		0	1	8681.6	8680.1
		±2		8687.0	8685.9
		3	0	8687.7	8682.5
		±1		8700.3	8701.7
		3	1	8715.6	8724.9
		±2		8741.0	8741.9
		±1		8773.1	8770.6
		0	0	—	8782.7
$^5I_5$		±1		11239.1	11239.3
		3	0	—	11274.4
		±2		11256.9	11254.9
		3	1	—	11242.0
		±2		11292.9	11290.1
		±1		11319.5	11320.6
		0	1	—	11335.6

3.2.4. Ho^{3+} in $(Ho_{0.1}, Y_{0.9})(OH)_3$. $^5I_8$: The four lowest crystal-field components were determined by Scott (1970). Now, two further components could be assigned from measurements at 70 K.

$^5I_7$: The two lowest doublets $\bar{\mu} = ±1$, the lower doublet $\bar{\mu} = ±2$ and the singlet $\bar{\mu} = 3$, $S = 0$ could be determined unequivocally from the spectra. The lower singlet pair $\bar{\mu} = 0$ is degenerate. Magnetic dipole transitions from the first excited singlet fixing the quantum number S could be observed at 30 K, and at 70 K magnetic dipole transitions could be detected from the second excited singlet of the ground term.

Table 5. Crystal-field parameters for the different compounds in cm^{-1}.

	YVO$_4$	YAsO$_4$	HoPO$_4$	Y(OH)$_3$
$B_0^{(2)}$	−183	−41	372	466
$B_0^{(4)}$	369	57	26	−499
$B_4^{(4)}$	−722	−663	−639	—
$B_0^{(6)}$	−719	−662	−760	−650
$B_4^{(6)}$	131	19	−29	—
$B_6^{(6)}$	—	—	—	550

Strong absorptions were observed for all polarizations at about 5260 cm^{-1}. According to the crystal-field calculation, these should correspond to the upper four crystal-field components which lie close together. Aside from $\bar{\mu} = 0$, $S = 1$ all these components could be verified through at least one additional unambiguous transition out of the ground-term components.

$^5I_6$: All absorptions could be assigned. Nearly all crystal-field components were found. The singlets $\bar{\mu} = 0$, $S = 0$ could not be determined because all transitions from the thermally populated ground-state components are forbidden by selection rules.

$^5I_5$: The energies of the doublets were assigned by Scott (1970). The singlet $\bar{\mu} = 0$, $S = 1$ could not be assigned because the allowed transition from the excited singlet $\bar{\mu} = 3$, $S = 1$ of the ground term $^5I_8$ was not observed. There is some evidence from the spectra that the energies of the singlets $\bar{\mu} = 3$, $S = 0$ and $\bar{\mu} = 3$, $S = 1$ should be 11 252.1 cm^{-1} and 11 257.1 cm^{-1}, respectivley. But these energies badly contradict the result of the crystal-field calculation. Thus these singlets remain uncertain and should be confirmed by extended investigations measuring, for example the circular polarization and the Zeeman effect at low temperatures.

4. Conclusion

The analysis of the infrared absorption spectra of Ho^{3+} in HoVO$_4$, HoAsO$_4$, HoPO$_4$ and (Ho$_{0.1}$, Y$_{0.9}$)(OH)$_3$ allowed the determination with great certainty of nearly all crystal-field components of the terms $^5I_{7,6}$, and in the latter two also of the term $^5I_5$. The experimentally found components could be verified with excellent agreement by a calculation using an appropriate crystal-field operator.

Acknowledgment

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