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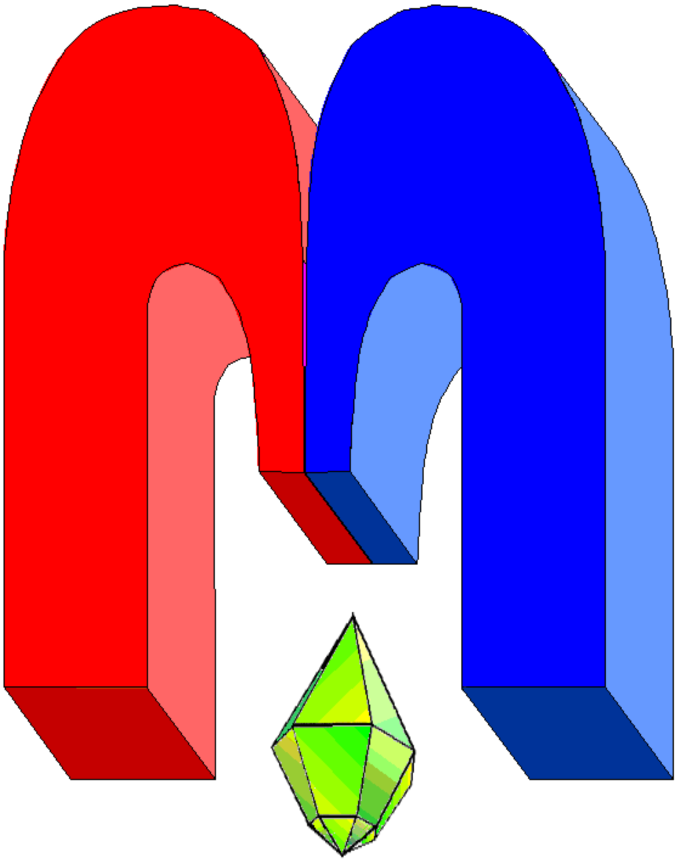

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Low-temperature luminescence spectrum of forbidden $4f^{13}5d$–$4f^{14}$ transitions in $\mathrm{CaF_2{:}Lu^{3+}}$ crystal

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The $\mathrm{Lu^{3+}}$ $4f^{13}5d$–$4f^{14}$ VUV luminescence in $\mathrm{CaF_2{:}Lu^{3+}}$ crystal at 8 K was studied with a high spectral resolution using synchrotron radiation excitation. Absence of a zero-phonon line in the recorded spectrum was explained and features in the recorded spectrum were reproduced by simulation based on the microscopic model of electron-phonon interaction and the developed theory of non-Condon spectra.

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Keywords: $5d$–$4f$ luminescence, electron-phonon interaction, non-Condon effect, lanthanides, $\mathrm{CaF_2{:}Lu^{3+}}$.

Dedicated to the 80th birthday of
Prof. Boris Zalmanovich Malkin

1. Introduction

During the past two decades there has been a considerable interest in vacuum ultraviolet (VUV) spectra of rare earth (RE) compounds, on the basis of which new efficient VUV lasers, phosphors and scintillator materials can be designed. Absorption (excitation) and emission spectra of $4f^n$–$4f^{n-1}5d$ transitions have been recorded for different RE ions in various host crystals and theoretical modeling of energy level patterns and transition intensities in such spectra was carried out for a lot of systems. However, a significant part of intensity of the $4f^n$–$4f^{n-1}5d$ transitions falls in broad vibronic bands with widths up to a thousand of wavenumbers even at liquid helium temperature complicating analysis of the spectra. In literature until 2007 $4f^n$–$4f^{n-1}5d$ vibronic bands were commonly approximated simply with Gaussian functions with a set of adjustable parameters: offset, bandwidth, intensity ratio of zero-phonon line (ZPL) to vibronic band, etc. [1].

