

Spectroscopy and crystal-field analysis of $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 255402

(<http://iopscience.iop.org/0953-8984/21/25/255402>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 20:14

Please note that [terms and conditions apply](#).

Spectroscopy and crystal-field analysis of $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$

Marjorie Mujaji^{1,3} and Jon-Paul R Wells²

¹ School of Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa

² Department of Physics and Astronomy, University of Canterbury, PB4800, Christchurch 8020, New Zealand

E-mail: Marjorie.Mujaji@wits.ac.za

Received 20 March 2009, in final form 18 May 2009

Published 1 June 2009

Online at stacks.iop.org/JPhysCM/21/255402

Abstract

A laser excitation and infrared absorption study of the single C_{4v} symmetry centre in $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$ is presented. Comparatively weak upconversion fluorescence is observed and can be attributed to an energy-transfer excitation mechanism proposed previously. Fifty one crystal-field energy levels for seven Ho^{3+} multiplets ($^5\text{I}_8$, $^5\text{I}_7$, $^5\text{I}_6$, $^5\text{F}_5$, $^5\text{S}_2$, $^5\text{F}_4$ and $^5\text{F}_3$) have been deduced. A crystal-field analysis has been performed, with excellent agreement found between experimental and calculated energy levels.

1. Introduction

The unit cell of KY_3F_{10} is a $2 \times 2 \times 2$ face centred cubic structure in which $[\text{KY}_3\text{F}_8]^{2+}$ and $[\text{KY}_3\text{F}_{12}]^{2-}$ ionic complexes alternate along the cube axes. Y^{3+} ions occupy cube face centre positions which coincide with the vertices of regular octahedron. The K^+ ions are at the cube corners and the F^- ions are positioned within the K^+ cubes, along the face and edge centres of the $[\text{KY}_3\text{F}_8]^{2+}$ and $[\text{KY}_3\text{F}_{12}]^{2-}$ complexes, respectively. The lattice constant is 11.544 Å at room temperature [1, 2].

The lattice is transparent over a wide region, thermally and chemically stable and is isotropic [1–3]. As such it is an ideal host for optical studies and laser applications [2, 3]. Trivalent rare-earth ions (RE^{3+}) introduced into the lattice replace the Y^{3+} ions, resulting in a C_{4v} symmetry centre [2]. RE^{3+} ions for which the most comprehensive studies have been reported in KY_3F_{10} crystals include Pr^{3+} [4], Sm^{3+} [5], Eu^{3+} [6–8], Er^{3+} [9–11], Tm^{3+} [12] and Yb^{3+} [13–15].

Laser excitation studies of both $\text{KY}_3\text{F}_{10}:\text{Pr}^{3+}$ and $\text{KY}_3\text{F}_{10}:\text{Sm}^{3+}$ have been performed. For Pr^{3+} the energy levels up to the $^3\text{P}_0$ multiplet were assigned [4] whilst for Sm^{3+} most energy levels up to $^4\text{G}_{5/2}$ were deduced [5]. KY_3F_{10} doped with samarium is complicated by the co-existence of the divalent species which are speculated to be present due to fluorine vacancies. For both Pr^{3+} and Sm^{3+} crystal-field analyses yield good agreement to the observed energy levels. However to adequately treat the Pr^{3+} $^1\text{D}_2$ multiplet, a spin

correlated crystal-field approach was required. One of the earlier works on rare-earth doped KY_3F_{10} comprehensively treated the Eu^{3+} ion [6–8] with crystal-field and Judd–Ofelt analyses used as a basis for an analysis of radiative lifetimes and non-radiative relaxation. Likewise several studies have been performed utilizing the erbium ion [9–11] and these have tended to focus upon analysis of the crystal-field levels of Er^{3+} using subtly different experimental techniques. Absorption and emission studies of $\text{KY}_3\text{F}_{10}:\text{Tm}^{3+}$ are reported [12]; crystal-field energy levels for the multiplets from $^3\text{H}_6$ to $^1\text{D}_2$ are presented together with the corresponding calculated levels and lifetimes for some of the multiplets. For $\text{KY}_3\text{F}_{10}:\text{Yb}^{3+}$, the optical spectroscopy and some laser parameters are presented in [13] whilst electron paramagnetic resonance studies are presented in [14, 15].

