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Absorption spectra and Zeeman effect of the trivalent holmium ion in compounds with tetragonal zircon structure: II. Ho^{3+} in YAsO_4

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Abstract. The optical absorption spectrum of Ho^{3+} in $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$ and HoAsO_4 and its Zeeman effect in magnetic fields along the crystal c axis were studied between 11 000 and 28 000 cm^{-1} at temperatures below 2.2 K and up to 85 K. In addition to the commonly used linearly polarised spectra, circularly polarised spectra with light propagation along the direction of the magnetic field were taken to ascertain the symmetry types of the singlets of the excited terms. The data of almost all crystal-field components could be determined with great reliability.

1. Introduction

As a continuation of our investigations on the trivalent holmium ion in crystals with point symmetry $\bar{4}2m$ of the rare-earth ion site (Enderle *et al* 1990, to be referred to as I), this paper deals with the optical absorption spectrum of Ho^{3+} in YAsO_4 and HoAsO_4 . Changing the host lattice but not the crystal symmetry results in a different strength of the crystal field and its multipole components, while its symmetry remains unaffected. Consequently, the energetic sequence of the crystal-field components may be exchanged and the contributions of the free-ion eigenfunctions $|\gamma JM\rangle$ to a given crystal-field state may differ, but the symmetry types and their respective basic states (composed of free-ion eigenfunctions) are the same (see table 1 of I). Most apparent are the differences in the splitting of the ground term 5I_8 . In YAsO_4 , Ho^{3+} has a doublet ground state and therefore experiences magnetic ordering at $T_N = 0.557$ K (Becher and Kalbfleisch 1973). Furthermore, the assignment of excited singlets using magnetic fields perpendicular to the crystallographic c axis (as described in I) cannot be performed because the quantum numbers ν and S are not defined for the doublet ground state. The energies of all crystal-field components can, however, be determined even at low temperatures, at least in principle.

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Table 1. Energies, crystal quantum numbers and Zeeman splitting factors.

J term	Centre of gravity (cm ⁻¹)	Energy of the component (cm ⁻¹)	Crystal quantum numbers			Splitting factor
			$\bar{\mu}$	ν	S	
⁵ I ₈		0.0	±1			-8.17
		7.7	0	0	0	
		27.8	±1			0.50
		29.5	2	1	0	
		59.5	2	0	1	
		108.9	2	1	0	
		182.1	±1			
		190.3	2	0	1	
		220.2	±1			
	229.3	0	1	1		
⁵ I ₅	11 217.9	11 189.3	2	0	1	
		11 189.7	±1			-1.5
		11 210.4	0	1	1	
		11 214.9	±1			3.1
		11 227.7	2	1	0	
		11 234.5	0	0	0	
		11 235.4	±1			0.6
	11 255.0	0	1	1		
⁵ F ₅	15 472.4	15 417.6	2	0	1	
		15 420.7	±1			0.15
		15 429.5	0	1	1	
		15 464.7	±1			4.9
		15 481.9	0	0	0	
		15 518.6	2	1	0	
		15 523.3	±1			-0.6
	15 531.3	0	1	1		
⁵ S ₂	18 406.8	18 395.8	2	0	1	-1.2
		18 404.4	0	0	0	-0.16
		18 406.4	±1			1.5
		18 420.8	2	1	0	0.9
⁵ F ₄	18 539.6	18 508.8	0	0	0	
		18 509.0	±1			-3.2
		18 540.2	0	1	1	-4.32
		18 546.1	±1			0.78
		18 548.4	0	0	0	4.43
		18 562.2	2	0	1	
		18 586.6	2	1	0	
⁵ F ₃	20 593.6	20 549.6	±1			-0.85
		20 558.2	2	1	0	
		20 615.9	±1			-1.75
		20 626.0	0	1	1	
		20 639.7	2	0	1	
⁵ F ₂	21 049.0	21 003.9	2	0	1	
		21 045.2	±1			
		21 053.3	0	0	0	
		21 097.6	2	1	0	
³ K ₈	21 344.7	21 299.4	0	0	0	-6.0
		21 301.1	0	1	1	