In the mid-2000s Prof. B.Z. Malkin proposed a method that allowed to simulate uniformly the energy level structure and the sophisticated lineshape of electron-vibrational $4f^n$–$4f^{n-1}5d$ bands, being based on a microscopic model of electron-phonon interaction and implementing the real phonon spectrum of the host crystal lattice. Ref. [2] was the first paper written that presented this method and approbated it for several light RE ions in $\mathrm{LiYF_4}$ crystal. One of the authors of the present paper O.V.S., being B.Z. Malkin's graduate student at that time, was much inspired by the potential of this method, on the one hand – and, on the other hand, he was fascinated by the experimental results revealed on VUV luminescence spectra of the $\mathrm{Lu^{3+}}$ ion in $\mathrm{LiYF_4}$ crystal by other authors of the present paper. Namely, no ZPLs were found in those spectra, indicating that the corresponding electric dipole $4f^{13}5d$–$4f^{14}$ transitions are forbidden. A natural idea arose – to extend the B.Z. Malkin's method of modeling of electron-vibrational $4f^n$–$4f^{n-1}5d$ bands to forbidden transitions, for which Condon approximation is inapplicable. So, a fruitful combination of high quality experimental data on $\mathrm{LiYF_4{:}Lu^{3+}}$ spectra and its interpretation using the novel theoretical approach was published in the article [3] , which was issued on paper even before the original article [2] due to faster reviewing procedure in Physical Review B. Several more publications came out in which the method was successfully applied to different compounds; at some point Prof. Malkin wrote himself on his personal page on the University website in the section 'The most important recent result': "A method of modeling of interconfigurational electron-vibrational $4f^n$–$4f^{n-1}5d$ spectra of rare earth ions in dielectric crystals".

Celebrating the collaboration arisen in the 2000s, in the present study we investigate yet another low-temperature $4f^{13}5d$–$4f^{14}$ luminescence spectrum, which also corresponds to forbidden electric dipole transitions in the Lu^{3+} ion – this time in CaF$_2$ crystal. The high resolution spectrum recorded in the VUV spectral region at the famous SUPERLUMI station using synchrotron radiation excitation is compared with the results of simulation, based on the B.Z. Malkin's microscopic model of electron-phonon interaction and the expressions for non-Condon luminescence, that we derived and reported in [3, 4].

2. Experiment and simulation details

High-resolution emission spectrum was studied at the SUPERLUMI station of HASYLAB at DESY, the only facility in the world enabling such research under synchrotron radiation excitation generated by the DORIS storage ring [5–7]. Single crystal of CaF$_2$ doubly doped with 0.04 mol % Lu^{3+} and 0.02 mol % Ce^{3+} was grown by the vertical Bridgman method in a fluorine atmosphere. VUV emission spectrum was recorded using an open position-sensitive microchannel-plate detector coated with CsI in combination with a 1-m NIM VUV monochromator, achieving spectral resolution better than 0.5 Å in the second order. More experimental details can be found in [8].

Impurity Lu^{3+} ions substitute for Ca^{2+} ions in CaF$_2$ crystal. No local deformations of CaF$_2$ lattice were introduced, we considered the O$_h$ point symmetry for Lu^{3+} sites (non-local charge compensation). In the nearest surrounding of the Ca^{2+} site, there are eight fluorine ions which form a cube with the distance 2.3642 Å from the Ca^{2+} ion. Lattice vibrations were considered in the harmonic approximation. Vibration spectrum of the CaF$_2$ crystal lattice was studied in [9]. The maximum phonon frequency of this crystal equals 477 cm^{-1}. Results of optical absorption and neutron inelastic scattering experiments were described successfully in the framework of the shell model [10]. Using parameters of this model, we computed frequencies and polarization vectors of vibrations for 216000 wave vectors distributed over the Brillouin zone. The electron-phonon interaction, linear in dynamic displacements of the lattice ions, was considered within the cluster approximation: modulation of the crystal field by ligand' shells vibrations was considered only. Imaginary parts of the lattice advanced Green's functions for the displacements of shells in the cluster Ca^{2+}F$_8^-$ were calculated at the equally spaced 954 points on the frequency axis by numerical integration over the Brillouin zone.

