Absorption spectra and Zeeman effect of the trivalent holmium ion in compounds with tetragonal zircon structure. III. $HoPO_4$

Absorption spectra and Zeeman effect of the trivalent holmium ion in compounds with tetragonal zircon structure: III. HoPO$_4$

M Enderle†, B Pilawa and H G Kahle

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

Abstract. The optical absorption spectrum of the transitions $^5I_8 \rightarrow {}^3K_7$ and $^5I_8 \rightarrow {}^3H_6$ of Ho^{3+} in HoPO$_4$ and its Zeeman effect in magnetic fields along the crystal c axis were studied at temperatures below 5 K. The quantum numbers $\bar{\mu}$ of the excited terms $^3K_7$ and $^3H_6$ were determined using linearly and circularly polarised transitions from the ground state. A short comparison of the experimental results for Ho^{3+} in (Ho$_{0.1}$,Y$_{0.9}$)VO$_4$, (Ho$_{0.1}$,Y$_{0.9}$)AsO$_4$ and HoPO$_4$ shows striking similarities but also remarkable differences.

1. Introduction

An almost complete analysis of Ho^{3+} in (Ho$_{0.1}$,Y$_{0.9}$)PO$_4$ in the range from 15 400 to 27 600 cm^{-1} has already been given by Becker *et al* (1969), who also investigated the Zeeman effect and the line intensities and calculated crystal-field parameters (Becker 1970, 1971). In order to complete the experimental investigations of Ho^{3+} in crystals with the tetragonal point symmetry $\overline{4}2m$ of the rare-earth site, the former analysis was checked and extended to the excited terms $^3K_7$ and $^3H_6$ using Ho^{3+} in HoPO$_4$. The possible symmetry types of crystal-field states and their respective basic states (composed of free-ion eigenfunctions) as well as the selection rules needed for the analysis are given in Enderle *et al* (1990a, to be referred to as I). In HoPO$_4$, Ho^{3+} has a doublet ground state with mainly $|M = \pm 7\rangle$ (Becker *et al* 1969) just as in (Ho$_{0.1}$,Y$_{0.9}$)AsO$_4$; thus the analysis could be performed as described in Enderle *et al* (1990b, to be referred to as II).

2. Experimental details

Single crystals of HoPO$_4$, which crystallise in the zircon structure I4$_1$/amd, were grown by a flux method (Hintzmann and Müller-Vogt 1969) and had thicknesses between 0.1 and 1 mm. The absorption spectrum and its Zeeman effect in fields along the crystal c axis were investigated with linear and circular polarisation at temperatures below 5 K. The experimental equipment was the same as described in I and II.

† Present address: Institut für Physik, Universität Mainz, D-6500 Mainz, Federal Republic of Germany.

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	
$^3K_7$	26 164.2	26 144.1	±1			−6.5
		26 153.0	0	1	1	−3.92
		26 153.0	0	0	0	
		26 156.1	±1			−3.3
		26 159.8	2	1	0	−1.43
		26 162.9	±1			5.0
		26 166.3	2	0	1	
		26 177.4	±1			0.9
		26 182.2	2	1	0	−5.6
		26 182.2	2	0	1	
		26 185.4	0	1	1	
$^3H_6$		27 720.1	2			
		27 739.0	2			
		27 745.0	±1			1.8
		27 763.1	0			
		27 781.1	0			
		27 838.6	2			
		27 862.4	±1			−0.6
		27 872.4	0			

3. Experimental results

3.1. Tabular summary of the findings

The measured energies, splitting factors and crystal quantum numbers, determined in undiluted $HoPO_4$, are given in table 1. The energies are related to the lowest component of the ground term $^5I_8$. As in the arsenate compounds, the transition energies of the undiluted $HoPO_4$ are shifted by 1.0 to 1.5 cm⁻¹ to higher values with respect to those of probes diluted with Y^{3+}.

