Journal of Alloys and Compounds 275–277 (1998) 196–199

Journal of
ALLOYS
AND COMPOUNDS

Resonant electron–phonon coupling of Yb^{3+} in YAG

A. Lupei[a,*], V. Enaki[b], V. Lupei[a], C. Presura[a], A. Petraru[a]

[a]Institute of Atomic Physics, Bucharest 76900, Romania
[b]Chisinau State University, Chisinau, Moldova

Abstract

An analysis of Yb^{3+} spectra in YAG in terms of the splitting of the zero-phonon lines in the case of near resonance between Stark levels and sharp peaks in the phonon spectrum is presented. The theoretical relations allow estimation of the position of the electronic level and vibronic coupling strength from the intensity ratio and spectral shifts. A new energy level scheme for the $^2F_{5/2}$ Yb^{3+} multiplet in YAG is proposed. © 1998 Elsevier Science S.A.

Keywords: Laser crystals; Optical spectroscopy; Resonant electron–phonon coupling; Yb^{3+}:YAG

1. Introduction

The investigation of electron–phonon coupling of Yb^{3+} ($4f^{13}$) is an interesting theoretical and experimental problem considering the increasing use of this ion as a laser activator or as a sensitiser for solid state laser systems. The optical spectra of Yb^{3+} should be simple, its electronic structure consisting of only two multiplets, $^2F_{7/2}$ and $^2F_{5/2}$, but in many matrices they are very complex, the multitude of spectral features being associated with the electron–phonon coupling.

In YAG ($Y_3Al_5O_{12}$), Yb^{3+} preponderantly replaces Y^{3+} in *c*-dodecahedral sites of D_2 local symmetry; the degeneracy of the two multiplets is raised and only seven Stark electronic levels are expected (four for the ground and three for the excited state). To explain the observed complex spectral structure, lines of vibronic nature have been considered. There are several reports that have attempted to separate the electronic Stark levels from vibronics [1–4], but the assignments are still ambiguous [5–7]. A crystal field calculation performed on the basis of structural data [6] suggested the necessity of the revision of some previous assignments of Stark levels, especially in the $^2F_{5/2}$ Yb^{3+} excited multiplet [6,7].

The purpose of this paper is to attempt to reanalyse the Yb^{3+} spectra in YAG taking into account the possibility of resonant (quasiresonant) vibronic effects. The splittings of zero-phonon lines due to resonant electron–phonon coupling have been considered to explain some features of Yb^{3+} spectra in $YAlO_3$ [8] and recently in apatites [9] and $CaBaBO_3F$ [10].

The Stark splittings of rare earth (RE^{3+}) ions are of the order of lattice phonons. If the distance between two Stark levels is in near resonance with peaks in the phonon spectrum, the electron–phonon interaction creates modified (nonadiabatic) vibronic states. This leads to changes in the optical spectral lineshapes (broadening, asymmetries or splitting). Splittings of zero-phonon lines of rare earth ions could appear if the phonon densities contain sharp peaks and electron–phonon coupling is nonnegligible. Such effects have been reported in organic and inorganic [8–15] compounds, especially for RE^{3+} ions at the beginning and end of the lanthanide series. Resonant effects could appear for Yb^{3+} in YAG since this ion manifests a strong vibronic coupling [14,15] and in YAG the phonon density presents intense sharp peaks, as demonstrated by IR, Raman or vibronic sidebands [18–21].

The first part of this paper presents a theoretical treatment for the near resonant electron–phonon coupling in the case of RE^{3+} nondegenerate electronic Stark levels [8,22–24] developed for the case of the resonance with phonon peaks between Stark levels close to the final state of an electronic transition. Data for optical Yb^{3+} spectra in YAG are subsequently presented and analysed in terms of resonant effects theory, and characteristic parameters are evaluated.

2. Theoretical background

The theory refers to transitions between electronically

---

*Corresponding author.

PII: S0925-8388(98)00302-8

nondegenerate levels. The transition from an initial pure electronic isolated state $|i\rangle$ to a final state $|f\rangle$, that is separated by another electronic level r with $\Delta_{fr} = E_f - E_r > 0$, is calculated taking into account the resonant electron–phonon interaction; the interaction Hamiltonian being considered in the linear approximation.