Table 1. (contd)

<i>J</i> term	Centre of gravity (cm^{-1})	Energy of the component (cm^{-1})	Crystal quantum numbers			Splitting factor
			$\bar{\mu}$	ν	<i>S</i>	
		21 314.1	0	0	0	-7.0 ^a
		21 314.1	0	1	1	
		21 317.7	± 1			-1.48
		21 322.7	± 1			3.35
		21 336.7	2	0	1	
		21 347.0	2	1	0	
		21 365.2	2	0	1	
		21 370.9	2	1	0	
		21 378.8	± 1			1.28
		21 384.9	0	0	0	
		21 394.4	± 1			-7.60
⁵ G ₆	22 108.8	21 997.7	0	0	0	
		21 999.2	± 1			1.7
		22 026.4	2	0	1	
		22 080.2	± 1			3.2
		22 103.0	0	1	1	
		22 124.2	2	1	0	-5.5
		22 140.5	2	0	1	5.5
		22 207.2	0	0	0	
		22 212.7	± 1			-0.7
		22 231.5	2	1	0	
⁵ F ₁	22 274.8	22 270.4	0	1	1	-0.23
		22 277.0	± 1			0.0
⁵ G ₅		23 872.6	2	1	0	
		23 876.0	± 1			-0.70
		23 887.1	0	1	1	
		23 923.6	± 1			4.75
		23 937.6	0	0	0	
		23 996.3	± 1			0.15
		24 015.7	0	1	1	
⁵ G ₄	25 813.2	25 757.5	2	1	0	
		25 769.9	2	0	1	
		25 798.9	0	0	0	-4.58
		25 798.9	0	1	1	4.76
		25 814.9	± 1			1.08
		25 849.0	± 1			-3.28
		25 865.9	0	0	0	
³ K ₇ ^b	26 128.5	26 113.6	± 1			-6.58
		26 118.1	0	1	1	-3.88
		26 118.1	0	0	0	
		26 121.2	± 1			-4.23
		26 125.9	2	1	0	-1.90
		26 127.5	2	0	1	2.10
		26 127.8	± 1			5.99
		26 138.6	± 1			0.88
		26 145.3	2	1	0	-5.68
		26 145.3	2	0	1	
		26 145.5	0	1	1	

Table 1. (contd)

<i>J</i> term	Centre of gravity (cm ⁻¹)	Energy of the component (cm ⁻¹)	Crystal quantum numbers			Splitting factor
			$\bar{\mu}$	ν	<i>S</i>	
³ H ₅	27 574.3	27 523.3	0	1	1	1.15
		27 527.3	±1			
		27 548.0	2	1	0	-1.45
		27 581.0	±1			
		27 581.0	2	0	1	
		27 586.8	0	0	0	
		27 616.2	0	1	1	4.6
		27 622.6	±1			
³ H ₆		27 700.9	±1			1.75
		27 702.6 ^b	0			1.7
		27 729.8 ^b	2			
		27 763.5	±1			
		27 777.8 ^b	2			
		27 819.9 ^b	2			0.07
		27 829.1	±1			
		27 834.0 ^b	0			

^a From energies in magnetic fields below 1 T (linear shift of degenerate singlets).

^b Energies of Ho³⁺ in HoAsO₄ (~1.5 cm⁻¹ higher than those in (Ho_{0.1},Y_{0.9})AsO₄).

2. Experimental details

Single crystals of (Ho_{0.1},Y_{0.9})AsO₄ and HoAsO₄, both of which crystallise in the zircon structure I4₁/amd, were grown by a flux method (Hintzmann and Müller-Vogt 1969). They had thicknesses between 0.1 and 1 mm. The spectroscopic equipment was the same as described in I. Circularly polarised spectra were observed in magnetic fields along *c* using a prism polariser and a Babinet–Soleil compensator (adjusted to a quarter of the mean measured wavelength) in front of the entrance slit of the spectrograph. Thereby the propagation vector was adjusted parallel to the crystallographic *c* axis.