Further to this, intensity and lifetime studies are reported for Eu^{3+} and Tb^{3+} ions [16] while energy-transfer processes have been investigated in KY_3F_{10} crystals co-doped with heterogeneous pairs such as $\text{Yb}^{3+}:\text{Dy}^{3+}$ and $\text{Tm}^{3+}:\text{Dy}^{3+}$ [17] as well as $\text{Yb}^{3+}:\text{Tm}^{3+}$ [18]. Laser action has been achieved in KY_3F_{10} crystals singly doped with Tm^{3+} (at a wavelength of 1.85 μm) [19], Pr^{3+} (at 644.5 nm) [20] as well as co-doped with Yb^{3+} and Tm^{3+} ions (at wavelengths of 1.5 μm , 2.3 μm , 450 nm and 480 nm) [18, 21], for example.

In this work, we report results from a laser selective excitation and infrared absorption study of a KY_3F_{10} crystal containing 0.1 mol% of Ho^{3+} ions. From absorption, fluorescence and excitation spectra obtained in the temperature range 8–77 K, the crystal-field energy levels for seven of the

³ Author to whom any correspondence should be addressed.

Ho^{3+} multiplets have been deduced. Corresponding energy level positions from a crystal-field fitting routine are included, with good agreement.

For KY_3F_{10} doped with Ho^{3+} , it appears that only EPR studies and some levels of the ground ($^5\text{I}_8$) multiplet are reported in the literature [22, 23]. $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$ is interesting since in addition to being a high symmetry system it has a close-lying singlet pair as its $^5\text{I}_8$ ground state in a similar fashion to $\text{CaF}_2:\text{Ho}^{3+}$ [24, 25]. This is partly our motivation in presenting this fundamental study since reliable and comprehensive wavefunctions for the crystal-field levels are required in order to do justice to any studies of the hyperfine structure. In the ground state this arises from the pseudo-quadrupole (second order magnetic-dipole) interaction between the $Z_1\gamma_1$ and $Z_2\gamma_2$ states which can be connected by the J_z operator since it transforms as a γ_2 under C_{4v} symmetry. The system also has potential as a laser material.

2. Experimental details

Crystals of KY_3F_{10} doped with trivalent holmium at a concentration of 0.1 mol% were prepared using the Bridgman–Stockbarger technique in a two zone furnace. The start materials were mixed in stoichiometric quantities before being placed into graphite crucibles in the furnace. After evacuation to better than 10^{-6} mbar, the crystal growth was performed under a slight positive pressure of purified argon gas to minimize evaporative losses. The as grown crystals were clear and of excellent optical quality.

Optical absorption and laser selective excitation studies were carried out. For both experiments, the sample was mounted onto a copper sample holder which was attached to the cold finger of a Janis CCS-150 closed cycle refrigeration cryostat. A thin layer of Apiezon N grease was applied for good thermal contact. The temperature of the sample as detected by a silicon diode was regulated by a LakeShore 331 temperature controller.

For absorption measurements, the sample was illuminated by a 150 W tungsten filament lamp and light transmitted through the 2 mm length of crystal focused onto the entrance slit of a Jarrell-Ash 1 m double Czerny–Turner 25–100 spectrometer. The spectrometer is equipped with a thermo-electrically cooled Burle C31034-A02 photomultiplier tube, an EG&G Princeton Applied Research model 1121A preamplifier/discriminator and model 1112 photon counter. Spectra over the ranges 15 760–15 360 cm^{-1} and 18 700–18 400 cm^{-1} which cover absorption transitions from the ground $^5\text{I}_8$ multiplet to the $^5\text{F}_5$ and $^5\text{S}_2$; $^5\text{F}_4$ multiplets of Ho^{3+} , respectively, were recorded at 8 K.

For selective laser excitation measurements, the 514.5 nm laser radiation from a Spectra-Physics 171 argon ion laser was used to pump a Coherent 599 dye laser. The DCM dye used emits laser radiation in the region which covers absorption transitions to the $^5\text{F}_5$ multiplet of Ho^{3+} . The dye laser output was calibrated using a Coherent WaveMate wavelength meter. With the dye laser wavelength set to coincide with a particular absorption transition, fluorescence was collected using a 90° geometry and focused onto the entrance slits of the