The lineshape for an absorption transition induced by light of frequency Ω takes the form

$$F(\Omega) = \frac{1}{2\pi}\sum_f |\langle i|M|f\rangle|^2 \frac{\Gamma(\Omega)}{[\Omega - \Omega_{fi} - \Sigma(\Omega)]^2 + (\Gamma^2(\Omega)/4)} \tag{1}$$

where $|\langle i|M|f\rangle|^2$ is proportional to the intensity of the zero-phonon line (M being the electronic transition operator) in the absence of the near resonant electron–phonon interaction. At low temperatures the shift $\Sigma(\Omega)$ and widths $\Gamma(\Omega)$ of the line for the resonant case [22,23] contain only the phonon emission part

$$\Gamma(\Omega) = 2\pi\sum_r \int \mathrm{d}\omega\, A_r(\omega)\rho(\omega)[n(\omega)+1]\delta(\Omega - \Omega_{fi} + \Delta_{fr} - \omega)$$

$$\Sigma(\Omega) = \sum_r P\int \mathrm{d}\omega \frac{A_r(\omega)\rho(\omega)[n(\omega)+1]}{(\Omega - \Omega_{fi} + \Delta_{fr} - \omega)} \tag{2}$$

The parameters A_r are associated with the matrix elements of the electron–phonon coupling operator and can be estimated in various approximations [22,23], but in this paper they are considered as adjustable parameters; $n(\omega)$ is the phonon occupation number, $\rho(\omega)$ the effective phonon density and P the principal value of the integral. For the resonance with one phonon $\omega_0 \sim \Delta_{fr}$, if the effective phonon density around resonance is described as $\rho(\omega) = a\delta(\omega - \omega_0) + \rho'(\omega)$, with a small deviation from a δ-function, the problem could be simplified. The energy spectrum is given by solution of the equation $\Omega - \Omega_{fi} = \Sigma(\Omega)$. Neglecting ρ' in the phonon density, this equation can be written as

$$\Omega' - \Delta_{fr} - \frac{B}{\Omega' - \omega_0} = 0$$

and has two solutions:

$$\Omega'_{12} = \frac{\Delta_{fr} + \omega_0}{2} \pm \frac{1}{2}[(\Delta_{fr} - \omega_0)^2 + 4B]^{1/2} \tag{3}$$

where $\Omega' = \Omega - \Omega_{ri}$, i.e. the spectrum is measured from the zero-phonon line $i \to r$ and $B = a*A$ is a measure of the vibronic coupling (including the phonon density) and will be considered as a global parameter that can be estimated from experiment. The zero-phonon line $i \to f$ is split into two components and the intensity ratio of the components (using Eq. (1)) is approximately given by

$$\frac{I_1}{I_2} = \frac{\Omega'_2 - \Delta_{fr}}{\Delta_{fr} - \Omega'_1} \tag{4}$$

From experimental data for Ω'_1, Ω'_2 and I_1/I_2 one can estimate ω_0, Δ_{fr} and B which can then be used in numerical simulations where the phonon peak can be taken not as a δ-function, but with a dispersion around the resonance frequency ω_0. One could replace the phonon density around the resonance with a Lorentz function [22]. The quasiresonant problem in the case of more phonon peaks in the resonance region could be solved numerically if one makes some assumptions about the phonon density, such as taking it as a sum of weighted Lorentz functions centred on the phonon peaks. However, this induces many adjustable parameters.

3. Results

Czochralski grown samples of YAG doped with 5–10 at% Yb^{3+} were measured at 10, 77 and 300 K with a Cary 17 spectrometer. Fig. 1 presents the absorption spectrum corresponding to the $^2\mathrm{F}_{7/2} \to {}^2\mathrm{F}_{5/2}$ transitions of Yb^{3+} (5 at%) in YAG at 77 K, measured from zero-phonon line A (10 327 cm^{-1}). It should contain three zero-phonon lines corresponding to Stark splitting of the $^2\mathrm{F}_{5/2}$ multiplet in D_2 local symmetry.