3. Selection rules

The selection rules have already been given in I (tables 2 and 3). A magnetic field along *c* breaks all symmetry elements, apart from the fourfold inversion axis parallel to *c*, and therefore removes the selection rules except those in $\bar{\mu}$ and *M*. With the propagation vector along *c*, right- and left-circularly polarised transitions can be observed between the singlets and the doublet components $|+1\rangle$ and $|-1\rangle$, respectively, which are split by the magnetic field along *c*. With $k \perp c$, σ_+ as well as σ_- are observed as linearly polarised transitions.

4. Procedure of the analysis

Since the lowest crystal-field component of the ground term ⁵I₈ is a doublet (just as in

HoPO_4 ; Becker *et al* 1969), transitions to all excited crystal-field components are allowed from the ground state. Thus the energy of all components may be determined from measurements at low temperatures. Singlet states should appear as σ -polarised and doublet states as π -polarised transitions. The excited ground-term singlet levels can be assigned at higher temperatures by considering the number of π -polarised electric dipole transitions from such a component to an excited term and the number of magnetic dipole transitions to singlets of a term with $J = 7, 8$ or 9 . Subsequently one can obtain the symmetry types of the singlets of the excited terms from singlet–singlet transitions. Independently, the crystal quantum number $\bar{\mu}$ can be obtained from the splitting factor of the respective component in most of the investigated terms. In addition to that, the assignment of $\bar{\mu}$ can be proved by means of circularly polarised spectra taken with $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{k} \parallel \mathbf{c}$ at low temperatures: at 1.4 K and 2 T only the lower-lying doublet component $|+1\rangle$ with mainly $M = -7$ remains thermally populated. Singlets with $\bar{\mu} = 0$ can be observed as σ_+ -polarised electric dipole transitions from $|+1\rangle$, singlets with $\bar{\mu} = 2$ as σ_- -polarised transitions, so they can easily be separated in terms with $J \neq 7, 8$ and 9 , where no magnetic dipole transitions occur.

5. Experimental results

5.1. Tabular summary

The results of former studies of our group (Schwab 1973) and of our latest investigations are collected in table 1. The data given are those of $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$ if not indicated otherwise. The energies are related to the lowest component of the ground term 5I_8 . Its errors are $\pm 0.2 \text{ cm}^{-1}$ as a rule.

5.2. Discussion of the individual terms

In the following, some characteristics and peculiarities are described, which appeared in the analysis of the individual terms. Unequivocal results regarding energy, crystal quantum numbers and splitting factor are not discussed.

5.2.1. 5I_8 . Ten of the 13 crystal-field components were found. The splitting factor of the lowest doublet was determined from transitions to singlets of the terms 5F_4 , 5S_2 and 5G_4 .

5.2.2. 5I_5 . All crystal-field components were assigned from measurements at different temperatures.

5.2.3. 5F_5 . The lines are rather broad. The transition to the lowest-lying doublet appears slightly depolarised. Besides the assigned ones, additional satellite lines of lower intensity were observed.

5.2.4. 5S_2 . The singlet $|201\rangle$ was only noticed by a weak transition from $|+1\rangle$ with a magnetic field applied along \mathbf{c} but it showed the correct circular polarisation σ_- and a reasonable splitting factor. Its energy was extrapolated for $B \rightarrow 0$ from the measurements with applied magnetic field.

5.2.5. 5F_4 . The transition $|\pm 1\rangle \rightarrow |210\rangle = |M = 2\rangle_s$ is very weak, while $|\pm 1\rangle \rightarrow |201\rangle = |M = 2\rangle_a$ is rather intense. In order to reproduce the measured Zeeman energies accord-

ing to section 4 of I, one has to choose different g -factors for the singlets (1.3) and the doublets (1.2), respectively, which might be caused by J mixing. The g -factor of the singlets is bigger than the value obtained from the splitting factors given in table 1 (which are determined at 3 T) since these factors are reduced due to the quadratic shifts of the singlets.

