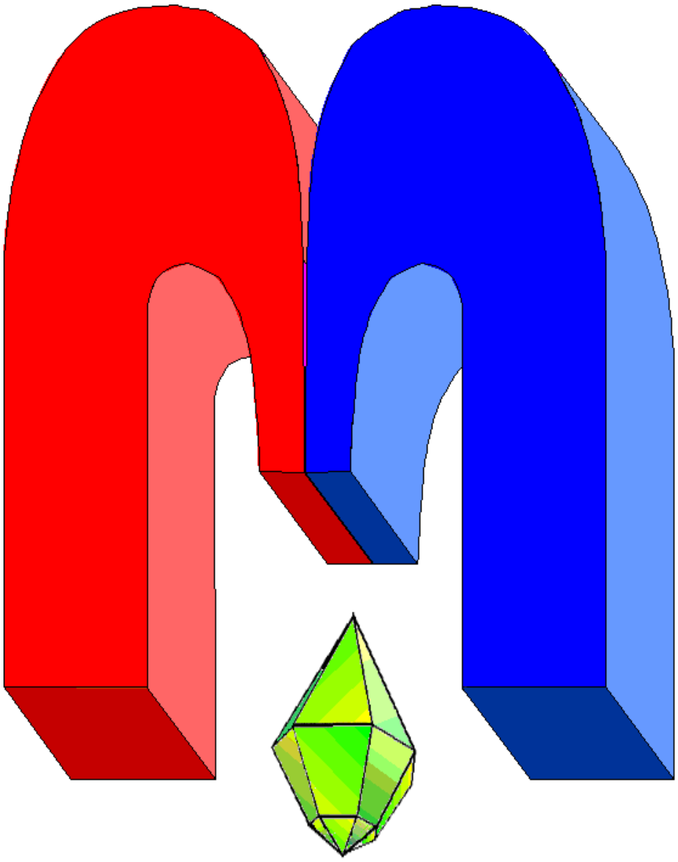
ISSN 2072-5981



agnetic Resonance in Solids

Electronic Journal

Volume **11,** *No.* **1,**
pages **14-19,**
2009

http://mrsej.ksu.ru

Established and published by Kazan State University
Sponsored by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press, August 2, 1996
First Issue was appeared at July 25, 1997

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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Electron-phonon interaction in the $4f^{12}5d$ electronic configuration of the Tm^{2+} ion in CaF_2

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(*Received October, 28, 2009; accepted November, 8, 2009*)

The low temperature $4f^{13}$–$4f^{12}5d$ absorption and emission band shapes of the impurity Tm^{2+} ions have been simulated within adiabatic approximation on the basis of a microscopic model operating with the real phonon spectrum of the host CaF_2 lattice. Crystal field parameters and electron-phonon coupling constants were treated in the framework of the exchange charge model. Results of simulations of the spectral envelopes agree satisfactorily with the experimental data available from literature.

PACS: 78.20.Bh; 78.40.Ha

Keywords: 4f–5d spectra, electron-phonon interaction, CaF_2

1. Introduction

A method for calculation of energy level patterns and transition intensities in the $4f^n$–$4f^{n-1}5d$ spectra of divalent impurity rare earth ions in cubic crystal field was developed in [1,2]. However, to simulate the $4f^n$–$4f^{n-1}5d$ optical spectra, it is necessary to take into account interaction between the electronic and lattice excitations. Most of intensity of the $4f^n$–$4f^{n-1}5d$ transitions is in broad vibrational bands with widths up to a thousand of wave numbers even at liquid helium temperature due to interaction of a 5d electron with the host lattice. Simulations of such vibrational bands have not been presented in literature, bands are usually approximated as Gaussians with three adjustable parameters: the offset, the bandwidth and the intensity ratio of the zero-phonon line to the vibrational band [3,4].

The goal of the present work is to simulate uniformly the energy level structure and the electron-vibrational band shapes for absorption and emission $4f^{13}$–$4f^{12}5d$ spectra of the impurity Tm^{2+} ions in CaF_2 crystal and to compare the results with the recent experimental data [5].