The assignments given by various authors for the electronic Stark structure of Yb^{3+} in YAG are given in Table 1. One can see that the data are contradictory; even the latest published data [7] present some ambiguity for the $^2\mathrm{F}_{5/2}$ multiplet. The difficulty in assignment comes from interferences with intense vibronics. In previous assignments, the absorption and emission spectra (or high temperature absorption) folded around line A were compared. Assuming that electron–phonon coupling does not depend on the electronic state, the same vibronic lines should appear in both absorption and emission spectra [3,4] and the electronic lines would be those that do not appear in pairs; these were B, C and C′ (Fig. 1). However,

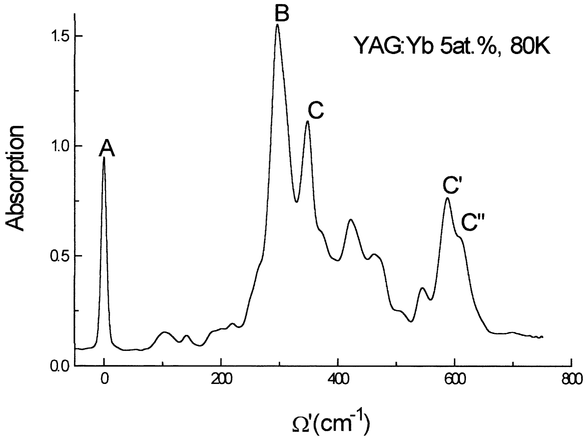

Fig. 1. Absorption spectrum corresponding to the $^2\mathrm{F}_{7/2} \to {}^2\mathrm{F}_{5/2}$ transitions of Yb^{3+} (5 at%) in YAG at 80 K, measured from zero-phonon line A.

Table 1
Energy levels of Yb^{3+} in YAG

Term	Energy (cm^{-1})				T (K)	Ref.
$^2F_{7/2}$	0	140	490	620	77	[1]
	0	611	696	782	77	[3,5]
	0	565	612	785	77	[4,7]
	0	584	635	783		[6]
$^2F_{5/2}$	10336	10640	10929		77	[1]
	10321	10620	10674		77	[3,5]
	10327	10624	10679		77	[4]
	10328	10752	10917			[6]
	10327	10624[a]	10679[a]	10 912	77	[7]
	10327	10650	10923		10, 80	This work

[a] Denotes a nondefinite assignment.

the temperature dependence of C′ is an argument for its rejection as a zero-phonon line [3].

Our measurements show that the opposite temperature shift of C′ compared with A, B and C is only apparent and is determined by the increase and broadening of the C″ line. Therefore, one electronic line could be in the (C′, C″) region as proposed in Refs. [6,7] and the other in the (B, C) region. If one compare Yb^{3+} absorption spectra at 10 K (assuming as before that all sidebands are associated with zero-phonon line A) with all available data on phonon peaks (sidebands), two intense phonon peaks are missing: one around 325–328 cm^{-1} (observed as a very strong sideband in Eu^{3+}, Nd^{3+} and Cr^{3+} [19,20] or Er^{3+} [21] spectra in YAG) and another around ~595–602 cm^{-1} (with medium intensity [19,20]). These facts give us ground to consider the possibility of resonant splitting due to interaction with these very active phonons in YAG.

The proposed model is presented schematically in Fig. 2. Thus, we assume that the B and C lines are associated with the resonant splitting of the second Stark level E_2 of $^2F_{5/2}$, while the C′ and C″ lines correspond to the splitting of the third Stark level E_3.

Although two sharp phonon peaks in YAG were previously observed as sidebands in other RE^{3+} spectra at ~546 and ~600 cm^{-1} [19,20], in Yb^{3+} spectra (Fig. 1) only the first is present. However, if the C′ and C″ lines are considered as resonantly split, relation (4) gives $\Delta_{fr} \sim 596\ cm^{-1}$ ($E_3 \sim 10\,921\ cm^{-1}$), $\omega_2 \sim 603\ cm^{-1}$ (in very good agreement with the phonon peak [19,20]) and $B^{1/2} \sim 13\ cm^{-1}$.

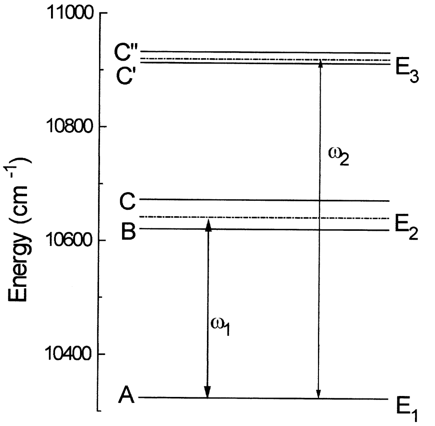

Fig. 2. Model of the assignment of Stark components of the $^2F_{5/2}$ multiplet of Yb^{3+} in YAG in terms of resonant effects.