To simulate spectral envelopes for the CaF$_2$:Lu^{3+} crystal luminescence, we used the microscopic model of electron-phonon interaction derived by Prof. B.Z. Malkin in [2]. The simulations involved: calculation of crystal field parameter $B_0^4(5d)$ (there is only independent parameter for the O_h point symmetry; here and further we use crystallographic axes) for the $5d$ electron as an explicit function of lattice ion's coordinates in the framework of the exchange charge model, B.Z. Malkin's famous development in crystal field theory [11] (lattice contribution to the Coulomb part of $B_0^4(5d)$ was estimated using the Ewald method); 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 ($4f^{14}$) and excited ($4f^{13}5d$) electronic configurations (configuration interactions were neglected); calculations of the $5d$ electron-phonon coupling constants as derivatives of crystal field parameters with respect to coordinates of crystal lattice ions; electron-phonon interaction was neglected for the $4f$ electrons as it is much smaller than for the $5d$ electron due to much more contracted space distribution of $4f$ wavefunctions. The calculated spectral lineshape was convoluted with the Gaussian with the full width at half maximum $19\,\mathrm{cm}^{-1}$ to take into account the inhomogeneous broadening induced by random lattice strains.

Radial moments of the $5d$ electron density, overlap integrals between the $5d$ electron and the ligands' outer electronic shells, bipolar expansion coefficients, which account for extended charge distributions of these electrons, were calculated using the $2s$, $2p$ functions of the F^{-} ion from [12] and the $5d$ function of the Lu^{3+} ion, which was obtained by modifying the Yb^{2+} function [13] to conform the moments of $5d$ electron density, calculated in [14] for Lu^{3+} with the use of standard program packages of atomic physics. Note, that the calculated bipolar expansion coefficients are negative, thus indicating the strong overlap between charge distributions of a $5d$ electron and ligands' outer electrons is to be considered strictly [15].

We derived analytical expressions for the shape of low-temperature non-Condon absorption and luminescence spectra of impurity centers in dielectric crystals in [4]. A solution of the Schrödinger equation for an electronic subsystem within the adiabatic approximation was considered in the first order of perturbation theory for the electron-vibrational interaction linear in normal coordinates of the vibrational subsystem (the Kubo-Toyodzawa approach [16]). It was proved that if an optical transition is forbidden in Condon approximation due to symmetry selection rules, the low-temperature non-Condon absorption and luminescence spectra are mirror symmetric and do not contain a zero-phonon line. The derived shape of the non-Condon spectrum of a symmetry forbidden electric dipole transition is determined by a lattice advanced Green's function diagonal over perturbation of the electric dipole moment matrix element due to electron-vibrational interaction: transition becomes allowed through borrowing the intensity from allowed transitions via electron-vibrational interaction. Conditions under which a symmetry forbidden electronic transition becomes allowed within the established approximations due to interaction with vibrations have been determined in [4].