2. Simulation of $4f^{13}$–$4f^{12}5d$ optical spectra of the Tm^{2+} ion in CaF_2 crystal

To simulate inter-configuration $4f^{13}$–$4f^{12}5d$ spectral envelopes for CaF_2:Tm^{2+} crystal, we used the approach derived in [6] for trivalent impurity rare earth ions in $LiYF_4$ crystal. This approach involves calculations of crystal field parameters for a 5d electron as explicit functions of lattice ion's coordinates in the framework of the exchange charge model [7], numerical diagonalization of the effective impurity ion Hamiltonian containing energies of electrostatic Coulomb and exchange interactions between electrons, spin-orbit interactions and the crystal field interactions for the ground ($4f^{13}$) and excited ($4f^{12}5d$) electronic configurations; calculations of the 5d electron-phonon coupling constants, and simulations of the band shapes within adiabatic Condon approximation for low temperatures by making use of the realistic phonon spectrum of the host crystal lattice. Since a 5d electron, having a more extended orbital, interacts with the lattice much stronger than 4f electrons, it is possible to neglect interaction of 4f electrons with phonons.

Impurity Tm^{2+} ions substitute for Ca^{2+} ions in CaF_2 crystal in sites with the O_h point symmetry. In the nearest surrounding of the Ca-site, there are eight fluorine ions which form a cube with distance $R = 2.3642$ Å from the Ca^{2+} ion. Since the effective ionic radii of Tm^{2+} and Ca^{2+} do not differ much, no local deformations of CaF_2 lattice were introduced.

The crystal field energy of the localized electron can be defined as

$$H_{cf} = \sum_{p,k} B_k^p C_k^{(p)} . \tag{1}$$

Here B_k^p are the crystal field parameters, $C_k^{(p)}$ are the components of one-electron spherical tensor operators $\boldsymbol{C}^{(p)}$. Crystal field parameters for the 5d electron, as functions of ligand coordinates, were calculated as a sum of contributions from lattice point charges and exchange charges, which account for overlap with the ligands' outer electronic shells ns^2 and np^6:

$$B_k^p(5\text{d}) = e^2 \sum_{L,s} \{ -q_{Ls} < 5\text{d}|r^p|5\text{d} > \beta_p(R_{Ls}) + \frac{2(2p+1)}{5} R_{Ls}^p S_p^{(5\text{d})}(Ls) \} \cdot (-1)^k C_{-k}^{(p)}(\vartheta_{Ls}, \varphi_{Ls}) / R_{Ls}^{p+1} , \tag{2}$$

where the sum is taken over all ions in the host lattice with charges eq_{Ls} and the spherical coordinates R_{Ls}, θ_{Ls}, φ_{Ls} (unit cells and ions in the cell are labeled by L and s, respectively); $< 5\text{d}|r^p|5\text{d} >$ are the moments of the 5d electron density. The field of exchange charges is defined by quadratic forms of the overlap integrals $<5\text{d}l_z|\text{n}l l_z>$ ($S_s = <5\text{d}0|\text{ns}0>$, $S_\sigma = <5\text{d}0|\text{np}0>$, $S_\pi = <5\text{d}1|\text{np}1>$)

$$S_p^{(5\text{d})}(Ls) = G_s S_s^2(Ls) + G_\sigma S_\sigma^2(Ls) + \gamma_p G_\pi S_\pi^2(Ls) , \ \gamma_2 = 1, \gamma_4 = -4/3; \tag{3}$$

G_s, G_σ, G_π are the phenomenological parameters of the model. The coefficients $\beta_p(R_{Ls})$ [8] account for extended charge distributions of an impurity ion 5d electron and its ligands' outer electrons and were calculated exactly utilizing bipolar expansion.