5.2.6. 5F_3 . The transition between the ground doublet and the upper doublet of 5F_3 is very weak, although this doublet is not a pure $|M = \pm 3\rangle$ ($s = -1.75$).

5.2.7. 5F_2 . The Zeeman effect of this term was not investigated.

5.2.8. 3K_8 . The transitions are very sharp with linewidths of 5 cm^{-1} and less. Figure 1 shows the measured Zeeman shifts and the calculations, which are described in section 4 of I.

The highest doublet with $s = -7.6$ is excited from the ground doublet not by electric but by magnetic dipole radiation in accordance with the selection rules in M , which have to be met in the considered case of initial and final states being rather pure $|M = \pm 7\rangle$. The magnetic dipole transition to the doublet with $s = 1.28$ is much weaker than the corresponding electric dipole transition. If the involved crystal-field states were pure $|M\rangle$ states, one would not expect a magnetic dipole transition at all in this case according

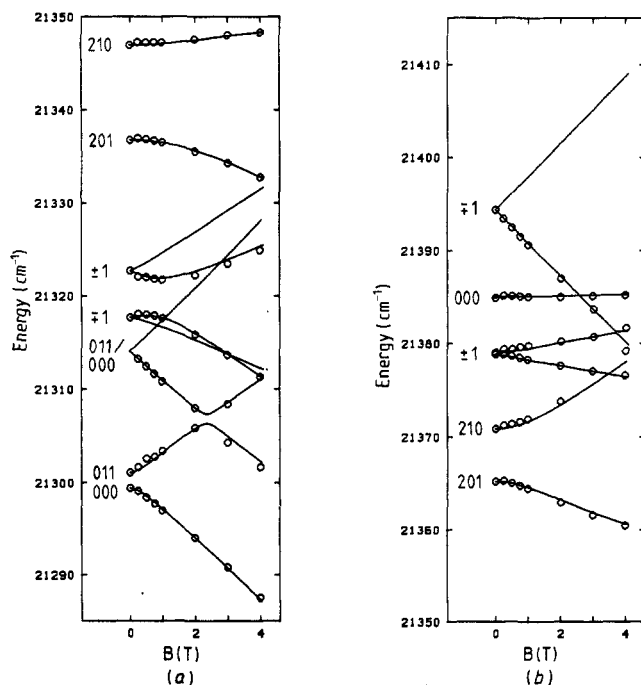


Figure 1. Comparison of measured (open circles) and calculated (full curves) Zeeman effect with $B \parallel c$ of the term 3K_8 in $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$ at 1.4 K. (a) Crystal-field components below 21350 cm^{-1} . (b) Crystal-field components above 21350 cm^{-1} . The labels are the crystal quantum numbers μ, ν and S of the components.

to the selection rules in M . The lower pair of doublets is only excited by electric dipole radiation. The small energy gap between them (5 cm^{-1}) leads to non-linear Zeeman shifts even below 1 T.

The singlet states form degenerate or quasi-degenerate pairs of equal $\bar{\mu}$ and M and different ν . The lowest $|000\rangle$ - $|011\rangle$ pair with a splitting factor $s = \pm 6$ appears with much higher intensity as an electric dipole transition than as a magnetic one. The middle $|000\rangle$ - $|011\rangle$ pair at $21\,314 \text{ cm}^{-1}$ is excited by electric as well as by magnetic dipole radiation in accordance with its splitting factor of ± 7 and the selection rules in M . As expected, the upper singlet $|011\rangle$ of this pair (mainly $M = +8$, perhaps also $M = +4$) does not appear in magnetic fields. Both pairs show approximately linear Zeeman splittings up to 2 T, where the middle components seem not to cross but to repel. The highest singlet $|000\rangle$ (mainly $M = 0$) has equal intensity in electric and magnetic dipole transition, indicating contributions $|M = \pm 8\rangle_s$. The singlets with $\bar{\mu} = 2$ also form pairs, but the respective gaps are wider than those of the $\bar{\mu} = 0$ pairs. The magnetic dipole transitions to the upper pair are more intense than those to the lower one.

