Journal of Alloys and Compounds, 207/208 (1994) 69–73
JALCOM 3017

Electronic energy level structure of Tb^{3+} in $LiYF_4$

G.K. Liu and W.T. Carnall
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 (USA)

Raymond P. Jones and R.L. Cone
Physics Department, Montana State University, Bozeman, MT 59717 (USA)

Jin Huang
Department of Physics and Astronomy, University of Wisconsin at Eau Claire, Eau Claire, WI 54702 (USA)

Abstract

We report the experimental results and theoretical modeling for the electronic energy level structure of Tb^{3+} in laser crystal $LiYF_4$. Using polarized one- and two-photon spectroscopic methods, crystal field levels of the Tb^{3+} ion have been obtained from the ground multiplet up to 42 000 cm^{-1} and unambiguously identified. The observed spectra have been analyzed using an effective operator Hamiltonian. Free-ion and crystal field parameters were determined in non-linear least-squares fitting of the calculated energy states to 165 observed levels. Excellent correlation (rms = 9.7 cm^{-1}) was obtained between the experiments and the computed energy level structure.

1. Introduction

In previously reported experiments in the present series, Liu *et al.* [1] analyzed the crystal field splitting of the $^5D_4$ multiplet and studied the electronic Zeeman effect and hyperfine spectral hole-burning for Tb^{3+}:$LiYF_4$. Huang *et al.* [2] reported observation of the $^5G_6$ multiplet near 40 000 cm^{-1} probed using direct two-photon absorption. In this paper, we report a detailed analysis of the optical spectra of Tb^{3+}:$LiYF_4$ using a variety of techniques and report the observed energy level structure up to 42 000 cm^{-1}. Several types of two-photon absorption experiments [2,3] have been carried out to resolve the complicated Tb^{3+} crystal field levels in the energy range from 39 000 cm^{-1} to 42 000 cm^{-1}. Energy levels of Tb^{3+} below that region were obtained with polarized one-photon absorption and fluorescence experiments, and frequency-doubled one-photon absorption experiments. From the one- and two-photon spectra, 165 observed energy levels have been assigned for determining the free-ion and crystal field parameters and for calculating the complete energy level structure and eigenstates of $4f^8$ configuration below 50 000 cm^{-1}.

Although extensive spectral analyses for most other rare earth ions in laser crystal $LiYF_4$ have been published in the literature, spectroscopic results for Tb^{3+} in $LiYF_4$ do not appear to have been analyzed previously, even though it is a key member near the center of the $4f^n$ series. The reason that ions in the center of the series, from Eu^{3+} to Tb^{3+}, generally have been less studied arises from the limited number of states in the visible region. Morrison and Leavitt [4] listed some of the energy levels of Tb^{3+}:$LiYF_4$ in their review article. Some years ago, Christensen [5] reported a spectroscopic analysis of the similar compound $LiTbF_4$, based on the observed energy levels of ^7F_J ($J = 0, 1, 2, 3$) and $^5D_4$ groups. By exploiting a variety of techniques of non-linear spectroscopy and the complementary polarization selection rules associated with those techniques, we have overcome the difficulties for Tb^{3+}:$LiYF_4$.

2. Experimental details

Experiments on 1% Tb^{3+}:$LiYF_4$ were performed both at Montana State University and Argonne National Laboratory. Absorption and fluorescence experiments utilized tunable dye lasers pumped by pulsed Nd:YAG or nitrogen lasers. Visible and near infrared fluorescence from the lowest component of $^5D_4$ was dispersed by a monochromator to obtain energy levels of the ^7F_J multiplets. Two dye lasers operating at independently variable wavelengths were used in two-photon experiments for probing highly excited states; in these experiments, the 418 nm fluorescence from $^5D_3$ to $^7F_5$

SSDI 0925-8388(93)03017-D

was used to monitor absorption. A frequency-doubling system (Inrad Autotracker II) was used to generate second harmonic frequencies of a tunable dye laser (Molectron DL-16A) pumped by a Q-switched Nd:YAG laser (Quanta Ray DCR-2A); four KDP frequency-doubling crystals were required to excite the Tb^{3+} ion into states spanning the range from 28 000 cm^{-1} to 38 000 cm^{-1}. Absorption spectra from 26 000 cm^{-1} to 28 000 cm^{-1} were recorded using a Cary Model-17 spectrophotometer.