Ion charges q_{Ls} were fixed as +2 (Ca^{2+}), –1 (F^-). The moments of the 5d electron density $< 5\text{d}|r^p|5\text{d} >$, overlap integrals $<5\text{d}l_z|2l l_z>$ and the $\beta_p(R_{Ls})$ coefficients were calculated using the analytical radial 5d function of the Tm^{2+} ion presented in [9] and the 2s, 2p functions of the F^- ion from [10]. The calculated moments equal $< 5\text{d}|r^2|5\text{d} > = 1.6546$ Å^2, $< 5\text{d}|r^4|5\text{d} > = 4.7826$ Å^4. The dependences of overlap integrals on the distance R (for $2.2\,\text{Å} < R < 2.5\,\text{Å}$) between the Tm^{2+} and the F^- ions were approximated as

$$S_s = < 5\text{d}0 \,|\, 2\text{s}0 > = 1.23302 - 0.68714 \cdot R + 0.1 \cdot R^2 , \tag{4a}$$

$$S_\sigma = < 5\text{d}0 \,|\, 2\text{p}0 > = 0.00443 + 0.18757 \cdot R - 0.05429 \cdot R^2 , \tag{4b}$$

$$S_\pi = < 5\text{d}1 \,|\, 2\text{p}1 > = 1.00553 - 0.59507 \cdot R + 0.09286 \cdot R^2 . \tag{4c}$$

The following approximations were obtained for the $\beta_p(R)$ coefficients (for $2.2\,\text{Å} < R < 2.5\,\text{Å}$):

$$\beta_2(R) = -5.73565 + 4.09841 \cdot R - 0.64083 \cdot R^2 , \tag{5a}$$

$$\beta_4(R) = -1.5127 - 0.72504 \cdot R + 0.46358 \cdot R^2 . \tag{5b}$$

The calculated $\beta_4(R_{Ls})$ coefficients are negative, thus indicating the strong overlap between charge distributions of a 5d electron and ligands' outer electrons is to be considered strictly.

Integral intensities of 4f^{13}–4f^{12}5d transitions, proportional to the squared matrix elements of the electronic dipole moment, were calculated by making use of the impurity ion Hamiltonian eigenfunctions.

The 5d electron-phonon interaction, linear in dynamic displacements of the lattice ions, was considered within the cluster approximation: modulation of the crystal field by ligand vibrations was considered only. The 5d electron-phonon coupling constants were obtained by direct differentiation of corresponding crystal field parameters with respect to the lattice ion coordinates.

Lattice vibrations were considered in the harmonic approximation. The vibration spectrum of the $\mathrm{CaF_2}$ crystal lattice was studied in [11]. The maximum phonon frequency of this crystal equals 477 $\mathrm{cm^{-1}}$. Results of optical absorption and neutron inelastic scattering experiments were described successfully in the framework of the shell model [12]. Using parameters of this model, we computed frequencies and polarization vectors of vibrations for 216000 wave vectors distributed over the Brillouin zone. Imaginary parts of the lattice advanced Green's functions for the displacements of ions in the cluster $\mathrm{Ca^{2+}F^-_8}$ were calculated at the equally spaced 954 points on the frequency axis by numerical integration over the Brillouin zone. Spectral density for shell motion relative to the ion core is much smaller than spectral density for ion vibrations, thus we neglected the difference in Green's functions for the displacements of ions and shells.

Symmetrized displacements of a cubic cluster are given in [13]. We needed the explicit expression of the only full symmetric displacement of the cluster: it corresponds to radial displacements towards the central ion of all eight fluorine ions.

3. Results and discussion

The ground configuration $4\mathrm{f}^{13}$ of the $\mathrm{Tm^{2+}}$ ion in $\mathrm{CaF_2}$ crystal consists of 5 levels, which correspond to O_h group irreducible representations Γ_{7u}, Γ_{8u}, Γ_{6u} (term ${}^2F_{7/2}$), Γ_{7u}', Γ_{8u}' (term ${}^2F_{5/2}$) in the order of energy increase. Level energies are determined by three parameters: crystal field parameters $B_0^4(4\mathrm{f})$ and $B_0^6(4\mathrm{f})$ (in the crystallographic system of coordinates) and spin-orbit interaction constant $\zeta(4\mathrm{f})$. These parameters were varied to fit the level energies, obtained in [14] by measurements of $\mathrm{CaF_2{:}Tm^{2+}}$ (0.05%) crystal $4\mathrm{f}-4\mathrm{f}$ optical spectra. The calculated $4\mathrm{f}^{13}$ level energies, relative to the ground Γ_{7u} level energy, equal (in $\mathrm{cm^{-1}}$, the measured values [14] are in parenthesis): Γ_{8u} 554 (557), Γ_{6u} 672 (symmetry forbidden, was not observed), Γ_{7u}' 8933 (8961), Γ_{8u}' 9386 (9377). The obtained values of the varied parameters equal $\zeta(4\mathrm{f}) = 2508$ $\mathrm{cm^{-1}}$, $B_0^4(4\mathrm{f}) = -1647$ $\mathrm{cm^{-1}}$, $B_0^6(4\mathrm{f}) = 333$ $\mathrm{cm^{-1}}$.