5.2.9. 5G_6 . Figure 2 shows the spectrum at 1.4 K and 2 T along c in different polarisations. The overall splitting is remarkably large ($\sim 250 \text{ cm}^{-1}$). The transitions to the singlet states are clearly circularly polarised. The quantum numbers ν were determined from measurements at higher temperatures. The middle $|210\rangle$ - $|201\rangle$ pair with mainly $M = \pm 6$ (large symmetric Zeeman splitting) is framed by two outer singlets $|201\rangle$ and $|210\rangle$ (mainly $M = \pm 2$) with nearly the same centre of gravity. In order to get agreement between measured and calculated Zeeman energies, as in 5F_4 , the g -factor of the singlets had to be chosen different (1.25) from that for the doublets (1.4), possibly because of J mixing.

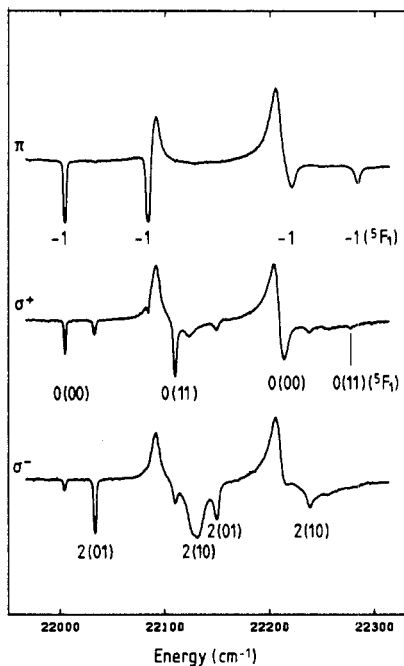


Figure 2. Transitions to the terms 5G_6 and 5F_1 in $(\text{Ho}_{0.1}\text{Y}_{0.9})\text{AsO}_4$ at $B = 2 \text{ T}$, $T = 1.4 \text{ K}$. The two emission lines belong to the spectrum of the Xe lamp used. In this and the following corresponding figures, the values of the crystal quantum numbers in parentheses cannot be determined from the shown measurements, where only transitions from the lowest component of the ground term are considered. They only follow from the high-temperature spectrum.

5.2.10. 5F_1 . The spectra of this term are presented in figure 2, together with those of 5G_6 . The observed transitions ${}^5I_8 \rightarrow {}^5F_1$ are not allowed ($|\Delta J| > 6$) unless the 5F_1 and/or the 5I_8 is mixed by the crystal field with other terms having appropriate J values. The transition $|\pm 1\rangle \rightarrow |011\rangle$ is very weak but shows the correct Zeeman shift ($s = 0$) and circular polarisation (σ_+).

5.2.11. 5G_5 . The transitions to the doublets are much more intense than those to the singlets. The doublet-doublet transitions also appear in the spectra taken with propagation vector along c , where they are forbidden. The singlet $|201\rangle$ ($= |M = \pm 2\rangle_a$) could not be observed, which cannot be explained by selection rules in M . Since the singlet $|210\rangle$ exhibits only a negligible Zeeman shift, the $|201\rangle$ cannot be very close to it.

5.2.12. 5G_4 . The degenerate singlet pair $|000\rangle - |011\rangle$ splits linearly with $B \parallel c$. The upper component (mainly $M = +4$) can only be observed above 2 T; the respective transition is very weak, as expected from the selection rules.

5.2.13. 3K_7 . The crystal-field splitting of this term is extremely small (32 cm^{-1}) and the transition lines are very sharp ($\leq 5 \text{ cm}^{-1}$). The quantum numbers $\bar{\mu}$ and parts of ν were assigned by means of circularly and linearly polarised measurements of the Zeeman effect at low temperatures. The spectra at $B = 2 \text{ T}$ and the Zeeman effect at 1.4 K are shown in figure 3. The quantum numbers ν , which did not result from these measure-

