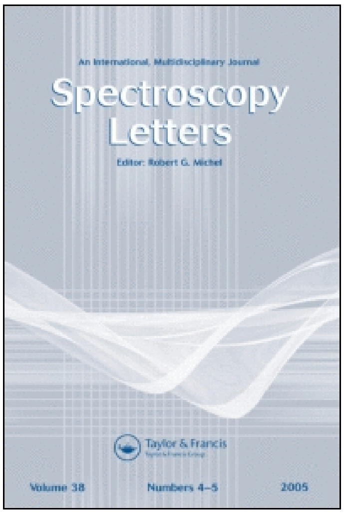

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ABSTRACT Crystal field absorption and emission spectra originated by $^5I_8 \leftrightarrow {}^5F_5$ transitions, due to Ho^{3+} (1% molar fraction) in a YPO_4 single crystal, were investigated in the 15000 to 16000 cm^{-1} range. Fourier Transform high resolution absorption measurements, performed in the 9 to 300 K range, and photoluminescence, monitored at 10 K upon 540 nm excitation, supplied the sublevel separations within both $^5I_8$ and $^5F_5$ manifolds. The sublevel positions were compared to those calculated by diagonalization of the full 4*f*-configuration matrix in the framework of a single-ion model. The results are discussed also in relation with experimental data previously reported for similar systems containing Ho^{3+}.

KEYWORDS crystal field splitting, Ho^{3+} ion, hyperfine structure, luminescence

INTRODUCTION

Yttrium orthophosphate YPO_4 is a widely investigated material that has proved to be important for many applications in the field of optical materials and devices. For instance, undoped YPO_4 has been recently demonstrated to be a stimulated Raman scattering active crystal with non-linear laser properties of possible application in the visible, near- and mid-IR spectral ranges.[1] On the other hand, YPO_4 doped with trivalent lanthanide ions (Ln^{3+}, in particular Ce^{3+}, Pr^{3+}, and Nd^{3+}) shows strong broad-band 5*d*-4*f* luminescence in the UV,[2,3] and therefore can find applications in the field of fast scintillating materials.

Although the 4*f*-4*f* spectroscopy of Ln^{3+} ions in YPO_4 is in general rather well known, in the case of the Ho^{3+} ion no very detailed studies have appeared in the literature. Ho^{3+} (as other Ln^{3+} ions) substitutes for the eightfold coordinated Y^{3+} and probes a D_{2d} site symmetry within the tetragonal YPO_4 (space group $D_{4h}^{19}-I4_1/amd$).[1] Y^{3+} and Ho^{3+} are both trivalent cations: no charge compensation is required and, as a consequence, no further local symmetry lowering can be caused by charge compensating defect(s). Absorption measurements were performed 40 years ago on $HoPO_4$ and YPO_4 doped with 10% Ho^{3+}:[4] crystal field energies and parameters have been extracted.[5,6] However, YPO_4:Ho^{3+} has been reported to be non-luminescent at room temperature[7] and so far only the multiphonon relaxation rate of the Ho^{3+} excited levels ($^5F_4$, $^5S_2$) has been investigated in detail.[8] On this basis a thorough study of high resolution

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optical spectra of YPO_4:Ho^{3+} single crystals was initiated by us in view of unveiling possible hyperfine structures due to ^{165}Ho, an ion endowed with nuclear spin I = 7/2. In the present paper the transitions connecting the sublevels of the $^5I_8$ and $^5F_5$ manifolds are analyzed by measuring high resolution absorption spectra, over a wide temperature range (9 to 300 K), and low temperature luminescence spectra.