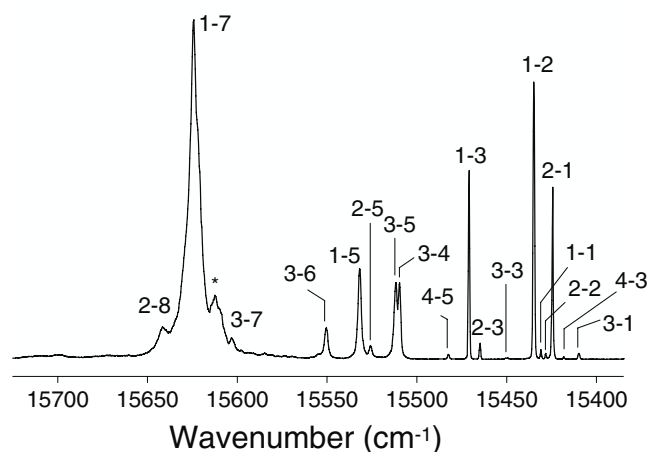


Figure 1. 10 K laser excitation spectrum of the $Z \rightarrow D$ transitions of the C_{4v} symmetry centre in $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$ crystals. Transitions are identified by numerical labels for the crystal-field energy levels giving rise to the transition; the first label identifies the originating level in the ground (Z) multiplet while the second label is the terminating level in the D multiplet. Transition marked * is unassigned.

same spectrometer as used for absorption measurements. The signal detection set-up was as for absorption measurements. The sample temperature was varied between 8 and 77 K for fluorescence and excitation spectral measurements.

Infrared absorption was performed at 0.25 cm^{-1} resolution with a Bio-Rad FTS-45 Fourier Transform infrared spectrometer equipped with a closed cycle cryostat and temperature controller.

3. Results

Trivalent holmium has a $4f^{10}$ configuration. As such its ground multiplet is $^5\text{I}_8$ and its first and second excited multiplets are $^5\text{I}_7$ and $^5\text{I}_6$ respectively. We adopt the notation of a letter plus a numerical subscript for labelling the various LSJ multiplets and their crystal-field levels. That is, the ground multiplet is labelled Z with the ground state labelled Z_1 and the first excited multiplet is labelled Y. Thereafter, as the multiplets ascend in energy, we follow the letters of the alphabet as embodied in the standard Dieke diagram [26]. Thus the $^5\text{I}_6$ is labelled A, $^5\text{I}_5$ is labelled B and so on.

The crystal-field energy levels of Ho^{3+} transform as one of the irreps γ_1 to γ_5 of the C_{4v} symmetry point group. The number of crystal-field energy levels in a given multiplet and the expected inter-multiplet transitions can be readily determined from the electric- and magnetic-dipole selection rules via the tables of Koster *et al* [27] and Butler [28].

3.1. Optical absorption, laser excitation and fluorescence

Although the absorption transitions of Ho^{3+} doped KY_3F_{10} recorded in the 15 500 and 18 500 cm^{-1} regions were weak due to the small size of the sample available, that for the red region showed the same transitions as in the excitation spectrum (figure 1). Selective excitation of each of the $^5\text{I}_8(\text{Z}) \rightarrow ^5\text{F}_5(\text{D})$