The sample grown by H.J. Guggenheim of AT&T Bell Laboratories was X-ray oriented and mounted in a cryostat with the *c*-axis perpendicular to the incident laser beam. The ultraviolet absorption and frequency-doubled one-photon absorption were performed at 4.2 K, and all other experiments in this work were performed at 1.3 K.

Signals from the photomultiplier were averaged using a DEC minicomputer. The optogalvanic effect in a uranium hollow cathode lamp was used for wavelength calibration of the excitation spectra. Emission from krypton and neon lamps was simultaneously recorded with the Tb^{3+} fluorescence spectra for calibration.

3. Summary of results

3.1. The $^5D_4$ state

There are two long-lived emitting states, $^5D_4$ and $^5D_3$, in this system. We have measured a lifetime of 5 ms at 4.2 K for the emitting state $^5D_4$ and 2.8 ms for the $^5D_3$. The crystal field levels of the isolated $^5D_4$ multiplet were probed in absorption and excitation. The selection rules for electric dipole transitions allow one to observe the Γ_1 and $\Gamma_{3,4}$ states in π and σ polarization, respectively. The observed energy levels of the $^5D_4$ multiplet split only 90 cm^{-1} reaching from 20 554 cm^{-1} to 20 645 cm^{-1} [1]. The lowest two levels of the $^5D_4$ multiplet are Γ_1 and $\Gamma_{3,4}$ separated only by 5 cm^{-1}. After laser excitation at 4.2 K, about 20% of the excited state population stays in the higher $\Gamma_{3,4}$ level, thus emission from both levels could be present in fluorescence spectra. Emission from the higher level of the $^5D_4$ multiplet was eliminated when the sample temperature was reduced to 1.3 K.

3.2. The septet ^7F_J multiplets from fluorescence

The crystal field energy levels of the septet ^7F_J ($J = 0$–6) multiplets have been observed in the emission spectra of both $^5D_4$ and $^5D_3$ states. The crystal field components of the lowest multiplet $^7F_6$ were found to spread over a range of 360 cm^{-1}. The ground state consists of two Γ_2 singlets separated by 0.9 cm^{-1} as previously observed in electron spin resonance [6]. In our experiments, these two levels were well resolved in the absorption and excitation spectra. The $^7F_5$ multiplet consists of a total of eight distinct levels separated into two groups. There are five levels between 2110 cm^{-1} and 2196 cm^{-1}; the second group has three states near 2400 cm^{-1}. These results are consistent with those reported for Tb^{3+}:$CaWO_4$ [4], but are different from the previous assignment for Tb^{3+}:$LiYF_4$ reported also in ref. 4, where all eight levels of this multiplet were assigned between 2108 cm^{-1} and 2197 cm^{-1}.

The Zeeman effect provided an independent identification of the $\Gamma_{3,4}$ and Γ_1 (Γ_2) states in the ^7F_J multiplets. In a magnetic field, a $\Gamma_{3,4}$ doublet splits linearly into two components, while Γ_1 and Γ_2 singlets have no linear Zeeman effect; instead, the energy levels of Γ_1 and Γ_2 vary non-linearly due to coupling to adjacent Γ_1 (Γ_2) levels. External magnetic field up to 50 kG parallel to the *c*-axis of the Tb^{3+}:$LiYF_4$ crystal was applied to clearly reveal these effects.