EXPERIMENTAL

Single crystals of YPO_4 were grown by spontaneous nucleation from a PbO-P_2O_5 flux (1:1 molar ratio).[9] The reagents employed were $NH_4H_2PO_4$, PbO (both reagent grade), Y_2O_3 (99.99%) and Ho_2O_3 (99.99%). The batch was put in a covered Pt crucible and heated up to 1300°C inside a horizontal furnace. After a soaking time of about 15 h, the temperature was lowered to 800°C with a rate of $\approx 1.8°C\,h^{-1}$, the crucible was then drawn out from the furnace and quickly inverted to separate the flux from the crystal grown at the bottom of the crucible. The flux was dissolved by using hot diluted nitric acid. Single crystals of good optical quality were obtained, having a size up to $1.0 \times 0.8 \times 8\,mm^3$ and elongated in the direction of *c*-axis of the tetragonal structure. The Ho^{3+} nominal concentration in the YPO_4 samples employed in the present work was 1% molar fraction (m.f.). The choice of a more diluted solid solution, with respect to the systems already investigated,[4] is aimed at obtaining sharper line spectra.[10,11]

The optical absorption spectra were monitored by means of a Fourier Transform spectrophotometer Bomem DA8 operating in the 500 to 17000 cm^{-1} range and capable of a nonapodized resolution as fine as 0.01 cm^{-1}. In the following the absorption lines are labeled by their position (wave number) as measured at 9 K, unless otherwise stated. To improve the signal to noise ratio the spectra were acquired by co-adding at least 400 scans. The sample temperature was controlled in the 9 to 300 K range by means of a 22 model Cryodine Refrigerator of CTI Cryogenics equipped with KRS5 and fused silica windows.

Luminescence spectra were obtained using an Optical Parametric Oscillator (OPO Quanta Ray) as excitation source. This OPO provides 10 ns pulses with an average energy of 10 mJ and wavelength tunability from about 400 nm to about 2000 nm. The emitted light was focused onto a double-grating monochromator (SPEX 500 M), followed by a CCD-Si detector. Measurements were made at 10 K by using a liquid He cryostat.

RESULTS AND DISCUSSION

Figure 1 displays the unpolarized high resolution (0.1 cm^{-1}) absorption spectra of a 0.4 mm thick YPO_4:Ho^{3+} 1% m.f. sample in the 15430 to 15580 cm^{-1} range (i.e., in the region of the $^5I_8 \rightarrow {}^5F_5$ transition) for a few temperatures in the 9–100 K range. At 9 K only seven lines are monitored (curve a): two of them, at 15451.5 and 15463.2 cm^{-1}, are rather narrow (FWHM ~ 1.5 cm^{-1}), while two (at 15532.7 and 15557.2 cm^{-1}) are much broader and apparently show a structure, which, however, cannot be resolved, in spite of the high instrumental resolution employed. No changes are monitored at 20 K (curve b). By increasing the temperature in the 40 to 100 K ranges (curves c–f), new lines grow on the low energy side, while the original ones displayed by curve a gradually lose intensity. A further temperature increase up to 300 K causes the appearance of other lines at even lower energies and a general broadening and weakening of the whole spectrum, as shown in Fig. 2 by curves g–n, related to the 120 to 270 K range. Such a behavior can be interpreted by assuming that at 9 K only the lowest sublevel of the ground manifold, $^5I_8$, is populated and all the

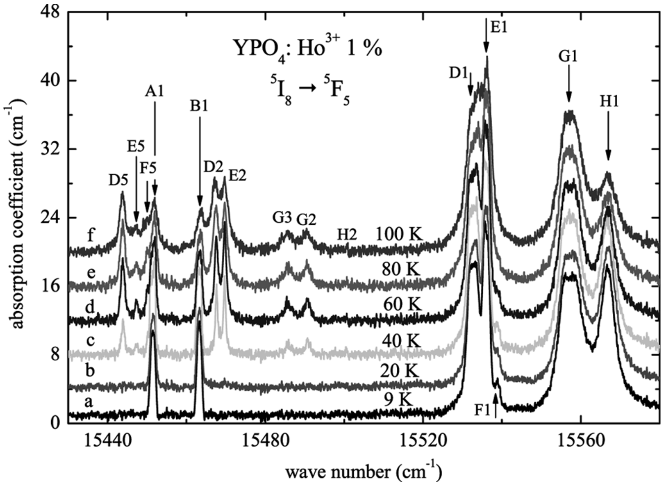

FIGURE 1 Optical absorption spectra (res. 0.1 cm^{-1}) measured at different temperatures on a 0.4 mm thick YPO_4:Ho^{3+} 1% m.f. sample. Curve a: 9 K; curves b–f: from 20 to 100 K by steps of 20 K. The curves are vertically shifted for clarity.