3. Results and discussion

The ground configuration $4f^{14}$ of the Lu^{3+} ion is a nondegenerate state with a wavefunction transforming according to the identical irreducible representation Γ_{1g} of the O_h point symmetry group. The Lu^{3+} ion excited $4f^{13}5d$ configuration consists of 140 states and splits in the O_h symmetry crystal field into 58 levels: 6 singlets Γ_{1u}, 5 singlets Γ_{2u}, 12 doublets Γ_{3u}, 18 triplets Γ_{4u} and 17 triplets Γ_{5u}. Since vector components transform according to the irreducible representation Γ_{4u}, electric dipole $4f^{13}5d$–$4f^{14}$ transitions are allowed only for the 18 $4f^{13}5d$ triplets of the Γ_{4u} type. Transitions for all other $4f^{13}5d$ levels are symmetry forbidden in Condon approximation. If we go beyond this approximation, they can become allowed due to admixture of Γ_{4u} levels by electron-vibrational interaction; the shape of corresponding low-temperature non-Condon spectra can be calculated using formulas derived in [4]. It is quite symbolic that symmetrized displacements of a cubic cluster were revealed also by B.Z. Malkin in [17]: there are 5 types of even displacements, which correspond to irreducible representations Γ_{1g} (totally symmetric), Γ_{3g}, Γ_{4g} (corresponds to rotations of the cluster and therefore can be neglected), Γ_{5g} (two sets of displacements). Only interaction with totally symmetric vibrations contributes in adiabatic approximation to the Condon form of an optical band. Now let us consider a non-Condon spectrum corresponding to a symmetry forbidden electric dipole $4f^{13}5d(\Gamma_{3u})$–$4f^{14}$ transition. Since $[\Gamma_{3u}\times\Gamma_{3u}]^{\mathrm{symm}}=\Gamma_{1g}+\Gamma_{3g}$ and $\Gamma_{3u}\times\Gamma_{4u}=\Gamma_{4g}+\Gamma_{5g}$, such a transition becomes allowed within adiabatic approximation due to interaction with vibrations of Γ_{5g} symmetry. As for a symmetry forbidden electric dipole $4f^{13}5d(\Gamma_{5u})$–$4f^{14}$ transition, since $[\Gamma_{5u}\times\Gamma_{5u}]^{\mathrm{symm}}=\Gamma_{1g}+\Gamma_{3g}+\Gamma_{5g}$ and $\Gamma_{5u}\times\Gamma_{4u}=\Gamma_{2g}+\Gamma_{3g}+\Gamma_{4g}+\Gamma_{5g}$, such a transition remains forbidden within the established approximations even with electron-phonon interaction taken into account.

The Lu^{3+} ion $4f^{13}5d$ energy levels are determined by the following impurity ion Hamiltonian parameters: crystal field parameter $B_0^4(5d)$ (which is in turn determined within the exchange charge model by three adjustable parameters G_s, G_σ, G_π), crystal field parameters $B_0^4(4f)$, $B_0^6(4f)$, spin-orbit interaction constants $\zeta(4f)$, $\zeta(5d)$, parameters of electrostatic interaction $F^{(2)}(fd)$, $F^{(4)}(fd)$, $G^{(1)}(fd)$, $G^{(3)}(fd)$, $G^{(5)}(fd)$, energy shift of the excited $4f^{13}5d$ configuration. One of the principles of the present study was to vary as few Hamiltonian parameters as possible. Spin-orbit interaction constants were taken from data on gaseous Lu^{3+} [18]: $\zeta(4f)=3406\,\mathrm{cm}^{-1}$, $\zeta(5d)=1939\,\mathrm{cm}^{-1}$. Exchange charge model parameters $G_s=2.3$, $G_\sigma=2.282$, $G_\pi=0.1$ were taken from our unpublished investigation of CaF$_2$:Ce^{3+} spectra; these values are also very close to the values that we established in our investigation of Tm^{2+} spectra in CaF$_2$ crystal [19]. Corresponding calculated $5d$ crystal field parameter equals $B_0^4(5d)=-31492\,\mathrm{cm}^{-1}$; this is nearly 1.5 times smaller than the $B_0^4(5d)$ value for the Ce^{3+} ion in CaF$_2$ that was used in [1]. Similarly, we fixed the $4f$ crystal field parameters at the level of 2/3 of the values that were used in [1] for CaF$_2$:Ce^{3+}: $B_0^4(4f)=-1267\,\mathrm{cm}^{-1}$, $B_0^6(4f)=333\,\mathrm{cm}^{-1}$. Also, 4 out of 5 parameters of electrostatic interaction were taken from our investigation of LiYF$_4$:Lu^{3+} spectra [3, 15]: $F^{(2)}(fd)=19727\,\mathrm{cm}^{-1}$, $F^{(4)}(fd)=10477\,\mathrm{cm}^{-1}$, $G^{(3)}(fd)=5640\,\mathrm{cm}^{-1}$, $G^{(5)}(fd)=7807\,\mathrm{cm}^{-1}$. The only actually fitted parameter (not taking into account the excited configuration energy shift) was the $G^{(1)}(fd)$ parameter of electrostatic interaction; we obtained the following value $G^{(1)}(fd)=3210\,\mathrm{cm}^{-1}$.