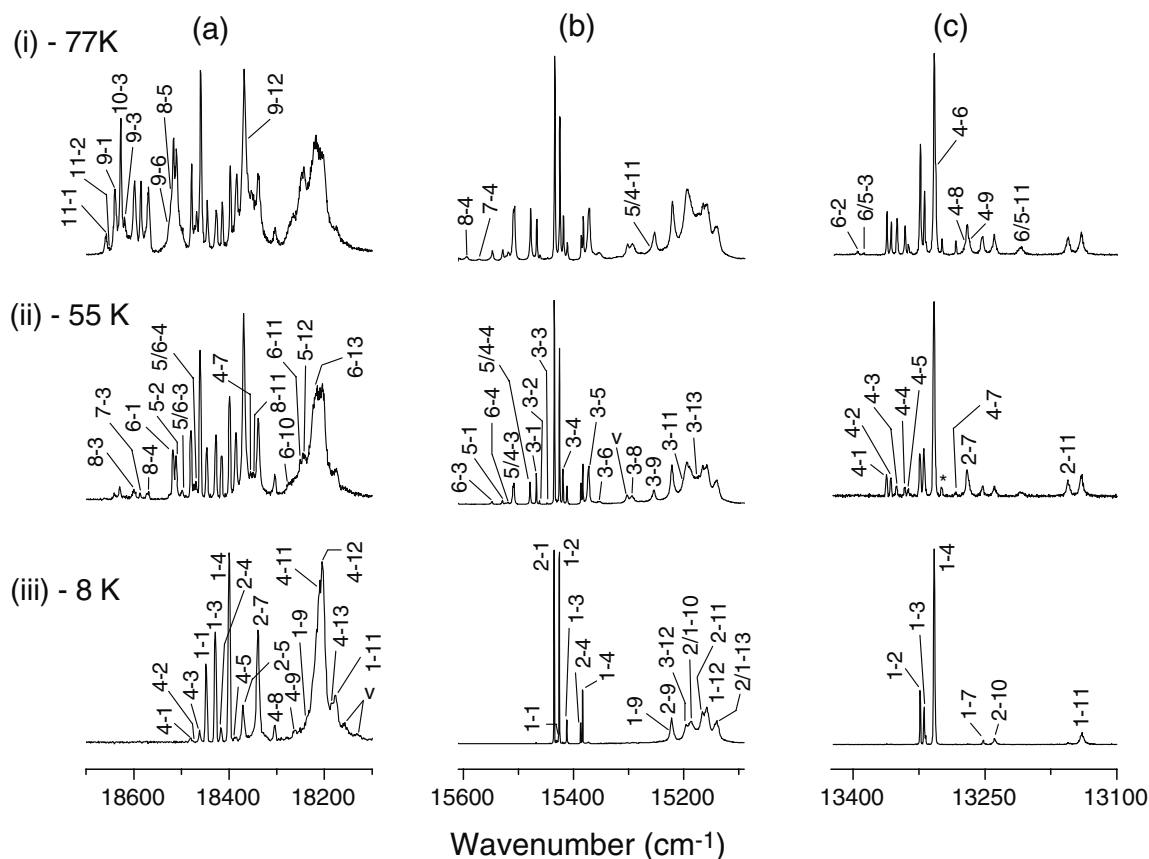


Figure 2. Fluorescence spectra of the (a) $E \rightarrow Z$, (b) $D \rightarrow Z$ and (c) $E \rightarrow Y$ transitions of the C_{4v} symmetry centre in $KY_3F_{10}:0.1\%Ho^{3+}$ crystals, as measured at (i) 77 K, (ii) 55 K and (iii) 8 K. The numerical labels identify the crystal-field energy levels involved; the first label identifies the originating E or D multiplet crystal-field energy level and the second identifies the terminating energy level in the Z or Y multiplet. ν identifies vibronic transitions while the transition marked * is unassigned. Only new transitions (i.e. absent or weaker at the lower temperature) are indicated in the 55 and 77 K spectra.

transitions yielded the same fluorescence spectra, confirming the presence of a single Ho^{3+} site. Representative fluorescence spectra recorded at 8, 55 and 77 K are presented in figure 2.

At 8 K, all the direct fluorescence transitions present (figure 2(b) (iii)) are consistent with a D_1-D_2 energy level separation of 3.5 cm^{-1} . The small D_4-D_5 splitting of 2.0 cm^{-1} is clearly visible in the excitation spectrum (figure 1) as well as the direct fluorescence transitions to Z_3 , at both 55 and 77 K (figure 2(b) (ii) and (i) respectively).

Upconversion fluorescence from the 5S_2 and 5F_4 (E) multiplets (figures 2(a) and (c)) was weak and that from the 5F_3 (F) multiplet was significantly weaker, hence the F levels are less accurately determined. At 8 K, $E \rightarrow Z$ fluorescence transitions emanate from the $E_1\gamma_1$, $E_2\gamma_3$ and $E_4\gamma_5$ levels which are spread over $\sim 33\text{ cm}^{-1}$, while transitions to the first excited multiplet (Y) are mainly from $E_1\gamma_1$. Transitions from higher-lying excited multiplet levels become apparent above 20 K. A careful search from $21\,000\text{ cm}^{-1}$ up to $30\,000\text{ cm}^{-1}$ did not reveal any other fluorescence transitions. As proposed in other fluorite hosts [29], interaction of close-lying Ho^{3+} ions leads to population of the 5F_2 ; 3K_8 (G, H) multiplets at $\sim 22\,000\text{ cm}^{-1}$. The phonon cut-off frequency of $\sim 500\text{ cm}^{-1}$ [30] allows non-radiative decay to the F and E multiplets at $\sim 20\,500$ and $\sim 18\,500\text{ cm}^{-1}$, respectively, from where radiative decay then occurs, resulting in the observed upconversion fluorescence.