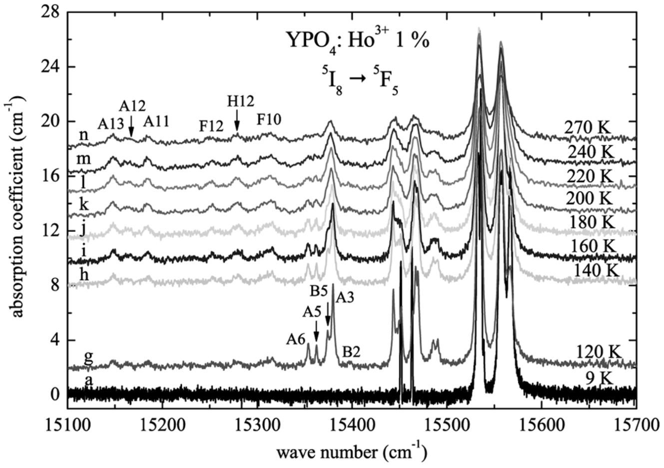

FIGURE 2 Optical absorption spectra measured at different temperatures on a 0.4 mm thick YPO$_4$:Ho^{3+} 1% m.f. sample. Curve a: 9 K, res. 0.1 cm^{-1} (from Fig. 1 and reported here for comparison); curves g: 120 K, res. 0.5 cm^{-1}; curve h: 140 K, res. 0.5 cm^{-1}; curve i: 160 K, res. 0.5 cm^{-1}; curve j: 180 K, res. 0.5 cm^{-1}; curve k: 200 K, res. 1 cm^{-1}, curve l: 220 K, res. 1 cm^{-1}; curve m: 240 K, res. 1 cm^{-1}; curve n: 270 K, res. 1 cm^{-1}. The curves are vertically shifted for clarity.

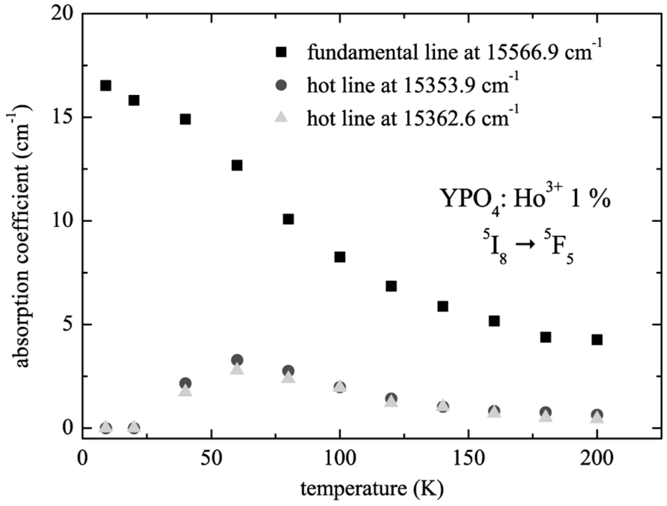

FIGURE 3 Temperature dependence of the amplitude for a few lines detected in a 0.4 mm thick YPO$_4$:Ho^{3+} 1% m.f. sample. Squares: fundamental line at 15566.9 cm^{-1}; circles: hot line at 15353.9 cm^{-1}; triangles: hot line at 15362.6 cm^{-1}.