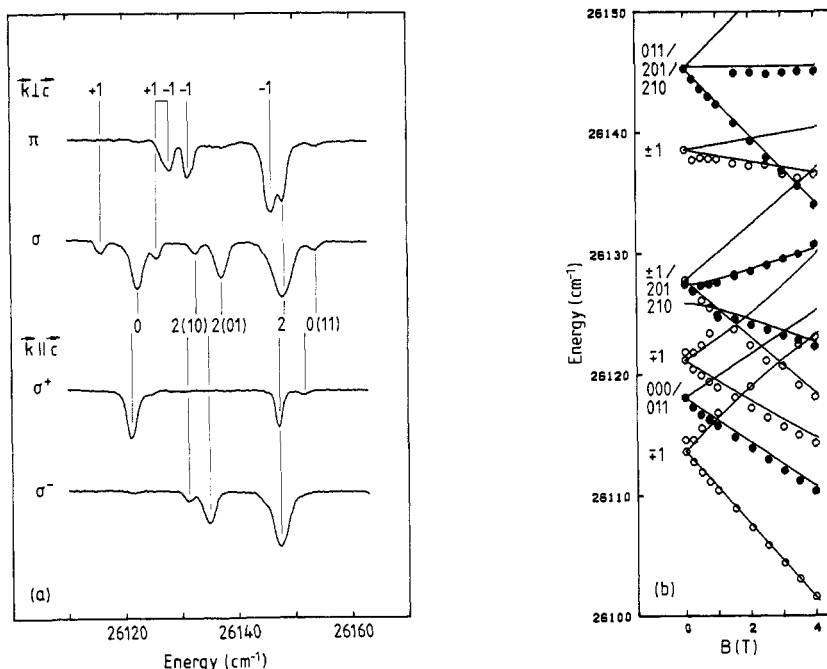


Figure 3. (a) Transitions to the term 3K_7 of Ho^{3+} in HoAsO_4 at $B = 2 \text{ T}$, $T = 1.4 \text{ K}$. The energy shift between the spectra with $k \perp c$ and $k \parallel c$ is caused by the different demagnetising factors of the probes. The reason for not indicating the crystal quantum numbers ν and S in some cases is that they are not defined for two singlets with the same $\bar{\mu}$ being (nearly) degenerate. (b) Comparison of measured (open circles, doublets; full circles, singlets) and calculated (full curves) Zeeman effect with $B \parallel c$ at $T = 1.4 \text{ K}$.

ments were determined at 5 K via transitions from the first excited ground-term singlet $|000\rangle$ at 9.4 cm^{-1} in pure HoAsO_4 . In the spectra at 1.4 K the components $| -1\rangle$ of all doublets are excited by π -polarised electric dipole radiation from the lower component $| +1\rangle$ of the ground doublet; the components $| +1\rangle$ of the lower two doublets also appear in $\sigma(k \perp c)$ as magnetic dipole transitions. Because of the hyperfine interaction, each doublet component is split into eight hyperfine components (Lausch *et al* 1975). At low temperatures, this leads to a small shift between the centres of gravity of the transitions to the components $| +1\rangle$ and $| -1\rangle$, respectively, caused by the thermal population of the hyperfine components and the different selection rules for electric and magnetic dipole transitions. This shift can be observed at $B = 0$ (see figure 3(b)). The upper two doublets with mainly $M = \pm 1$ and $M = \pm 5$, respectively, cannot be excited by magnetic dipole radiation according to the selection rules in M . The singlets form almost degenerate pairs of equal $\bar{\mu}$ and M and different ν except for the highest $|011\rangle$. Their Zeeman shifts are almost linear and the s values indicate approximately pure $|M\rangle$ states. The three singlets $|000\rangle$ and $|011\rangle$, which only consist of $|M = 0\rangle$ and $|M = \pm 4\rangle$, should not be excited by magnetic dipole radiation; they are allowed only in $\sigma(k \parallel c)$ or $\sigma(k \perp c)$. The upper singlet of the lower $|000\rangle$ - $|011\rangle$ pair (almost pure $M = +4$) does not appear with $B \parallel c$ since the transition is not allowed by the selection rules in M . The low intensity of the σ transition to the highest singlet $|011\rangle$ (mainly $M = 0$) can be explained in the same way; the corresponding π transition could be induced by a small admixture of the nearby $|M = \pm 1\rangle$. The singlets of the lower $|201\rangle$ - $|210\rangle$ pair ($s = -1.9$ and 2.1) are only observed as electric dipole transitions in σ_- and $\sigma(k \perp c)$, which confirms that they are almost pure $|M = \pm 2\rangle$ states. The upper pair $|201\rangle$ - $|210\rangle$ was assigned to a transition that appeared in all polarisations but with slightly less intensity in σ_+ and π . This indicates a singlet that may be excited by electric as well as by magnetic dipole radiation, i.e. a