Higher-lying levels of the D and E multiplets deduced from absorption spectra were confirmed from fluorescence spectra recorded at higher temperatures of up to 77 K. Selection rules allowed fluorescence transitions from higher-lying excited multiplet levels to the Z and Y multiplet levels enabled identification of several of the lower multiplet levels. Energy levels deduced for the Z, Y, D, E and F multiplets are presented in table 1. The Z_1-Z_2 energy level separation of 5.8 cm^{-1} obtained here is in agreement with that reported from EPR measurements [22, 23]. Electron-phonon coupling is evident through the presence of vibronic transitions associated with phonons of energies in the $142-496\text{ cm}^{-1}$ range [30].

3.2. Infrared absorption

The infrared absorption spectra of a $KY_3F_{10}:0.1\text{ mol}\% Ho^{3+}$ sample of thickness 1 mm are shown in figure 3. From the energy levels derived from fluorescence measurements, and utilizing the results of preliminary crystal-field calculations, we know that the ground state consists of a singlet state of γ_1 symmetry with a nearby γ_2 state only 5.8 cm^{-1} higher in energy. It might therefore be expected that transitions to states of γ_3 and γ_4 symmetry will not be observed as these are forbidden by both electric- and magnetic-dipole selection rules. However the relatively low-lying second and third excited

Table 1. Experimental and calculated energy levels (in cm^{-1}) for $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$. † indicates an energy level assigned from infrared absorption.

Multiplet	State and Symmetry	Experiment	Calculated
$^5\text{I}_8$	$Z_1\gamma_1$	0	-0.7
	$Z_2\gamma_2$	5.8	4.2
	$Z_3\gamma_5$	19.7	23.0
	$Z_4\gamma_5$	48.4	48.4
	$Z_5\gamma_3$	95.0	98.6
	$Z_6\gamma_4$	110.0	121.8
	$Z_7\gamma_3$	126.4	138.2
	$Z_8\gamma_4$	174.9	168.3
	$Z_9\gamma_5$	213.9	213.0
	$Z_{10}\gamma_1$	246.4	239.9
	$Z_{11}\gamma_5$	270.1	264.2
	$Z_{12}\gamma_2$	273.8	278.4
	$Z_{13}\gamma_1$	292.0	278.4
$^5\text{I}_7$	$Y_1\gamma_2$	5117.5	5115.5
	$Y_2\gamma_1$	5122.3	5121.0
	$Y_3\gamma_5$	5126.7	5125.8
	$Y_4\gamma_5$	5138.2	5138.9
	$Y_5\gamma_4$	5142.3	5138.5
	$Y_6\gamma_3$	5172.6	5176.9
	$Y_7\gamma_5$	5195.9	5193.5
	$Y_8\gamma_2$	5204.7	5202.5
	$Y_9\gamma_4$	5211.6	5216.6
	$Y_{10}\gamma_3$	5224.1	5217.4
	$Y_{11}\gamma_5$	5308.4	5319.3
$^5\text{I}_6$	$A_1\gamma_1$	8637.1†	8638.1
	$A_2\gamma_2$	—	8645.8
	$A_3\gamma_5$	8646.1†	8646.2
	$A_4\gamma_3$	—	8647.4
	$A_5\gamma_5$	8664.6†	8671.2
	$A_6\gamma_1$	8674.9†	8676.8
	$A_7\gamma_5$	8679.6†	8683.0
	$A_8\gamma_4$	8696.3†	8682.4
	$A_9\gamma_3$	—	8817.0
	$A_{10}\gamma_4$	—	8817.0
$^5\text{F}_5$	$D_1\gamma_2$	15432.7	15428.1
	$D_2\gamma_1$	15436.2	15432.1
	$D_3\gamma_5$	15469.0	15462.6
	$D_4\gamma_4$	15528.4	15519.4
	$D_5\gamma_5$	15530.4	15546.0
	$D_6\gamma_3$	15570.5	15576.7
	$D_7\gamma_5$	15623.0	15623.5
	$D_8\gamma_2$	15646.5	15647.4
$^5\text{S}_2, ^5\text{F}_4$	$E_1\gamma_1$	18445.9	18450.8
	$E_2\gamma_3$	18463.1	18454.8
	$E_3\gamma_4$	—	18470.6
	$E_4\gamma_5$	18479.2	18483.5
	$E_5\gamma_2$	18517.3	18520.8
	$E_6\gamma_1$	18518.6	18523.3
	$E_7\gamma_4$	18604.5	18613.9
	$E_8\gamma_3$	18618.8	18620.4
	$E_9\gamma_5$	18639.9	18629.0
	$E_{10}\gamma_5$	18648.4	18638.8
	$E_{11}\gamma_1$	18658.7	18662.5
$^5\text{F}_3$	$F_1\gamma_5$	20588	20586.3
	$F_2\gamma_2$	20618	20613.8
	$F_3\gamma_3$	—	20695.1
	$F_4\gamma_5$	20695	20698.5
	$F_5\gamma_4$	—	20736.9