The $\mathrm{Tm^{2+}}$ excited configuration $4\mathrm{f}^{12}5\mathrm{d}$ consists of 303 levels (910 states), which correspond to O_h group irreducible representations Γ_{6g} (75 levels), Γ_{7g} (76 levels), Γ_{8g} (152 levels). Level energies are determined by three parameters, discussed above, and eleven more parameters: crystal field parameter $B_0^4(5\mathrm{d})$, spin-orbit interaction constant $\zeta(5\mathrm{d})$, parameters of electrostatic interaction $F^{(2)}(\mathrm{ff})$, $F^{(4)}(\mathrm{ff})$, $F^{(6)}(\mathrm{ff})$, $F^{(2)}(\mathrm{fd})$, $F^{(4)}(\mathrm{fd})$, $G^{(1)}(\mathrm{fd})$, $G^{(3)}(\mathrm{fd})$, $G^{(5)}(\mathrm{fd})$, energy shift of the excited configuration Δ.

We used the values of electrostatic interaction parameters $F^{(2)}(\mathrm{fd})$, $F^{(4)}(\mathrm{fd})$, $G^{(1)}(\mathrm{fd})$, $G^{(3)}(\mathrm{fd})$, $G^{(5)}(\mathrm{fd})$, obtained for $\mathrm{Lu^{3+}}$ ion in $\mathrm{LiYF_4}$ crystal [6]. The value of spin-orbit interaction constant $\zeta(5\mathrm{d})$ was fixed at 1719 $\mathrm{cm^{-1}}$ (that is 90% of the value 1910 $\mathrm{cm^{-1}}$, calculated in [15] with the use of standard programs of atomic physics for the isoelectronic ion $\mathrm{Yb^{3+}}$).

Values of the other parameters – Δ, $F^{(2)}(\mathrm{ff})$, $F^{(4)}(\mathrm{ff})$, $F^{(6)}(\mathrm{ff})$ and $B_0^4(5\mathrm{d})$ – were varied to fit the experimental data on inter-configuration $4\mathrm{f}^{13}$–$4\mathrm{f}^{12}5\mathrm{d}$ optical spectra of $\mathrm{CaF_2{:}Tm^{2+}}$ crystal [5]. The obtained values equal $F^{(2)}(\mathrm{ff}) = 122544$ $\mathrm{cm^{-1}}$, $F^{(4)}(\mathrm{ff}) = 64210$ $\mathrm{cm^{-1}}$, $F^{(6)}(\mathrm{ff}) = 46243$ $\mathrm{cm^{-1}}$, $B_0^4(5\mathrm{d}) = -41000$ $\mathrm{cm^{-1}}$. The obtained values of the phenomenological parameters of the exchange charge model equal $G_s = 2$, $G_\sigma = 2.563$, $G_\pi = 0.2$. These values do not differ much from the values established for $\mathrm{Ce^{3+}}$ and $\mathrm{Lu^{3+}}$ ions in $\mathrm{LiYF_4}$ crystal [6]. The following contributions to the crystal field parameter $B_0^4(5\mathrm{d})$ can be distinguished: exchange charge field (–58219 $\mathrm{cm^{-1}}$), ligands' point charge field (14869 $\mathrm{cm^{-1}}$), lattice point charge field excluding ligands' contribution (2350 $\mathrm{cm^{-1}}$).

It is possible to interpret levels of the Tm^{2+} ion excited configuration by considering a superimposition of a 5d electron spectrum and a 4f^{12} electronic configuration spectrum and afterwards taking into account electrostatic interaction between a 5d electron and 4f electrons. Cubic crystal field splits the 5d states into a term e_g (ground level in eightfold surrounding) and a term t_{2g}. Terms of the 4f^{12} configuration are well known [16]: $^3H_6$, $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$, $^3F_2$, $^1G_4$, $^1D_2$, $^1I_6$, $^3P_0$, $^3P_1$, $^3P_2$ and $^1S_0$, in the order of energy increase.