3.2. Discussion of the individual terms

3.2.1. $^3K_7$. Figure 1 shows the spectrum and the Zeeman effect of the term at 1.4 K. The crystal-field splitting is extremely small (41 cm⁻¹) and the transitions are very sharp (<5 cm⁻¹). The upper two doublets are only observed as electric dipole transitions from the ground-state doublet (mainly $|M = \pm7\rangle$). This is in agreement with their splitting factors 5.0 and 0.9 and the selection rules $|\Delta M| \leq 6$ for electric and $|\Delta M| \leq 1$ for magnetic dipole radiation. The lowest doublet with the splitting factor −6.5 mainly consists of $|M = \pm7\rangle$; it can only be excited by magnetic dipole radiation ($\Delta M = 0$). The neighbouring doublet with the splitting factor −3.3 is also excited by magnetic but not by electric dipole radiation. This indicates contributions of $|M = \pm7\rangle$, since a pure $|M = \pm3\rangle$ should be excited neither by electric nor by magnetic dipole radiation if the selection rules in M hold. The transition to this doublet also appeared with $k \parallel c$ in σ_+ polarisation and, less intense, in σ_-. This is indicated by the broken line in figure 1(a). A possible
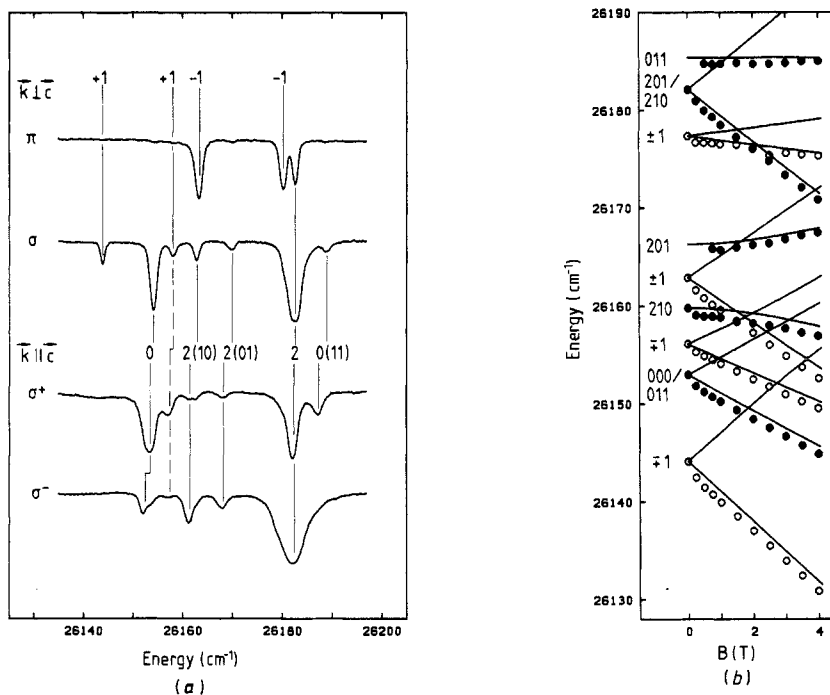
Figure 1. (*a*) Transitions to the term $^3K_7$ of Ho^{3+} in $HoPO_4$ at $B = 1$ T, $T = 1.4$ K. The energy shift between the spectra with $k \perp c$ and $k \parallel c$ is caused by the different demagnetising factors of the probes. For the meaning of the broken line and the crystal quantum numbers in parentheses, see the text. For the transitions indicated by $\bar{\mu}$ alone, two singlets are (nearly) degenerate so that ν and S are not defined. (*b*) Comparison of measured (open circles, doublets; full circles, singlets) and calculated (full curves) Zeeman effect with $B \parallel c$ at 1.4 K.