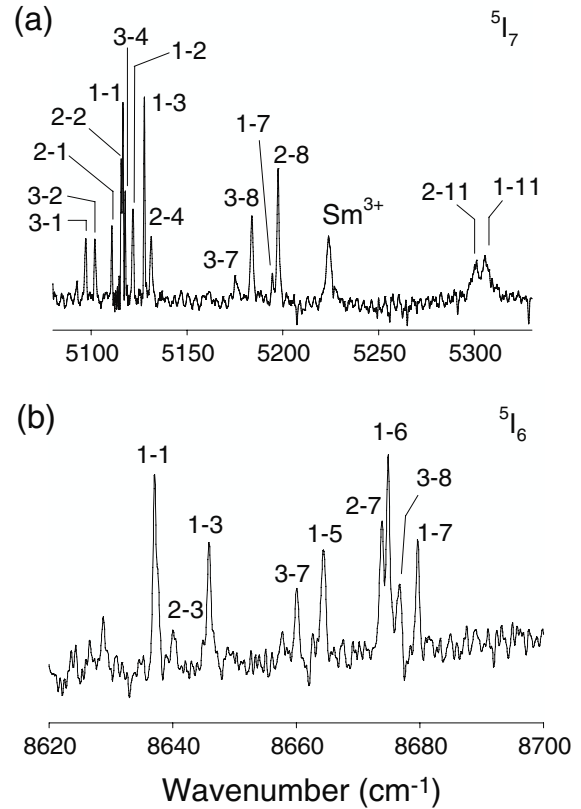


Figure 3. 15 K infrared absorption spectrum for the (a) $^5\text{I}_7$ and (b) $^5\text{I}_6$ multiplets.

states of the ground multiplet (see table 1) are both orbital doublets (γ_5) so in principle most of the $^5\text{I}_7$ and $^5\text{I}_6$ states could be observable albeit rather weak due to the low doping concentration and thin crystals available.

Transitions to the $^5\text{I}_7$ multiplet (shown in figure 3(a)) appear at the 1–2% absorption level. With transitions originating from the Z_1 , Z_2 and Z_3 levels many of the assignments made by laser excitation were able to be confirmed. A transition at 5224.2 cm^{-1} is assigned to the presence of unintentional Sm^{3+} impurities [5]. For the $^5\text{I}_6$ multiplet (see figure 3(b)), six states could be assigned as outlined in table 1. These were the $A_1\gamma_1$, $A_3\gamma_5$, $A_5\gamma_5$, $A_6\gamma_1$, $A_7\gamma_5$ and $A_8\gamma_4$ states and the irrep assignments are based on preliminary crystal-field calculations. Of these assignments, only the $A_8\gamma_4$ state which is placed at 8696.3 cm^{-1} is considered tentative. This is based on the observed 8676.9 cm^{-1} absorption line being associated with the $Z_3\gamma_5 \rightarrow A_8\gamma_4$ transition.

3.3. Crystal-field analysis

The calculations reported here employed a free ion Hamiltonian given by [31, 32]:

$$\begin{aligned}
 H_{f,i} = & \sum_{k=2,4,6} F^k f_k + \sum_i \zeta l_i \cdot s_i + \alpha L(L+1) \\
 & + \beta G(G_2) + \gamma G(R_7) \\
 & + \sum_{i=2,3,4,6,7,8} t_i T^i + \sum_{h=2,4} m_h M^h + \sum_{f=2,4,6} p_f P^f. \quad (1)
 \end{aligned}$$

Table 2. Optimized free ion and crystal-field parameters for $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$. All values are in wavenumbers, except for n , the number of experimental data points. The values in square brackets were not varied. Optimized results for other rare-earth ions are included for comparison.