lines displayed by curve a in Fig. 1 are due to transitions starting from that sublevel and reaching the sublevels of the excited $^5F_5$ manifold (fundamental lines). By increasing the temperature also the excited sublevels of the ground $^5I_8$ manifold become progressively populated, thus transitions starting from such sublevels originate the new lines (hot bands) appearing on the low-energy side (see curves c-n, in Figs. 1 and 2). The hot bands initially grow at the expenses of the fundamental lines, then decrease at higher temperatures in favor of other transitions starting from even higher sublevels within the ground manifold. Figure 3 shows, as an example, the amplitudes of a fundamental line, such as the one peaking at 15566.9 cm^{-1} (see Fig. 1, curve a), and of two hot bands at 15353.9 and 15362.6 cm^{-1} (see, for example, Fig. 1, curve c) plotted as a function of the temperature in the 9 to 200 K range. The careful analysis of the hot lines evolution over the 9 to 300 K range allowed the identification of the splitting of the sublevels belonging to the ground manifold $^5I_8$. Such results are summarized in Table 1, together with the sublevels of the excited $^5F_5$ manifold, which can be easily deduced from curve a in Fig. 1. The lines (and transitions) are labeled by Xn, where n = 1, 2, 3, … indicates the ground manifold sublevel (initial state of the absorption transition), and X = A, B, C,… indicates the sublevel within a given excited manifold (final state).[10,11] For example, the position of the sublevel 2 within the ground manifold was estimated from the difference between the wave numbers of 6 pairs of X1 and X2 lines, spanning over the spectral range of 15100 to 15700 cm^{-1}. The position mean value was calculated in this way for each sublevel of the $^5I_8$ manifold and reported in Table 1 (third column): the standard deviation was within 2%. The present data are compared in Table 1 with the experimental values obtained from measuring the HoPO$_4$ and YPO$_4$:Ho^{3+} 10% m.f. samples spectra at two temperatures (4.2 and 85 K).[4] A comparison is also given with the energy values calculated by diagonalization of the full 4*f*-configuration matrix in the framework of a single-ion model,[11] which originate from a preliminary fit of the experimental data acquired over a wide wave number range (500 to 25000 cm^{-1}). The complete set of the experimental levels and the calculation details will be presented in a forthcoming paper. The total r.m.s. deviation for the above fit is 14 cm^{-1}, which is as good as can be expected for a crystal-field model. While the ground manifold splittings are quantitatively well reproduced, the deviation for the states belonging to the $^5F_5$ manifold is slightly larger; on the other hand, the qualitative features of the calculated manifold splitting agree with the experimental data. There is an excellent agreement between the values obtained from absorption measurements of the present work and those reported by Becker et al.[4] for a few sublevels (1–5) belonging to the ground

TABLE 1 **Line Positions (cm^{-1}), as Obtained from the Absorption (at Different Temperatures T, see Footnotes) and Luminescence (T = 10 K) Measurements on YPO$_4$:Ho^{3+} 1% m.f. Samples (Third and Fourth Column, Respectively, Present Work), from Absorption Measurements on HoPO$_4$ and YPO$_4$:Ho^{3+} 10% m.f. Samples (T = 85 K, Ref. [4], Fifth Column) and from Calculations (Sixth Column, Present Work). The Manifolds, $^{2S+1}L_J$, and Sublevel Labels are Displayed in First and Second Column, Respectively**

$^{2S+1}L_J$	Sublevel	Experimental[1] (absorption)	Experimental[1] (luminescence)	Experimental[2] (absorption)	Calculated[1]
$^5I_8$	1	0	0	0	5.3D
	2	66.7[b]	67[3]	66.58	60.1
	3	71.1[b]	73[3]	71.73	74.0D
	4	81.8[b]	81[3]	80.86	81.7
	5	88.8[b]	89[3]	89.21	88.2
	6	96.1[b]	94[3]	160.42	101.1
	7	107.0[c]		188.09	143.9
	8	111.8[c]		250.21	144.6
	9	170.6[d]		279.36	199.0D
	10	234.4[d]	235[3]		244.5
	11	265.0[d]	266[3]		246.4
	12	285.4[d]	285[3]		262.9D
	13	304.8[d]	306[3]		278.0
				15432.11	
$^5F_5$	A	15451.5[a]	15452	15452.27	15429.0
	B	15463.2[a]	15463[3]	15463.68	15432.7D
	C	–	–	–	15438.4
	D	15532.7[a]*	15533	15532.79	15514.9D
	E	15535.9[a]*	15536[3]	15336.26	15523.9
	F	15539.0[a]		15539.05	15527.1
	G	15557.2[a]*	15557[3]	15557.01	15542.1D
	H	15566.9[a]	15567[3]	15567.29	15558.0