explanation is monoclinic distortions of the surroundings of the ion caused by thermal vibration of the lattice. They lead to admixtures of the nearby singlets with $M = \pm 4$ and $M = \pm 2$ to the doublet. The linear Zeeman shift (-3.92) of the singlet at 26 153.0 cm^{-1} requires the second singlet with $\bar{\mu} = 0$ and $M = +4$ to be degenerate. It cannot be observed in accordance with the selection rules in M. The other singlets except the uppermost $|011\rangle$ also form pairs of equal $\bar{\mu}$ and $|M|$. Their Zeeman shifts are almost linear and the s values point to approximately pure $|M\rangle$ states. In accordance with the selection rules in M, the lower $|201\rangle$–$|210\rangle$ pair with mainly $|M = \pm 2\rangle$ appears with higher intensity as electric than as magnetic dipole transition, while the singlet with $\bar{\mu} = 2$ and $|M = -6\rangle$ $(s = -5.6)$ is observed with high intensity in magnetic as well as in electric dipole radiation. Again the second degenerate singlet with $\bar{\mu} = 2$ and $|M = +6\rangle$ is required by the linear Zeeman shift but not observable, in agreement with the selection rules in M. Since the crystal-field splitting and the Zeeman effect are very similar to those of Ho^{3+} in $YAsO_4$, the second quantum numbers ν of the split lower $|201\rangle$–$|210\rangle$ pair were assigned by comparison with the level scheme of Ho^{3+} in $YAsO_4$, where ν could easily be determined by transitions from the first excited $|000\rangle$ of the $^5I_8$ at about 9 cm^{-1}.

3.2.2. $^3H_6$. This term could not be assigned completely; a doublet and a singlet with $\bar{\mu} = 2$ were not found. The quantum numbers ν were not determined. The transitions are

very broad and weak, not strongly polarised and show strange lineshapes. The doublet–singlet transitions appeared with much higher intensity than the doublet–doublet transitions; thus for the σ spectra a thinner crystal was used. The singlets could be assigned by comparing the intensities of the σ_+- and σ_--polarised spectra. The crossing of the components of $^3H_5$ and $^3H_6$ as postulated by Becker *et al* (1969) (they assumed a singlet of the $^3H_6$ to be quasi-degenerate with the upper doublet of the $^3H_5$) could not be confirmed. The doublet splitting factors are not very certain because of the large linewidths.

4. Comparison of the three compounds

Comparing the level schemes of Ho^{3+} in the three host lattices, YVO_4, $YAsO_4$ and $HoPO_4$, one notices great similarities in the crystal-field splittings and even in the Zeeman splitting factors for the terms $^5G_{4,5,6}$ and $^3K_{7,8}$, while larger differences are observed for $^5F_{3,4,5}$ and $^5I_8$. In the following the characteristic features of the investigated terms will be summarised, beginning with those terms bearing the greatest resemblance.

The components of the $^5G_4$ have rather pure M values, the singlets $|201\rangle$ and $|210\rangle$ are closely neighbouring, and $|000\rangle$ and $|011\rangle$ with $M = \pm4$ form a quasi-degenerate pair in all three lattices.

The $^3K_8$ also shows almost pure M states; the order of the doublet states is $M = \pm3$, ±5, ±1, ±7 with rising energy, and the two lower ones are widely separated from the higher ones. The singlets begin with an $M = \pm4$ pair followed by a quasi-degenerate $M = \pm8$ pair. The two $|201\rangle$ and the two $|210\rangle$ lie between the two doublet groups and the uppermost state $|000\rangle$ has mainly $M = 0$.

Remarkably small is the splitting of the $^3K_7$, which comes to about $40\ cm^{-1}$ in all three lattices. The states are almost pure M states. The doublets have $M = \pm7$, ±3, ±5, ±1 with rising energy; the singlets with $\bar{\mu} = 0$ form a degenerate $M = \pm4$ pair as the lowest components of the term while the $|M = 0\rangle$ is the uppermost. The states with $M = \pm2$ are slightly separated and have lower energy than the quasi-degenerate pair with $M = \pm6$.

The components of the $^5G_5$ consist of mixed M states; nevertheless, the splittings in the various host lattices resemble each other. The doublets have (with rising energy) a small negative, a large positive and a quasi-zero splitting factor, indicating similar composition of the states. The two singlets with $\bar{\mu} = 2$ as well as those with $\bar{\mu} = 0$ are widely separated, but the energetic order of the singlets is the same.

In $^5G_6$, too, the crystal-field states show the same order in spite of a wide splitting of the whole term (240 to $290\ cm^{-1}$) as well as of subgroups with the same quantum number ν. The Zeeman splittings differ slightly, but common to all are positive doublet splitting factors of the two lower doublets and a small negative one for the upper doublet. The splittings of the lower ones in $YAsO_4$ and YVO_4 are just exchanged.