3.3. Energy level structure from 26 300 cm^{-1} to 38 500 cm^{-1}

After a large energy gap of 5750 cm^{-1} between the $^5D_4$ to $^5D_3$ states, there are a total of 227 crystal field levels of the $4f^8$ configuration densely packed between 26 300 cm^{-1} ($^5D_3$) and 38 100 cm^{-1}. With the high density of the $4f^8$ states in this range, the energy levels of the Tb^{3+} ion are significantly mixed up by both spin-orbit coupling and crystal field interaction. Few energy gaps exist and superposition of the crystal field components of the nominally different free-ion states appear in the observed spectra.

The frequency-doubled output from a tunable dye laser provided a tunable ultraviolet laser source for probing higher energy levels of the Tb^{3+} ion. From 28 000 cm^{-1} to 38 500 cm^{-1}, σ and π polarized excitation spectra were recorded and analyzed in this work. Levels in the regions from 29 000 cm^{-1} to 31 600 cm^{-1} and from 33 100 cm^{-1} to 34 500 cm^{-1} were not probed in our experiments, as appropriate harmonic generation crystals were not available. The energy levels of Tb^{3+}:$LiYF_4$ between 26 300 cm^{-1} and 28 000 cm^{-1} were probed in conventional absorption experiments. The crystal field components in the ultraviolet absorption spectra were not completely resolved because of the low resolution of the spectrophotometer. Assignment of the observed levels in the ultraviolet absorption spectrum was made only after success in fitting the energy levels in low- and high-lying energy regions obtained from our laser experiments.

3.4. Energy level structure from 39 000 cm^{-1} to 42 000 cm^{-1} via twophoton absorption

From $^5K_9$ to $^5K_7$, 48 crystal field levels out of a total 70 in this energy region were observed in our two-photon absorption (TPA) experiments and two-step excitation (TSE) experiments. The crystal field spectra of the $^5G_6$ and $^5D_2$ multiplets near 40 000 cm^{-1} have been probed in the TPA experiments [2,3]. One laser was scanned while another was fixed at a wavelength below the transition to the intermediate state $^5D_4$. The energy summation of the two lasers was thus tuned to reach the energy levels from 39 500 to 40 500 cm^{-1}. Combinations of different polarization of the laser beams from the two independent lasers resolved 12 out of a total 14 components of the $^5G_6$ and $^5D_2$ groups. The electric dipole selection rules for two-photon transition were confirmed and the assignment of the observed energy level was unique.

Most energy levels of Tb^{3+} from 40 000 cm^{-1} to 42 000 cm^{-1} were obtained by a two-step excitation (TSE) technique using the long-lived $^5D_4$ as an intermediate state [3]. All upper energy levels probed by TSE are Γ_2 and $\Gamma_{3,4}$ states since the lowest $^5D_4$ Γ_1 level was used as the intermediate state, and Γ_1 to Γ_1 transitions were forbidden for the electric dipole transitions occurring in the second step of the TSE process. With the time delay between the two laser pulses in a few nanoseconds, energy transfer to the defect sites did not occur in the intermediate state and most lines observed in the TSE spectra were "intrinsic-site" lines. When the time delay was longer than a few nanoseconds, extra lines were observed in the TSE spectra due to excitation trapping in the $^5D_4$ intermediate state at perturbed crystal sites [3].

4. Analysis of the crystal field spectra

The crystal field spectra of the Tb^{3+} ion in $LiYF_4$ have been analyzed using a model Hamiltonian including effective operators for free-ion and crystal field interactions. The crystal field calculation was conducted using D_{2d} site symmetry. For the $4f^8$ configuration, a method of truncation was used to keep manageable matrix sizes and to cover energy levels from the ground state up to 50 000 cm^{-1}. The observed energy levels are below 42 000 cm^{-1}, and contributions of the states above 50 000 cm^{-1} to the crystal field states below 42 000 cm^{-1} are generally negligible.

