Temperature effect on the emission spectra of narrow band Mn$^{4+}$ phosphors for application in LEDs

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Temperature dependence of the luminescence shape and decay time of narrow band Mn$^{4+}$ fluoride phosphors: Rb$_2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$ was investigated. The temperature changes in the relative intensity between the zero-phonon line and both phonon sidebands were observed in both samples. The sideband spectra consist of three lines related to interaction with three different phonon modes labeled $\nu_3$, $\nu_4$ and $\nu_6$. We present a comprehensive quantum theory which allows calculation of the luminescence intensity and the luminescence lifetime by simultaneously taking into account odd parity crystal fields, odd parity phonon modes and spin–orbit coupling. Since we include all modes, for which the respective interaction strengths and energies of the phonons are known, our approach does not involve any free parameters. We also discuss our results in relation to the temperature dependence of the lifetime of the $^2E_g \rightarrow ^4A_{2g}$ transition, taking into account the quantum efficiency of the system and the migration of the excitation energy. The presented model is applicable to all materials doped with Mn$^{4+}$ ions and also to any narrow line emitting phosphor, where a zero-phonon line and phonon structure is simultaneously observed in the emission spectrum.

Introduction

Mn$^{4+}$ ions are known as substitutional dopants, located in oxides and fluorides$^{1-4}$ that exhibit efficient, red, sharp-line luminescence in the spectral range of 600–700 nm. Therefore, materials doped with Mn$^{4+}$ are suitable as red phosphors for white light emitting diodes (WLEDs). Recently, a general and convenient strategy based on an efficient cation exchange reaction for the synthesis of Mn$^{4+}$-activated fluorides with the formula A$_2$MF$_6$ (A = Na$^+$, K$^+$, Cs$^+$, Rb$^+$, M = Si$^{4+}$, Ge$^{4+}$, Sn$^{4+}$, Ti$^{4+}$, and Zr$^{4+}$) has been developed and used to modify the luminescence spectrum of Mn$^{4+}$ by changing the interaction between the emitting ion and the host.

Mn$^{4+}$ is a transition metal ion which has three electrons occupying the 3d atomic (ionic) orbitals (3d$^3$ system). The luminescence of the Mn$^{4+}$ ions strongly depends on the point symmetry of the cation site in the host. In fluorides, Mn$^{4+}$ is located in the centre of an octahedron formed by six F$^-$ ions.

The energetic structures and luminescence properties of Mn$^{4+}$ in an MnF$_6^{2-}$ system are described by the Tanabe-Sugano diagram,$^{17}$ which is parameterized by Racah parameters $B$ and $C$, describing the Coulomb and exchange interactions between 3d$^3$ electrons and the crystal field strength $D_q$, which describes the influence of the lattice host potential and depends on the Mn$^{4+}$–F$^-$ distance $R$, approximately as $R^{-5}$.

The value of $10D_q$ is the energy of the splitting of the 3d electronic manifold into triply degenerated state t and doubly degenerated state e. In the ground state $^4A_{2g}$ three electrons occupy the lower state (t$^3$ electronic configuration). Depending on the value of $D_q/B$ the first excited (emitting) state can either be the $^4T_{2g}$ state (the low crystal field case $D_q/B < 2.4$) where one electron is excited to the e state (t$^2$e electronic configuration) without changing the spin or the $^2E_g$ state (the high field case $D_q/B > 2.4$) where one electron from the t electronic configuration changes the spin (t$^2$ electronic configuration). In Fig. 1 a simplified Tanabe–Sugano diagram that includes the lowest states of a 3d$^3$ system is presented. Mn$^{4+}$ in fluorides is a high field system, which means that the lowest excited state is the $^2E_g$ (t$^2$) state. The typical energetic distance between the $^4T_{2g}$ and $^2E_g$ state in Mn$^{4+}$ in fluorides is equal to 3000–4000 cm$^{-1}$.

One notices that energies of the 3d electrons in different states depend in a different way on the crystal field. In particular, the energetic distance between $^2E_g$ (t$^2$) and the ground state $^4A_{2g}$ (t$^3$)
by the transition of the electron from the $t_3$ to the $t_{2e}$ electronic configuration.

The lattice expands to the value $Q_2$ where electronic energies are presented as a function of Mn$^{4+}$–F$^-$/C$_{22}$ ion distance described by single configurational coordinate $Q_1$, presented in Fig. 1b. The value $Q_E$ describes the distance of F$^-$ ions with respect to Mn$^{4+}$ when electrons in Mn$^{4+}$ occupy the $A_{2g}$ and $E_g$ states belonging to the $t^3$ electronic configuration. The lattice expands to the value $Q_1$ which represents the distance of F$^-$ ions when the system is in the $T_{2g}$ state belonging to the $t^7$ electronic configuration.