Calculated crystal field energies (relative to the ground 4f^{12}5d state energy) and the Huang-Rhys parameters for the Tm^{2+} 4f^{12}5d states, dependent on a state ordinal number, are given in Fig. 1. As seen from Fig.1, the lowest 200 4f^{12}5d states originate mainly from the 5d e_g term: the e_g states have the Huang-Rhys parameter nearly twice larger than the t_{2g} states (this was confirmed by simulation of a 4f–5d absorption spectrum for a cubic Ce^{3+} impurity center in CaF$_2$ crystal using the same approach). Transitions to these 200 states determine the 4f^{13}–4f^{12}5d absorption spectrum of CaF$_2$:Tm^{2+} crystal measured in [5]. These 200 states can be divided into 5 groups, corresponding to the 4f^{12} terms $^3H_6$, $^3F_4$, $^3H_5$, $^3H_4$ and $^3F_3$, superimposed on the 5d e_g term, as shown in Fig. 1. Thus, we can interpret the bands, observed in CaF$_2$:Tm^{2+} absorption spectrum [5], as shown in Fig. 2.

The 4f^{12} configuration $^3F_2$ term energy (~20000 cm^{-1} [16]) is close to the energy gap between the e_g and t_{2g} 5d terms, therefore a continuum of electronic states with different Huang-Rhys parameters is observed for the 4f^{12}5d states with ordinal numbers from 200 to 300 (see Fig. 1). The 4f^{12}5d electronic states with ordinal numbers from 300 to 450 and from 740 to 900 originate mainly from the 5d t_{2g} term.

We calculated the 4f^{13}–4f^{12}5d absorption envelopes for the lowest 200 Tm^{2+} 4f^{12}5d states in adiabatic Condon approximation at zero temperature. Only interaction with the full symmetric