Notes: [1]present work; [2]from Ref.[4]; [3]indirect evaluation (see text); [a]T = 9 K; [b]T = 40 K; [c]T = 80 K; [d]T = 120 K; *possible hyperfine structure; D = doublet.

manifold, $^5I_8$, and for all the sublevels of the excited $^5F_5$ manifold (compare third and fifth column in Table 1) except for the 15432.11 cm^{-1} level. No evidence of the related line was found in the present measurements, notwithstanding the high resolution employed and the rather closely temperature spaced (by 20 K steps over the 20 to 240 K range) spectra monitored (see Figs. 1 and 2). The agreement indicates that Ho^{3+} sublevels within the $^5F_5$ manifold are not affected by the Ho^{3+} concentration, from 1 (present work) to 100% m.f.,[4] i.e., neither shift nor additional lines are monitored, at variance, for example, with Er^{3+} in BaY$_2$F$_8$,[10] where Er^{3+} clustering phenomena occur. For what concerns the 6–9 sublevels within the ground manifold, $^5I_8$, the discrepancy between the present data and those reported by Becker et al.[4] may arise from the analysis of spectra measured only at two temperatures (4.2 and 85 K). The rather closely temperature spaced sequence of spectra, measured in the present work by 20 K steps over the 20 to 240 K range, is a necessary requirement to follow the progressive growth of the hot bands and to evaluate correctly the positions of all sublevels within the ground manifold.[11] In this way, the number of sublevels detected (13), see third column in Table 1, agrees with that expected on the basis of symmetry considerations for the $^5I_8$ manifold (i.e., $2J + 1 = 17$) of Ho^{3+} (a non-Kramers ion) embedded in the tetragonal YPO$_4$ matrix. In fact, the calculations performed in the framework of a single-ion model (see above) show that four among the $^5I_8$ sublevels are doubly degenerate (doublets, labeled with 'D', see sixth column in Table 1): the manifold degeneracy cannot be completely removed by the crystal field experienced by Ho^{3+}, sitting in a D$_{2d}$ symmetry site, within the tetragonal YPO$_4$ lattice (see Introduction). From the calculations sublevel degeneracy was found also within the excited $^5F_5$ manifold: the doubly degenerate sublevels are marked again with 'D' in Table 1 (sixth column). A further support to the $^5I_8$ and $^5F_5$ manifold splitting comes from the luminescence measurements.