Parameter	Pr^{3+} Ref. [4]	Nd^{3+} This work	Sm^{3+} Ref. [5]	Eu^{3+} Ref. [6]	Ho^{3+} This work	Er^{3+} Ref. [9]	Tm^{3+} Ref. [12]
F^2		69 894			94 063		
F^4		47 686			66 361		
F^6		27 774			51 637		
α		[21.34]			[17.15]		
β		[−593]			[−607.9]		
γ		[1445]			[1800]		
T^2		[298]			[400]		
T^3		[35]			[37]		
T^4		[59]			[105]		
T^6		[−285]			[−264]		
T^7		[322]			[316]		
T^8		[305]			[336]		
M^{tot}		[2.11]			[2.54]		
P^{tot}		[192]			[605]		
ζ		881			2142		
B_0^2	−644	−670	−600	−551	−669	−591	−556
B_0^4	−1543	−1484	−1388	−1360	−1269	−1339	−1275
B_4^4	343	569	410	345	344	407	227
B_0^6	891	698	596	394	525	426	403
B_4^6	−30	9	127	234	9	−10	−6
n		25			51		
σ		10.9			7.1		

The first two terms represent the inter-electronic Coulombic repulsion and spin–orbit interactions. The remaining terms represent the two-body configuration interaction (with parameters α , β and γ), the three-body configuration interaction (with parameters T^i), the spin–spin and spin–other–orbit interactions represented by the parameters M^h and the two-body electrostatically correlated magnetic interactions represented by the parameters P^f . As is standard, we will only treat the Slater parameters F^k and the spin–orbit parameter ζ as freely variable parameters with the remainder fixed at the values given by [32] and listed in table 2. Free ion calculations show that the three lowest energy multiplets of holmium are close to 95% LS coupled, whilst the higher-lying multiplets are progressively admixed through intermediate coupling.

To account for the crystal-field splittings, the measured energy levels are least squares fitted to a Hamiltonian appropriate for C_{4v} symmetry, using the entire configuration as basis states (that is, there is no truncation of the free ion states). The Hamiltonian has the form:

$$H_{C_{4v}} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_0^6 C_0^{(6)} + B_4^4 (C_4^{(4)} + C_{-4}^{(4)}) + B_4^6 (C_4^{(6)} + C_{-4}^{(6)}), \quad (2)$$

where all symbols are as defined in Wybourne [33]. Table 1 presents both the experimental data and the calculated crystal-field levels. As is evident from the standard deviation ($\sigma = 7.1$) presented in table 2, a good fit is obtained. Table 2 also compares the results of all other crystal-field analyses performed for rare-earth ions doped into KY_3F_{10} available in literature. The parameters for Nd^{3+} are based on a fit, using the Hamiltonian as described above, to the optical data obtained from [15]. As can be seen the Ho^{3+} parameters are entirely

consistent with the previously published values for other RE^{3+} ions.

4. Conclusions

Detailed spectroscopic analysis of $\text{KY}_3\text{F}_{10}:\text{Ho}^{3+}$ is presented. Direct fluorescence is strong even at 77 K while upconversion fluorescence is rather weak for excitation of the 5F_5 multiplet. A total of 51 crystal-field energy levels belonging to seven multiplets of Ho^{3+} have been deduced. The calculated crystal-field energy levels compare well with the experimental results and are consistent with the previously published parameters.

Acknowledgments

This work was supported by the University of the Witwatersrand in Johannesburg, South Africa, the University of Canterbury in Christchurch, New Zealand and the National Laser Centre of South Africa through research grants. We are grateful to Professor Mike Reid of the University of Canterbury in New Zealand, for providing his crystal-field fitting routines.

References

- [1] Friese K, Krüger H, Kahlenberg V, Balić-Žunić T, Emerich H, Gesland J-Y and Grzechnik A 2006 *J. Phys.: Condens. Matter* **18** 2677
- [2] Abdulsabirov R Yu, Dubiskii M A, Kazakov B N, Silkin N I and Yagudin Sh I 1987 *Sov. Phys.—Crystallogr.* **32** 559