Similarly the energetic order of the states in $^3H_5$ is the same in all three substances but the splitting factors differ, the signs and approximate values being the same in $YAsO_4$ and YVO_4 while $HoPO_4$ shows another behaviour.

In $^5F_3$ the splitting factors of the former two are again similar, while $HoPO_4$ has considerably differing values. The order of $|011\rangle$ and $|201\rangle$ is reversed from $YAsO_4$ to YVO_4.

In $^5F_4$ the splitting factors of $HoPO_4$ are completely different from those in $YAsO_4$ and YVO_4, which still resemble each other. Further, the upper $|000\rangle$–$|011\rangle$ pair in

$HoPO_4$ is widely separated from the lower $|000\rangle$ while in $YAsO_4$ and YVO_4 the distance is much smaller.

The energetic order of the components of $^5F_5$ is the same in all three host lattices but the Zeeman splitting factors of the doublets show no similarity at all, indicating completely different composition of the crystal-field states.

Finally, the lowest six states of the ground term $^5I_8$ have the same symmetry types but their order is different. $HoPO_4$ and Ho^{3+} in $YAsO_4$ have the same lowest state, even in the splitting factor, but the order of the singlets is changed. Ho^{3+} in YVO_4 and Ho^{3+} in $YAsO_4$ show similar singlet order but the two lower doublets have reversed splitting factors.

5. Outlook

The similarities in the features of Ho^{3+} in the three host lattices on the one hand and their differences on the other hand require explanation. This will be given in more detailed form in a forthcoming paper of one of the authors (Pilawa 1990), together with an analysis of the crystal-field splittings by improved theoretical models. Here only some ideas will be presented.

The three host lattices are isostructural, and the distances and the bond angles to the neighbours of a central Ho^{3+} ion differ only slightly (Wyckoff 1965). Expanding the crystal-field interaction for each J term in multipole components (k, q) by using spherical harmonics $Y_q^{(k)}$ or tensor operators $C_q^{(k)}$ ($k = 2, 4, 6, q = 0, \pm 4$), one can expect comparable strengths of the effective components (k, q) in the three lattices. This is almost true for most of the components (k, q) with one important exception, and that is the quadrupole component $(2, 0)$, which is much different in the three cases. Thus the question whether the individual term shows similarities or differences in the three lattices is decided by the relative size of the effective quadrupole component. If the influence of this contribution on the crystal-field splitting of a term is small in all three host lattices, the features of this term are similar. This is the case for the terms $^5G_{4,5,6}$ and $^3K_{7,8}$. If, on the contrary, the influence of the quadrupole for a term is not negligible in any of the three salts, the characteristics of this term are different. This holds, for example, for the terms ^5F.

For the terms $^3K_8$, $^3K_7$ and $^5G_4$ the crystal-field states proved to be almost pure $|M\rangle$ states. This indicates that the effective crystal-field components (k, q) with $q \neq 0$ are small compared with those with $q = 0$, bearing in mind that the mixing of the $|M\rangle$ states is caused by the components with $q \neq 0$. These terms experience a predominantly cylindrical symmetry. The other terms clearly perceive the entire influence of the tetragonal zircon structure.

References

Becker P J 1970 *Phys. Status Solidi* **38** 379–84
—— 1971 *Phys. Status Solidi* b **43** 583–90
Becker P J, Kahle H G and Kuse D 1969 *Phys. Status Solidi* **36** 695–704
Enderle M, Pilawa B, Schlaphof W and Kahle H G 1990a *J. Phys.: Condens. Matter* **2** 4685
Enderle M, Pilawa B, Schwab M and Kahle H G 1990b *J. Phys.: Condens. Matter* **2** 4701
Hintzmann W and Müller-Vogt G 1969 *J. Crystal Growth* **5** 274–8
Pilawa B 1990 *J. Phys.: Condens. Matter* at press
Wyckoff R W G 1965 *Crystal Structures* vol 3 (New York: Interscience) p 15–18