Figure 4 shows the 10 K unpolarized emission spectrum in the 15100 to 15500 cm^{-1} range, obtained upon excitation at 540 nm (18518.5 cm^{-1}), i.e., into the $^5I_8 \rightarrow {}^5S_2$ transition of Ho^{3+} ions. The emission spectrum was measured only in the energy range of interest for the present work, i.e., it involves transitions from the $^5F_5$ manifold (at ~15500 cm^{-1}, see Table 1) to the sublevels within the $^5I_8$ manifold. It should be remarked that difficulties are usually met to detect luminescence in YPO$_4$, due to a tight coupling between Ho^{3+} and the lattice.[8] In addition, part of the excitation energy is known to be delivered to lattice vibrations in terms of multiphonon (MP) process.[8] The MP transition rate for Ho^{3+} was found to be very high in YPO$_4$ and much higher with respect to similar host matrices as YAsO$_4$ and YVO$_4$, compare Fig. 7 with Figs. 5 and 6 in Reed and Moos.[8] A hint about the nature of 'phonons' involved may be found in Fig. 5, where the 9 K absorption spectrum of the YPO$_4$:Ho^{3+} 1% m.f. sample in the 600–4000 cm^{-1} range shows very strong absorptions around 1100 cm^{-1}, strong ones at ~2080 cm^{-1}, and a much weaker one at ~3000 cm^{-1}. Absorption peaks at 1070, 1030, 643.1, and 526.3 cm^{-1} were monitored in room temperature IR spectra of YPO$_4$-KBr (or CsI) pellets.[12] They were attributed to PO$_4^{3-}$ ionic group vibrations: the first two to stretching modes, while the last two to bending modes. Recent Raman scattering measurements have shown two peaks at ~1002 and 1058 cm^{-1}, which were attributed to totally symmetric $A_{1g}(\nu_1)$ and antisymmetric $B_{1g}(\nu_3)$ stretching vibrations of the PO$_4^{3-}$ complexes, respectively.[1] Thus the bands detected around 1100 cm^{-1} (Fig. 5, solid arrow) can be attributed to the fundamental absorption of IR active modes of PO$_4^{3-}$ groups. The peaks at ~2080 and ~3000 cm^{-1} in Fig. 5 (dashed arrows) can be regarded as due to absorptions of first and second overtones of PO$_4^{3-}$ IR active modes and of their combinations with Raman active modes, in analogy with the multi-mode absorptions of tetrahedral groups in sillenites.[13,14] Thus part of the excitation energy may be spent to change the vibrational state of one or more of the PO$_4^{3-}$ complexes neighboring Ho^{3+} in tetragonal YPO$_4$. The vibrational modes of tetrahedral VO$_4^{3-}$ and AsO$_4^{3-}$ units should occur at lower frequencies, as observed indeed in sillenites,[14] due to the larger atomic masses of V and As with respect to that of P. Such a consideration may account for the lower MP transition rate for Ho^{3+} in YAsO$_4$ and YVO$_4$, with respect to YPO$_4$.[8] OH$^-$ groups might also be responsible for luminescence quenching,[15] however the spectrum displayed in Fig. 5 does not show, for the present sample, any absorption which can be attributed to OH$^-$ modes.

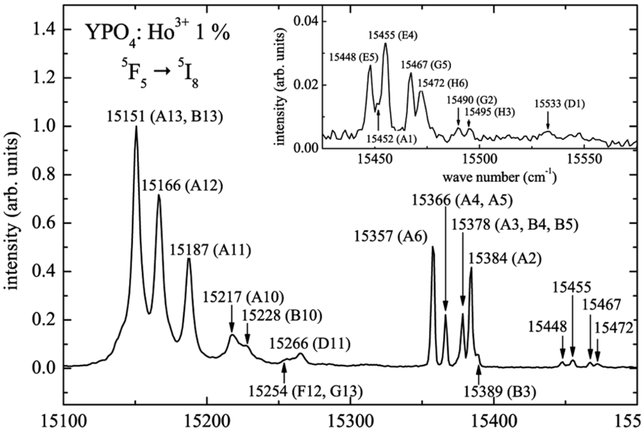

FIGURE 4 Unpolarized emission spectrum, in the range 15100 to 15500 cm^{-1}, measured at 10 K on a YPO$_4$:Ho^{3+} 1% m.f. sample upon excitation at 540 nm. The insert shows a magnification of the spectrum in the 15400–15600 cm^{-1} range.

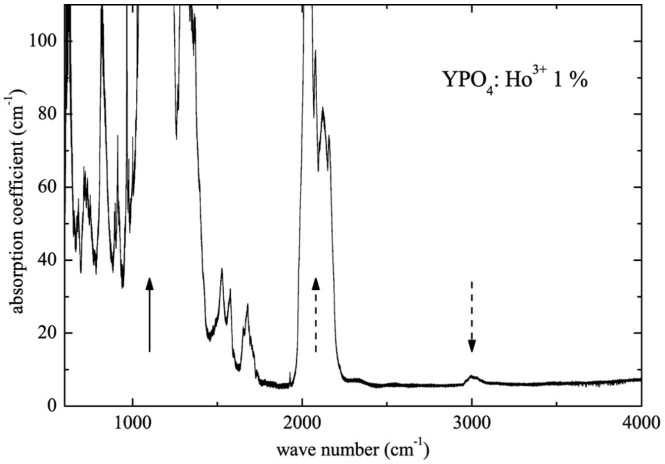

FIGURE 5 Optical absorption spectrum measured at 9 K on a 0.4 mm thick YPO$_4$:Ho^{3+} 1% m.f. sample in the 500–4000 cm^{-1} range. The solid arrow indicates the fundamental absorption of IR active modes of PO$_4^{3-}$ groups, while the dashed ones indicate the regions of the related first and second overtones.