- [3] Dubinskii M A, Khaidukov N M, Garipov I G, Dem'yanets L N, Naumov A K, Semashko V V and Malyusov V A 1990 *J. Mod. Opt.* **37** 1355
- [4] Wells J-P R, Yamaga M, Han T P J and Gallagher H G 2000 *J. Phys.: Condens. Matter* **12** 5297
- [5] Wells J-P R, Sugiyama A, Han T P J and Gallagher H G 1999 *J. Lumin.* **85** 91
- [6] Porcher P and Caro P 1976 *J. Chem. Phys.* **65** 89
- [7] Porcher P and Caro P 1978 *J. Chem. Phys.* **68** 4176
- [8] Porcher P and Caro P 1978 *J. Chem. Phys.* **68** 4183
- [9] Antic-Fidancev E, Lemaitre-Blaise M and Porcher P 1984 *Rare Earths Spectroscopy: Proc. Int. Symp. on Rare Earths Spectroscopy (Wroclaw, Poland)* ed B Jezowska-Trzebiatowska, J Legendziewicz and W Strek (Singapore: World Scientific) p 134
- [10] Heyde K, Binnemans K and Görrler-Walrand C 1998 *J. Chem. Soc. Faraday Trans.* **94** 1671
- [11] Boulma E, Diaf M, Jouart J P, Bouffard M, Doualan J L and Moncorgé R 2006 *J. Phys.: Condens. Matter* **18** 6721
- [12] Diaf M, Braud A, Labbé C, Doualan J L, Girard S, Margerie J, Moncorgé R and Thuau M 1999 *Can. J. Phys.* **77** 693
- [13] Ito M, Boulon G, Bensalah A, Guyot Y, Goutaudier C and Sato H 2007 *J. Opt. Soc. Am. B* **24** 3023
- [14] Yamaga M, Honda M, Wells J-P R, Han T P J and Gallagher H G 2000 *J. Phys.: Condens. Matter* **12** 8727
- [15] Abdulsabirov R Yu, Vinokurov A V, Ivanshin V A, Kurkin I N, Pudovik E A, Stolov A L and Yagudin Sh I 1987 *Opt. Spektrosk.* **63** 97
- [16] Andraud C, Denis J P, Blanzat B and Vedrine A 1983 *Chem. Phys. Lett.* **101** 357
- [17] Tigreat P Y, Doualan J L, Budasca C and Moncorgé R 2001 *J. Lumin.* **94/95** 23
- [18] Braud A, Girard S, Doualan J L, Thuau M, Moncorgé R and Tkachuk A M 2000 *Phys. Rev. B* **61** 5280
- [19] Braud A, Tigreat P Y, Doualan J L and Moncorgé R 2001 *Appl. Phys. B* **72** 909
- [20] Camy P, Doualan J L, Moncorgé R, Bengoechea J and Weichmann U 2007 *Opt. Lett.* **32** 1462
- [21] Rapaport A, Milliez J, Szpöcs F, Bass M, Cassanho A and Janssen H 2004 *Appl. Opt.* **43** 6477
- [22] Malkin B Z, Tarasov V F and Shakurov G S 1995 *JETP Lett.* **62** 811
- [23] Tarasov V F, Shakurov G S, Malkin B Z and Hutchison C A Jr 1997 *J. Alloys Compounds* **250** 364
- [24] Mujaji M, Jones G D and Syme R W G 1992 *Phys. Rev. B* **46** 14398
- [25] Wells J-P R, Jones G D, Reid M F, Popova M N and Chackalina E P 2004 *Mol. Phys.* **102** 1367
- [26] Henderson B H and Bartram R 2000 *Crystal-Field Engineering of Solid State Laser Materials* (Cambridge: Cambridge University Press)
- [27] Koster G F, Dimmock J O, Wheeler R G and Statz H 1963 *Properties of the Thirty-Two Point Groups* (Cambridge, MA: MIT Press)
- [28] Butler P H 1981 *Point Group Symmetry Applications* (New York: Plenum)
- [29] Mujaji M and Comins J D 1999 *Phys. Rev. B* **59** 6092
- [30] Silva E N, Ayala A P, Gesland J-Y and Moreira R L 2005 *Vib. Spectrosc.* **37** 21
- [31] Mortier M, Gesland J Y, Rousseau M, Pimenta M A, Ladeira L O, Machado da Silva J C and Barbosa G A 1991 *J. Raman Spectrosc.* **22** 393
- [32] Crosswhite H M and Crosswhite H 1984 *J. Opt. Soc. Am. B* **1** 246
- [33] Carnall W T, Goodman G L, Rajnak K and Rana R S 1989 *J. Chem. Phys.* **90** 3443
- [33] Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: Wiley-Interscience)