In the first step of the calculation, the choice of initial values for the parameters of the model Hamiltonian is critical. We relied on the previous work on Tb^{3+}:LaF_3 by Carnall *et al.* [7] for initial values of all 20 free-ion parameters. The initial values of the five crystal field parameters were set to those obtained by Christensen for $LiTbF_4$ [5]. The crystal field parameters were not allowed to vary freely until new values of the primary free-ion parameters F^k and ζ were reasonably established from our Tb^{3+}:$LiYF_4$ results. In subsequent calculations, a least-squares fitting program originally developed by Hannah Crosswhite [8] was used to diagonalize the complete Hamiltonian and optimize the values of chosen parameters. In the final results, both free-ion and crystal field parameters were varied freely for fitting the calculated crystal field splittings to the observed levels.

It was not surprising that fitting the isolated ^7F_J and $^5D_4$ groups in the low energy region alone did not yield a clear correlation between the calculation and the experimental data in the high energy region where dense superposition of levels occurs. This was understandable because the crystal field states in the high energy region have very different characteristics and sensitivities to the free-ion parameters than the pure ^7F_J or $^5D_4$ states in the low energy region. When only the ^7F_J and $^5D_4$ multiplets were fitted, most of the free-ion parameters could not be allowed to vary freely; any inappropriate constraint or fixed values for certain parameters would force the varied parameters to compensate and to produce improper energy levels in the region where no experimental data were assigned.

Assignment of the $^5G_6$ and $^5D_2$ multiplets obtained by two-photon absorption was a breakthrough in our modeling. Levels in that region were required to properly determine the free-ion parameters. After the calculation for these two multiplets and the ^7F_J and $^5D_4$ groups was locked to the observed energy levels by allowing the primary free-ion parameters (F^k, ζ, α, β and γ) to vary freely in the least-squares fitting, clear correlations between the calculation and the experimental results were obtained for the levels below the $^5D_2$ multiplet and above the $^5G_6$ multiplet. Then, we had no difficulty in assigning the observed energy levels from the TSE spectra and the frequency doubled excitation spectra, even in the regions where energy levels of different groups of free-ion levels were mixed. Subsequently, the crystal field parameters were allowed to vary freely, and the energy levels in the ultraviolet absorption spectrum were assigned. The final fit was based on the assignment of a total of 165 observed energy levels from the ground state $^7F_6$ up to the $^5K_7$ group near 42 000 cm^{-1}. The values of the free-ion and crystal field parameters that best fit the observed energy levels are listed in Table 1.

Whereas the primary free-ion parameters F^k, ζ, α, β and γ were well established in fitting the energy level structure, the three-particle parameters T^i were fixed throughout our analysis, and traditional constraints on M^h and P^f ($M^2=0.56M^0$, $M^4=0.31M^0$, $P^4=0.5P^2$, and $P^6=0.1P^2$) were maintained [7,8]. We believe that these three-particle parameters and the relativistic correction parameters would not be independently determined unless a larger number of experimental data characterizing the entire configuration are provided. Even the 165 observed energy levels covering the energy

TABLE 1. Free-ion and crystal-field parameters for Tb^{3+}:$LiYF_4$ (cm^{-1})

F^2	88897±59
F^4	63203±125
F^6	47317±84
ζ	1699±1.5
α	19.32±0.25
β	−577±8
γ	1475±39
M^0	3.0±0.1
P^2	586±36
B^2_0	400±12
B^4_0	−802±36
B^6_0	−57±22
B^4_4	1055±26
B^6_4	754±15
σ^a	9.8

[a] Deviation $\sigma = [\Sigma(\Delta_i)^2/(n-p)]^{1/2}$, where Δ_i is the difference between the observed and calculated energies, $n=165$ is the number of levels fit, and $p=14$ is the number of parameters freely varied.

range of 42 000 cm^{-1} still represent a small portion of the entire $4f^8$ configuration whose energy levels spread up to 190 000 cm^{-1}. Comparing the free-ion parameters of Tb^{3+}:$LiYF_4$ with those of Tb^{3+}:LaF_3 shows that there are only minor differences except for M^0 and P^2; thus, we conclude that for the Tb^{3+} ion, the free-ion parameters are weakly dependent on crystal field of the host materials.