On the basis of the sublevel positions determined by means of the present absorption measurements and listed in Table 1 (third column) it was possible to identify the transitions originating the single emission lines portrayed in Fig. 4: they are labeled according to the terminology adopted for the

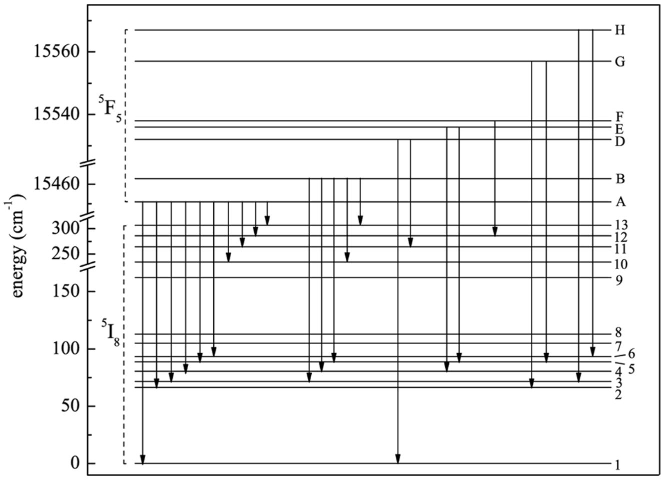

FIGURE 6 Energy level scheme for the fundamental $^5I_8$ and the excited $^5F_5$ manifolds of Ho^{3+} in YPO_4, according to the experimental absorption and luminescence results (see Table 1, third and fourth column). The arrows indicate the transitions originating the emission lines displayed in Fig. 4.

corresponding absorption lines, see Figs. 4 and 6. Only in a few cases, it was difficult to assign unequivocally the final state, as for the 15366 and 15378 cm^{-1} lines because the two possible final states (4 and 5, Table 1, third column) are rather close. Even an A3 line contribution might be hidden under the 15378 cm^{-1} line. For the strongest line at 15151 cm^{-1}, the starting sublevel may be either A or B: the line, being rather broad, may arise from the superposition of both A13 and B13 lines. Lines due to transitions starting from all the $^5F_5$ manifold sublevels (listed in Table 1, third column) were identified. The strongest lines are those appearing on the low energy side of the emission spectrum and are originated by transitions having as final states the highest sublevels of the $^5I_8$ manifold. Only the weak lines at 15533 and 15451 cm^{-1} correspond to transitions reaching the lowest sublevel of the ground manifold, see Fig. 6 and insert in Fig. 4. According to the above attribution it was possible to extract the position of the sublevels within the ground manifold, as the difference between the energy of the starting sublevel within the $^5F_5$ manifold (evaluated from the absorption measurements) and the energy at which each emission line is detected: the results are collected in Table 1, fourth column. The agreement with the figures obtained from the absorption spectra as a function of temperature (Figs. 1 and 2) is excellent (compare third and fourth column in Table 1).