Calculations show that two lowest $4f^{13}5d$ levels are a doublet Γ_{3u} and a triplet Γ_{5u} with very close energies, while the third excited level – a triplet Γ_{4u} – is situated more than $2000\,\mathrm{cm}^{-1}$ higher. Such an energy level structure is typical for this symmetry, the same one was obtained in [20] for Yb^{2+} in SrCl$_2$. Note that electric dipole transitions from the two lowest $4f^{13}5d$ levels to the ground configuration $4f^{14}$ are forbidden by symmetry. Therefore, to simulate the low-temperature luminescence spectrum for the CaF$_2$:Lu^{3+} crystal it is necessary to use the formulas for non-Condon lineshape derived in [4]. It follows from the analysis above that this spectrum becomes allowed for the doublet Γ_{3u} due to interaction with vibrations of Γ_{5g} symmetry; no ZPL should be observed in this spectrum. On the contrary, electric dipole transition to the ground configuration $4f^{14}$ is allowed for the third $4f^{13}5d$ level, so a ZPL should be observed in corresponding spectrum having a Condon shape.

These theoretical results agree with experiment very well. The CaF$_2$:Lu^{3+} emission spectrum measured with high resolution reveals no ZPL indeed. In Fig. 1 this spectrum measured at 8 K is compared with the simulated non-Condon luminescence spectrum corresponding to transitions from the $4f^{13}5d(\Gamma_{3u})$ level. The calculated energy of zero-phonon $4f^{13}5d(\Gamma_{3u})$–$4f^{14}$ transition is marked for convenience: $80310\,\mathrm{cm}^{-1}$. It is interesting to note that the energy positions of three maxima in the recorded spectrum are reproduced by simulation (but not their relative intensities): $170\,\mathrm{cm}^{-1}$, $250\,\mathrm{cm}^{-1}$ and $330\,\mathrm{cm}^{-1}$ with respect to the energy of zero-phonon transition. One more maximum in the measured spectrum is found at the energy of $780\,\mathrm{cm}^{-1}$ with respect to the energy of zero-phonon transition. It is not reproduced by calculations – actually the calculated spectral distribution vanishes at such high energies much exceeding the maxi-