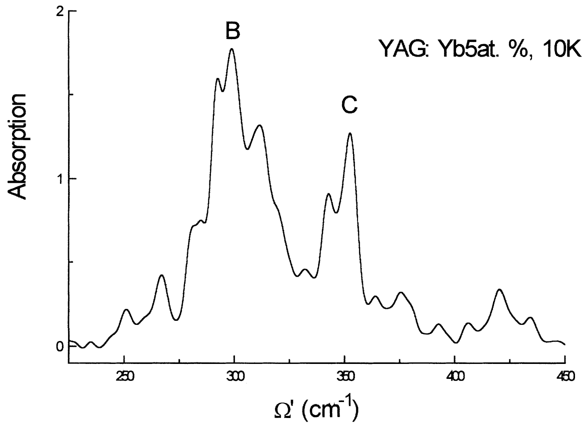

Fig. 3. Region of the absorption spectrum ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) of Yb^{3+} (5 at%) in YAG at 10 K, measured from zero-phonon line A.

The (B, C) region is more complex, as shown in Fig. 3, where part of the absorption spectrum at 10 K (measured from A) is presented. The relative intensities of various lines were obtained by decomposition with Lorentzian lineshapes. Assuming that B and C are resonantly split, fitting with relation (4) gives $\Delta_{fr} \sim 323\ cm^{-1}$ ($E_2 \sim 10\,650\ cm^{-1}$), $\omega_1 \sim 326\ cm^{-1}$ and $B^{1/2} \sim 26\ cm^{-1}$. The other peaks around B or C are vibronics that present an increase in intensity, although their position (in the limit of experimental errors of previously published data) is unshifted.

4. Discussion

The new proposed energy level scheme for the $^2F_{5/2}$ Yb^{3+} multiplet in YAG, based on resonant splitting, is given in Table 1. Several additional arguments in favour of our assignment can be invoked. (i) The larger crystal field splitting of the $^2F_{5/2}$ multiplet, suggested by calculations [6], is sustained by comparison with total splittings of the ground multiplet $^2F_{7/2}$ in different crystals such as YGG [3] and $YAlO_3$ [8]. The second Stark level of $^2F_{5/2}$ should be in the B, C region, otherwise one cannot explain the anomalous increase of vibronic intensities in this region. (ii) The similarity of the Yb^{3+} absorption in YAG to that in $Lu_3Al_5O_{12}$ (LuAG) [4]. The vibronics observed in LuAG are very similar to those in YAG [19,20]. This similarity comes from the fact that most of the vibration peaks in YAG can be associated with motion inside or outside AlO_4^{5-} tetrahedra. The Yb^{3+} spectra in YGG are different [3]. In this case the vibration peaks are also different [18] since they are essentially determined by GaO_4^{5-} tetrahedral vibrations [20].

The strength of the vibronic coupling estimated from resonant effects is rather large; however, parameter $B^{1/2}\sim$ 13 and ~26 cm^{-1} for interaction with phonons ω_2 and ω_1, respectively, are comparable to the interaction parameter $V\sim 10\ \mathrm{cm}^{-1}$ used in Ref. [9] to simulate the Yb^{3+} emission spectrum in apatites. Two factors could give strong coupling: one associated with the ion (the largest coupling for Yb^{3+} [16,17] as compared with other RE^{3+} ions in the same matrix) and the observation that intense vibronic satellites occur in inorganic compounds with tetrahedral groups (such as YAG) [11,19,20].

Most of the vibronics (not involved in resonance) for Yb^{3+}: YAG can be associated with line A (93, 104, 143, 184, 200, 220, 250, 267, 283, 292, 310, 343, 364, 376, 393, 406, 420, 433, 450, 463, 477, 512, 541, 700 cm^{-1}), but an anomalous increase in the intensities of the vibronics situated in the region of another electronic transition is observed in Figs. 1 and 3, even if their positions are not shifted [19,20]. This problem could be solved numerically by taking into account more phonons in the resonance regions.

5. Conclusions

Due to the intensive use of Yb^{3+} as an active or sensitiser ion in laser systems, its spectroscopic characteristics should be well understood. Since the published data concerning the energy levels of Yb^{3+} in YAG are contradictory, due mainly to strong vibronics, we reanalysed the Yb^{3+} absorption spectra in YAG in terms of the near resonant electron–phonon coupling effects. The fact that Yb^{3+} is an ion with strong electron–phonon coupling and the phonon density of YAG presents sharp peaks (associated with vibrations of tetrahedral group) were grounds for this approach. By comparing experimental data with theoretical expressions, the positions of the electronic levels and coupling strength have been estimated. A new electronic energy level diagram for the $^2F_{5/2}$ Yb^{3+} multiplet in YAG is proposed, the positions of the excited Stark levels being shifted from intense absorption lines. The electronic line intensity is shared by divided mixed vibronics created by resonant electron–phonon coupling.