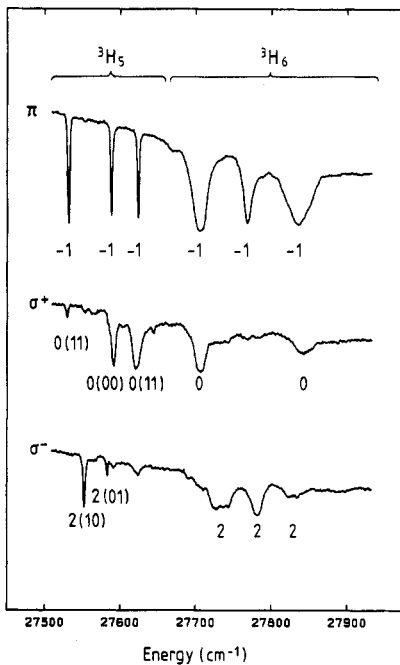


Figure 4. Transitions to the terms ${}^3\text{H}_5$ and ${}^3\text{H}_6$ at $B = 2\text{ T}$, $T = 1.4\text{ K}$: π polarisation, $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$; σ polarisation, HoAsO_4 . In the term ${}^3\text{H}_6$ the crystal quantum numbers ν and S were not determined.

singlet $\bar{\mu} = 2$ with $M = \pm 6$, which is proved by the splitting factor of this singlet ($s = -5.68$). The linear shift even at small field strengths (below 1 T) required a degenerate second singlet $\bar{\mu} = 2$, $M = \pm 6$ with the alternative value of ν . It cannot be observed in accordance with the selection rules in M .

5.2.14. 3H_5 . Figure 4 shows the spectrum of the terms 3H_5 and 3H_6 at $B = 2$ T, $T = 1.4$ K. All singlets appeared with the correct circular polarisation but with much lower intensity than the doublets. The transitions to $|201\rangle = |M = \pm 2\rangle_a$ and $|011\rangle$ were especially weak. The splitting factors of the doublets were calculated assuming a linear Zeeman shift of the components, although the splitting is not linear. The reason is that an adjustment as described in section 4 of I was not possible since the 'best fits' (which did not reproduce the measurements very well) were obtained with badly differing splitting factors and g -factors. This indicates that J mixing with other terms, mainly the neighbouring 3H_6 , cannot be neglected.

5.2.15. 3H_6 . In contrast to the immediately neighbouring 3H_5 , the transitions to 3H_6 observed at low temperatures were very broad and weak and the lines showed strange shapes (figure 4). Even from the spectrum of the undiluted HoAsO_4 , only a part of the singlets could be determined. Two singlets, one with $\bar{\mu} = 0$ and one with $\bar{\mu} = 2$, were not found at all. The quantum numbers ν were not determined. The doublets already appeared in the spectrum of the diluted $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$. Besides the lines assigned to electronic transitions, further lines of unknown origin were observed.

6. Conclusions

The spectrum of Ho^{3+} in $(\text{Ho}_{0.1}, \text{Y}_{0.9})\text{AsO}_4$ and HoAsO_4 was investigated from 11 000 to 28 000 cm^{-1} , performing measurements at various temperatures and using linear and circular polarisation with the magnetic field along the c axis at low temperatures. It was possible to analyse the spectrum completely and to assign the energies, the symmetry types and the Zeeman behaviour of almost all crystal-field components with great accuracy and reliability.

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