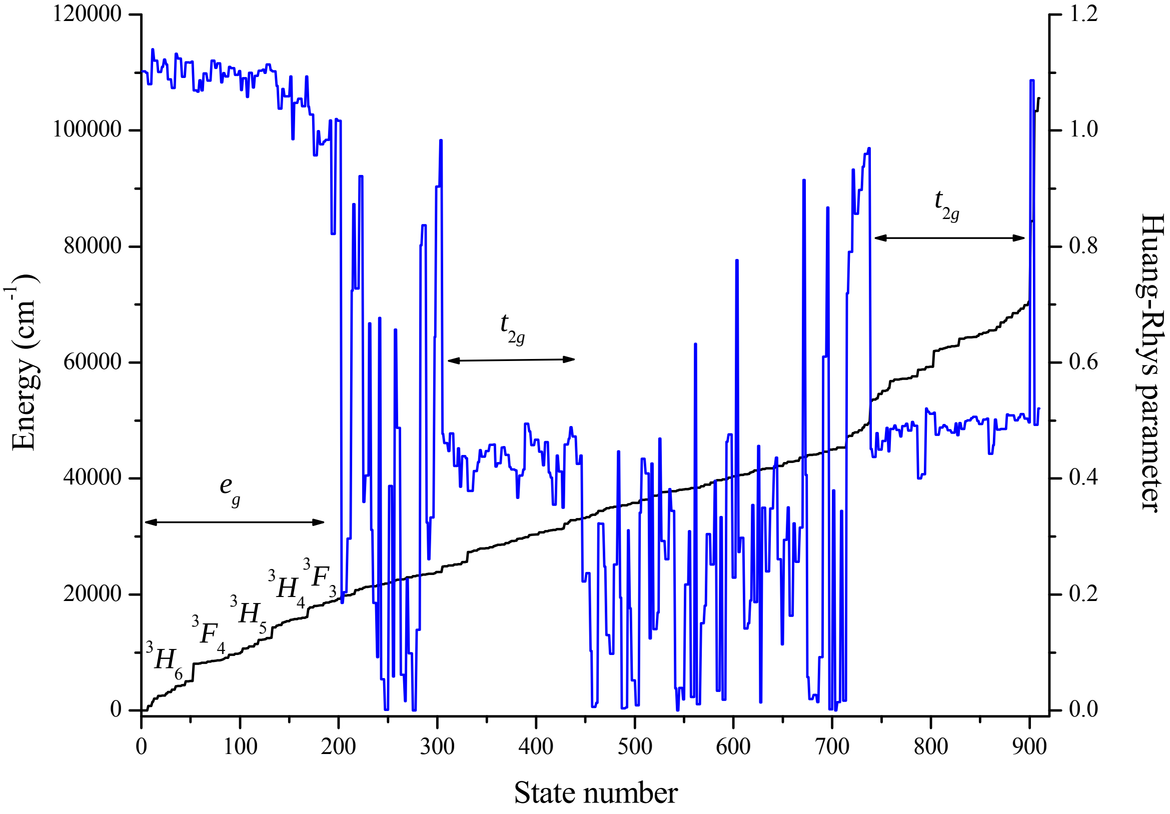

Figure 1. Calculated energies (black line, left scale) and Huang-Rhys parameters (blue line, right scale) of 4f^{12}5d states of the Tm^{2+} ion in CaF$_2$ crystal

displacement of the F^- cubic cluster was taken into account. The calculated band shapes were convoluted with the Lorentzian to take into account relaxation broadening. To estimate relaxation broadening width we calculated probabilities of spontaneous one-phonon transitions from each $4f^{12}5d$ state, induced by non-full symmetric phonons at zero temperature. In Fig. 2 calculated and measured [5] $4f^{13}$–$4f^{12}5d$ absorption spectra of CaF_2:Tm^{2+} crystal are compared. Agreement with experimental data is satisfactory; for example, calculated band widths are close to the measured ones. Pronounced fine structure is observed in the calculated spectrum, as it corresponds to transitions with the Huang-Rhys parameters close to 1. The calculated spectrum should be convoluted with the Lorentz distribution with a width ~250 cm^{-1} to conform experimental spectrum, which exhibits no fine structure (see Fig. 2). Calculated relaxation broadening widths are, in average, much smaller than 250 cm^{-1}.