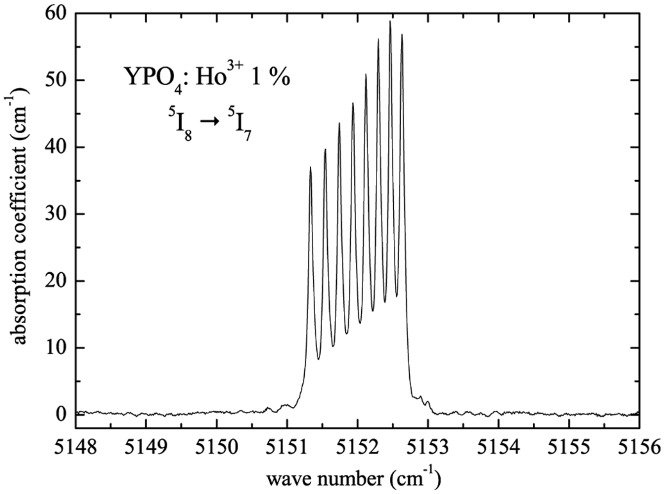

FIGURE 7 Hyperfine structure displayed by the absorption line at 5152 cm^{-1} in the region of Ho^{3+} $^5I_8 \rightarrow {}^5I_7$ transition. The spectrum is measured at 9 K with a non apodized resolution of 0.01 cm^{-1}.

It has been observed (see above) that two absorption lines (at 15532.7 and 15557.2 cm^{-1}) in the 9 K spectrum (Fig. 1, curve a) are rather broad (FWHM ~3.4 and 6.4 cm^{-1}, respectively) and show a nearly squared top. Such a feature deserves further insight and might be accounted for in terms of hyperfine splitting (hfs). ^{165}Ho has the highest nuclear spin ($I = 7/2$) among rare earths and a natural abundance of 100%. In addition to this, all the low-lying manifolds of Ho^{3+} are characterized by high J (up to $J = 8$ for the ground state), thus they are expected to display relatively large hyperfine separations: the hyperfine splitting depends both on the nuclear spin **I** and on the electronic total angular momentum **J**, being expressed as $H_{hf} = A_J\, \mathbf{J} \cdot \mathbf{I}$, where A_J is the hyperfine coupling constant for the considered multiplet.[16] Preliminary high resolution absorption measurements (non apodized resolution as fine as 0.01 cm^{-1}), performed at 9 K on the present YPO_4:Ho^{3+} 1% m.f. sample in the region of the $^5I_8 \rightarrow {}^5I_7$ transition, supply clear evidence that a few lines are affected by hfs. An example is portrayed in Fig. 7 regarding the A1 line at 5152 cm^{-1}. The comprehensive linewidth is ~1.4 cm^{-1} with a separation between the components of ~0.2 cm^{-1}. The number of components is that expected on the basis of nuclear spin, i.e., $2I + 1 = 8$.[16] In the case of the 15532.7 and 15557.2 cm^{-1} lines (Fig. 1, curve a) the lineshape suggests a possible hfs, however the rather large intrinsic linewidth does not allow its resolution. As a rule, the transitions to the highest sublevels of an excited manifold originate broader lines, as reported for Er^{3+} in BaY_2F_8:[10] a general explanation may be found by considering that the highest sublevels are not in thermodynamic equilibrium at 9 K, as observed for the upper sublevel of the $^5D_1$ manifold in YVO_4:Eu^{3+}, which shows a MP transition rate which is about 15 times that of the lower one.[17] High transition rate involves short lifetime and broad linewidth. This feature will be discussed more in detail in a forthcoming, more comprehensive paper dealing both with all the transitions occurring in a wider range (500 to 25000 cm^{-1}) and with the detailed analysis of different hyperfine structure patterns.

CONCLUSION

Optical spectroscopy (absorption and emission) measurements have been employed to supply the scheme of energy sublevels involved in the $^5I_8 \leftrightarrow {}^5F_5$ transitions of Ho^{3+} in a YPO_4 single crystal. More in detail the high resolution absorption spectra, monitored over the 9 to 300 K range at rather close temperature steps, have provided the level scheme which allowed to identify clearly, for each line displayed by the 10 K photoluminescence spectrum, the pair of sublevels connected by the related radiative transition. The sublevel positions were also calculated in the framework of a single-ion model and discussed in relation with the experimental data reported both in the present work and by Becker et al. for similar systems containing Ho^{3+}.[4] The possible role played by the vibrational modes of the tetrahedral PO_4^{3-} units in opening non-radiative de-excitation paths is also discussed. Preliminary high resolution spectroscopy measurements show that tetragonal YPO_4 single crystal is a suitable host for a successful analysis of the hyperfine structure displayed by a few $^{165}Ho^{3+}$ absorption lines.

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