The characteristics of the crystal field eigenfunctions computed in the modeling are very different between the low energy states and the high energy states. Whereas the admixtures of different J-multiplets are less than 0.5% in the ^7F_J and $^5D_4$ states, the states above 26 300 cm^{-1} are significantly mixed. In addition to intermediate coupling, contributions of different J-multiplets are generally higher than 15%, and in some states, J-mixing is as high as 50%.

The crystal field parameters are well determined, except that B^6_0 has a larger uncertainty. The variation of the crystal field parameters from the initial values likely reflects the local structure difference between the Tb^{3+} ion in $LiYF_4$ and in $LiTbF_4$. It was found that different magnitudes of the crystal field parameters could be obtained by separately fitting the experimental data in the low energy region and in the high energy region. If non-linear shielding of the crystal field is not important in this system, this suggests that inadequate experimental data could result in a false solution for the parameterization of crystal field energy structure. As previously obtained in the LaF_3 host [7] the rank 4 and 6 parameters B^4_0, B^4_4, and B^6_6 are likely to have a marked change from Eu^{3+} to Tb^{3+} across the center of the series. Our results show that the magnitudes of these parameters are compatible with the systematic trends in the second half of the series. Since less work has been reported on the first half of the series, variation of the rank 4 and 6 parameters in systematic trends across the entire series is not clear at present.

5. Conclusions

We have applied a variety of laser spectroscopic techniques in resolving the crystal field spectra of Tb^{3+}:$LiYF_4$, which remained as one of the most challenging cases for energy level study of the rare earth series. Combined results from two-photon absorption, two-step excitation, and frequency-doubled one-photon excitation have been used with clear polarization selection rules in probing the complicated Tb^{3+} crystal field spectra in the ultraviolet range. These experiments have greatly expanded our knowledge of highly excited states of rare earth ions in solids, many of which have received little attention. The present work also shows that the opportunities for better understanding and applying multiphoton processes of rare earth ions in solids are quite significant.

Modeling of the energy level structure of Tb^{3+} in $LiYF_4$ is successful based on our analysis of results from a variety of experimental techniques. Free-ion and crystal field parameters have been determined in the least-squares fitting of the 165 assigned energy levels. No constraints on the primary (F^k,ζ) and two-body (α, β and γ) free-ion parameters were necessary, and excellent correlation has been obtained between the experimental data and the computed energy level structure.

Acknowledgment

The work performed at Argonne National Laboratory was under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38. The work performed at Montana State University was supported by NSF/MONTS.

References

1 G.K. Liu, J. Huang, R.L. Cone and B. Jacquier, *Phys. Rev. B, 38* (1988) 11061.
2 J. Huang, G.K. Liu and R.L. Cone, *Phys. Rev. B, 39* (1989) 6348.
3 R.P. Jones, *M.S. Thesis,* Montana State University, 1990, unpublished.

4 C.A. Morrison and R.P. Leavitt, in K.A. Gschneidner, Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 5, North-Holland, Amsterdam, 1982, pp. 461–692.

5 H.P. Christensen, *Phys. Rev. B, 17* (1978) 4060.

6 I. Laursen and L.M. Holmes, *J. Phys. C, 7* (1974) 3765.

7 W.T. Carnall, G.L. Goodman, K. Rajnak and R.S. Rana, *J. Chem. Phys., 90* (1989) 3443.

8 H.M. Crosswhite, *Colloq. Int. CNRS, 255* (1977) 65; H.M. Crosswhite and H. Crosswhite, *J. Opt. Soc. Am. B, 1* (1984) 246.