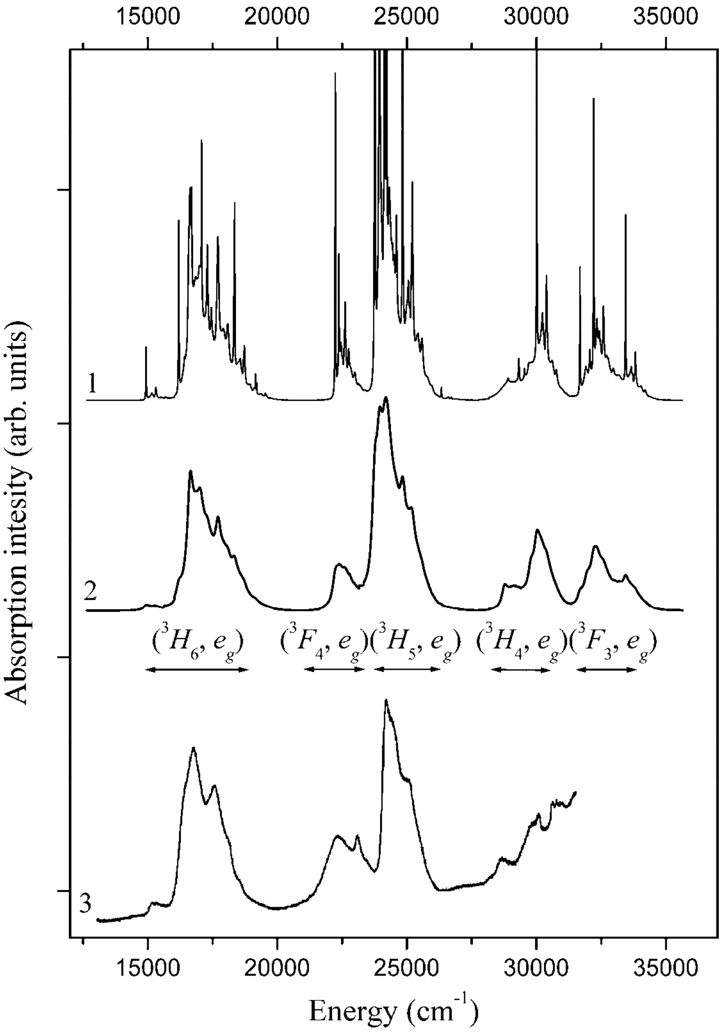

Figure 2. $4f^{13}$–$4f^{12}5d$ absorption spectra of CaF_2:Tm^{2+} crystal: calculated at zero temperature (1 – relaxation broadening widths are proportional to calculated probabilities of spontaneous one-phonon transitions, 2 – relaxation broadening width equals 250 cm^{-1}) and measured (3) at 10 K [5]. Bands interpretation obtained in the present paper is indicated

As follows from our calculations, the lowest Tm^{2+} $4f^{12}5d$ states are a Kramers doublet Γ_{6g} and a quadruple Γ_{8g}. Electric dipole transition to the ground Tm^{2+} $4f^{13}$ state Γ_{7u} is symmetry forbidden for the former and spin forbidden for the latter. In Fig. 3 calculated and measured [5] $4f^{12}5d$–$4f^{13}$ emission spectra of CaF_2:Tm^{2+} crystal are compared. Agreement with experimental data is very good (the calculated spectrum was convoluted with the Gauss distribution with the width 19 cm^{-1} to take into account inhomogeneous broadening). The vibrational band observed in emission spectrum [5] corresponds to transitions with the birth of one phonon. Shape of this band, with the maxima on 225 cm^{-1} and 375 cm^{-1} counting from the zero-phonon transition energy, is determined by spectral density of the full symmetric displacement of the F^- cubic cluster.

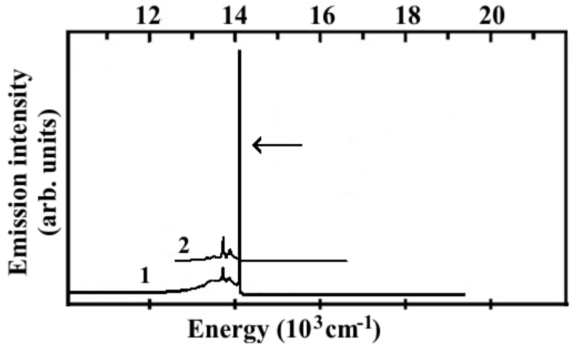

Figure 3. $4f^{12}5d$–$4f^{13}$ emission spectra of CaF_2:Tm^{2+} crystal, measured (1) at 10 K [5] and calculated (2) at zero temperature. Arrow marks the top of the calculated zero-phonon line

4. Summary

The following results have been obtained in this work. The $4f^{13}$–$4f^{12}5d$ absorption spectrum of CaF_2:Tm^{2+} crystal in the range 14000 – 34000 cm^{-1} is determined by transitions involving $4f^{12}5d$ electronic states that originate mainly from the e_g states of a 5d electron. The Huang-Rhys parameters of these transitions are close to 1 (intermediate electron-lattice coupling). Terms ($^{2S+1}L_J, e_g$), where $^{2S+1}L_J$ are terms of the $4f^{12}$ configuration, were put in correspondence to the bands, observed in CaF_2:Tm^{2+} absorption spectrum [5]. CaF_2:Tm^{2+} crystal emission at low temperatures has a Condon shape. Agreement between calculated and measured [5] $4f^{13}$–$4f^{12}5d$ absorption and emission spectra of CaF_2:Tm^{2+} crystal is satisfactory. It is necessary to consider multiphonon relaxation and interaction with the non-full symmetric phonons in simulation of $4f^{13}$–$4f^{12}5d$ CaF_2:Tm^{2+} absorption spectrum to achieve better agreement with the experimental data.

Acknowledgements

The author is grateful to B.Z. Malkin for valuable discussions. This work was supported by the Russian Foundation of Basic Research (Grant 09-02-00930) and by the Ministry of education and science of Russian Federation (Projects RNP 2.1.1.7348 and 2.1.1/2985).

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