The large resonant splittings of the electronic levels in this case are comparable to those observed for Yb^{3+} in other matrices [9,10] and to a theoretical evaluation for isoelectronic Tm^{2+} in fluoride crystals [25]. The estimated values of the electron–phonon coupling parameters from resonant splitting data for Yb^{3+} (13–26 cm^{-1}) in this work and for Tm^{3+} (~5 cm^{-1}) [15] in YAG, show the same trend of increasing towards the end of the lanthanide series as the recent data obtained from line broadening or vibronic sidebands [16,17].

References

[1] D.L. Wood, J. Chem. Phys. 39 (1963) 1671.
[2] J.A. Koningstein, Teor. Chim. Acta 3 (1965) 271.
[3] R.A. Buchanan, K.A. Wickersheim, J.J. Pearson, G.F. Herrmann, Phys. Rev. 159 (1967) 245.
[4] G.A. Bogomolova, D.N. Vylegzhanian, A.A. Kaminskii, Sov. Phys. JETF 42 (1976) 440.
[5] J.J. Pearson, G.F. Herrmann, K.A. Wickersheim, R.A. Buchanan, Phys. Rev. 159 (1967) 245.
[6] G.A. Bogomolova, L.A. Bumagina, A.A. Kaminskii, B.Z. Malkin, Sov. Solid State Phys. 19 (1977) 1439.
[7] A.A. Kaminskii, Laser Crystals, Springer, Berlin, 1981, p. 146.
[8] Yu.E. Perlin, A.A. Kaminskii, V.N. Enaki, D.N. Vilegzhanin, Pis'ma JETF 30 (1979) 426.
[9] L.D. DeLoach, S.A. Payne, W.L. Kway, J.B. Tassano, S.N. Dixit, W.F. Krupke, J. Lumin. 62 (1994) 85.
[10] K.I. Schaffers, L. De Loach, S.A. Payne, IEEE J. Quantum Electron. 32 (1996) 741.
[11] P. Caro, O.K. Moune, E. Antic-Fidancev, M. Lemaitre-Blaise, J. Less-Common Met. 112 (1985) 153.
[12] M. Dahl, G. Schaak, Phys. Rev. Lett. 56 (1986) 232.
[13] H. Gerlinger, G. Schaach, Phys. Rev. B 33 (1986) 7438.
[14] V.D. Savchenko, V.I. Tsaryuk, V.F. Zolin, Yu.K. Gusev, Spectroscopy of Crystals Activated by Rare earths and Transition Metal Ions, Proc. SPIE, Vol. 2706 (1996) 134.
[15] A. Lupei, V. Lupei, J. Phys.: Condensed Matter 9 (1997) 2807.
[16] A. Ellens, H. Andreas, M.L.H. ter Heerdt, R.T. Wegh, A. Meijerink, G. Blasse, Phys. Rev. B 55 (1997) 180.
[17] A. Ellens, H. Andreas, A. Meijerink, G. Blasse, Phys. Rev. B 55 (1997) 173.
[18] A.M. Hofmeister, K.R. Campbell, J. Appl. Phys. 72 (1992) 638.
[19] V.M. Markushev, V.I. Tsaryuk, V.F. Zolin, Opt. Spectrosc. 58 (1985) 583 (in Russian).
[20] V.F. Zolin, V.M. Markushev, A.T. Sobolev, V.I. Tsaryuk, Izv. Akad. Nauk 21 (1985) 286 (in Russian).
[21] V.I. Jekov, T.M. Murina, Yu.N. Polivanov, M.N. Popova, A.M. Prohorov, Sov. Solid State Phys. 25 (1985) 1510 (in Russian).
[22] Yu.E. Perlin, V.N. Enaki, Physical Processes in Semiconductors, Stiinta, Chisinau, 1981 (in Russian).
[23] V.N. Enaki, Nonequilibrium Processes in Multicomponent Crystals, Stiinta, Chisinau, 1988 (in Russian).
[24] O.L. Malta, J. Phys. Chem. Solids 56 (1995) 1053.
[25] I. Ignatiev, V. Ovsiankin, J. Lumin. 72–74 (1997) 679.