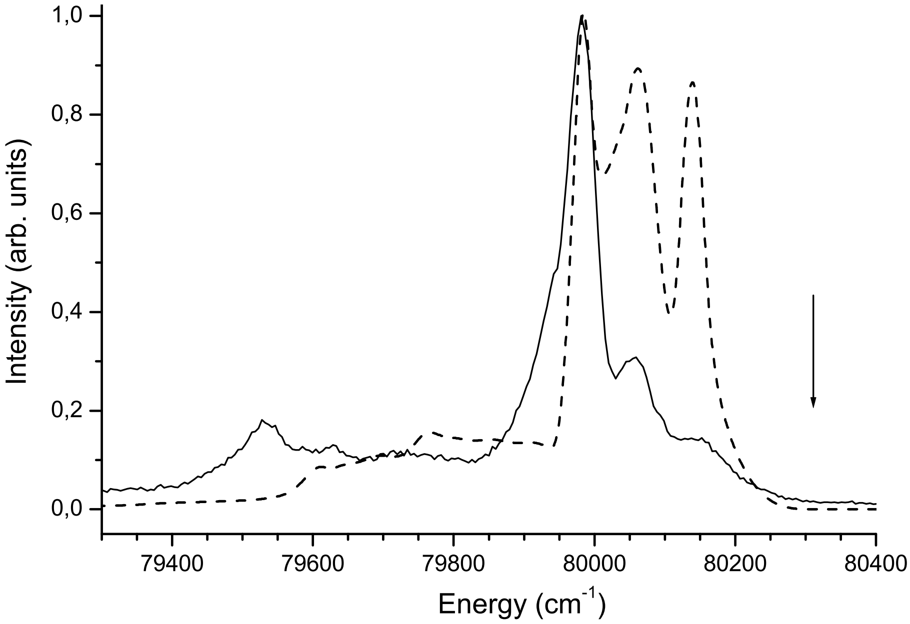

Figure 1. $4f^{13}5d$–$4f^{14}$ luminescence spectra recorded at 8 K (solid line) and simulated for 0 K (dashed line) of Lu^{3+} ion in the CaF$_2$:Lu^{3+} crystal. Arrow marks the calculated zero-phonon transition energy.

mum phonon energy of the CaF$_2$ crystal, perhaps indicating that a quadratic non-Condon effect should be considered in this case [21]. Whether it is possible to improve agreement between calculations and experimental data by fitting the model parameters, which were not varied in the present study for methodical reasons, remains an open question. However, it is obvious, that shape of a non-Condon spectrum is much more sensitive to variation of Hamiltonian parameters than the Condon shape, especially in the case when Condon contribution to a spectrum vanishes due to symmetry.

It is interesting to note that in [8] CaF$_2$:Lu^{3+} emission spectra were recorded, with a somewhat lower spectral resolution, for a set of temperatures ranging from 8 K to 200 K, and an additional band was observed with a maximum at about 80620 cm^{-1} for temperatures 140 K and above. However, our calculations show that there are no any additional energy levels close to this energy. We think that the band observed in [8] is simply the anti-Stokes component of the non-Condon luminescence spectrum considered above; the energy ≈ 80620 cm^{-1} of the observed additional maximum seems to be in agreement with the energy of the most intensive maximum revealed in the measured low-temperature luminescence spectrum (79980 cm^{-1}, see Fig. 1) mirrored with respect to the zero-phonon transition energy 80310 cm^{-1}. We are planning to publish a theoretical approach that would allow calculating the non-Condon shape of optical spectra at finite temperatures in the nearest future.

In [8] excitation spectrum of the CaF$_2$:Lu^{3+} crystal has also been investigated at 8 K. In agreement with the calculation results discussed above, a ZPL is indeed observed in this spectrum, which corresponds to the allowed transitions from the ground configuration $4f^{14}$ to the third $4f^{13}5d$ level (Γ_{4u} symmetry). The energy of the observed ZPL gives us the energy of zero-phonon transition for this $4f^{13}5d(\Gamma_{4u})$ level: 82420 cm^{-1}. Value of the only parameter varied in the present study – $G^{(1)}(fd)$ – was chosen in order to fit this energy, once the position of zero-phonon transition in Fig. 1 was fixed.

For clarity, we collected in Table 1 some specific spectral characteristics of the three lowest $4f^{13}5d$ levels of Lu^{3+} ion in CaF$_2$: the level number in the order of energy increase (N), O_h point

Table 1. Spectral characteristics of the lowest $4f^{13}5d$ levels in CaF$_2$:Lu^{3+}(energies given in cm^{-1}).

N	Ir. rep.	E_{CF}	E_{ZPL}	E_{ZPL} (exper.)
1	Γ_{3u}	80389	80310	Not observed (symmetry forbidden transitions)
2	Γ_{5u}	80389.4	80311	
3	Γ_{4u}	82505	82420	82420

symmetry group irreducible representation (Ir. rep.), the calculated eigenvalue of the effective impurity ion Hamiltonian, often called 'crystal field energy' (E_{CF}), the calculated zero-phonon line (or zero-phonon transition, to be more precise) energy (E_{ZPL}), the zero-phonon line energy derived from the experimental data (E_{ZPL} (exper.)).

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