The specific bandshape of the luminescence related to $E_g \rightarrow A_{2g}$, that consists of the zero-phonon line and phonon sidebands, results from the fact that the d-d transitions are parity forbidden. Therefore, both the $3d^{3}(E_g) \rightarrow 3d^{3}(A_{2g})$ and $3d^{3}(E_g) \rightarrow 3d^{3}(A_{2g})$ electric dipole transitions can take place only when the odd parity crystal field mixes the even parity d wave function with odd parity p or and f wave functions. In the materials where the point group describing the symmetry of the Mn$^{4+}$ ion contains the operation of inversion (no odd parity static field is present), the $E_g \rightarrow A_{2g}$ luminescence can only take place due to interaction with odd parity phonons which has the effect of admixing opposite parity wave functions into the emitting state. As a result, the luminescence spectrum consists of sharp lines called phonon sidebands with energies shifted from the energy of the $E_g$ state by values equal to the energies of the respective phonons. In the case when the group symmetry of the Mn$^{4+}$ ion does not contain the inversion symmetry the odd parity static crystal field allows for direct $E_g \rightarrow A_{2g}$ transition and the emission spectrum contains a zero-phonon line having energy equal to the energy of the $E_g$ state apart from (or instead of) the phonon sidebands. The situation is different in different fluorides. The emission spectrum of Mn$^{4+}$ in K$_2$TiF$_6$ and K$_2$SiF$_6$ does not contain the zero-phonon line, whereas Mn$^{4+}$ in Na$_2$SiF$_6$ KNaSiF$_6$ and Rb$_2$GeF$_6$ has emission, which consists of the zero-phonon lines and the phonon sidebands. Recently, it has been shown that the zero-phonon line appears in K$_2$SiF$_6$:Mn$^{4+}$ emission under high hydrostatic pressure and this effect is persistent after decompression.

The $E_g \rightarrow A_{2g}$ transition is strongly forbidden due to the parity selection rule as well as spin selection rule and can take place when both selection rules are broken. The structure of the $E_g \leftrightarrow A_{2g}$ transitions observed in the emission and absorption spectra has been known for at least 50 years and has been attributed to interaction with odd parity phonons and spin–orbit coupling. The standard absorption and emission spectroscopy as well as the two photon absorption method has been used to determine the phonon energies. It has been shown that the spin–orbit coupling that is responsible for the $E_g$ and $A_{2g}$ mixing is much smaller in crystals than in the free ion, which was explained as a result of the Ham effect. In the case of Mn$^{4+}$ in Cs$_2$SiF$_6$ the quenching of the spin–orbit coupling has been attributed to the strong Jahn–Teller effect in the $T_{2g}$ state. However, the exact calculations performed in the diabatic limit have shown that the reduction of the spin–orbit coupling may be caused by interaction of the 3d electrons in the $T_{2g}$ state with the symmetrical (breathing) $a_1$ lattice vibration mode. The luminescence related to $E_g \rightarrow A_{2g}$ transition has been described using the perturbation method either by considering the spin–orbit coupling of the $E_g$ and $T_{2g}$ states or by analysis of interactions with odd parity lattice distortion.

In this contribution, we present a comprehensive theory which allows the calculation of the luminescence intensity and the luminescence lifetime by taking into account the odd parity crystal field, odd parity phonon modes, and spin–orbit coupling. The developed theory is used to analyze the temperature dependence of the luminescence intensity and luminescence decay for Rb$_2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$. In both cases, the zero-phonon lines and the phonon sidebands are observed, and the sideband spectra consist of three lines related to interaction with three distinct odd phonon modes labelled $v_{12}$, $v_{14}$ and $v_{16}$. Since we include all interacting phonon modes and the energies of the phonons are known our model does not contain any free (fitting) parameters. The obtained model can be readily applied to any system, where there is a simultaneous interaction of an optical centre with an odd-parity static crystal field and odd-parity phonon modes.

**Experimental**

Information on the preparation and crystallographic structure of Rb$_2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$ can be found in

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**Fig. 1** (a) Simplified Tanabe–Sugano diagram of the octahedrally coordinated 3d$^3$ system. The low field and high field regions are separated by the dashed line. The absorption and emission transitions for the Mn$^{4+}$ system are indicated by solid arrows. (b) Configurational coordinate diagram representing the Mn$^{4+}$ system. Value $Q_k$ describes the position of F$^-$ ions when electrons in Mn$^{4+}$ occupy the $A_{2g}$ and $E_g$ states belonging to the $t^3$ electronic configuration, and value $Q_f$ represents the positions of F$^-$ ions when the system is in the $T_{2g}$ state.
ref. 16 and 13 respectively. In both cases the Mn$^{4+}$ ions occupy the octahedral sites of slightly distorted $O_h$ point symmetry. Analyses performed in this paper were based on the measurements of luminescence intensity and decay times of individual Mn$^{4+}$ lines as a function of temperature. The experimental data – emission spectra and decay profiles – were obtained simultaneously using time resolved emission spectroscopy (TRES), where the pulse excited luminescence intensity of a sample is measured simultaneously with respect to time and wavelength.

Light collected from a sample phosphor under excitation from a pulsed laser source passes through a two stage detection system. The first stage is a Bruker Optics 2501S spectrometer, where the incident light is dispersed by a diffraction grating producing a wavelength-resolved light beam stretched in the horizontal plane. Spectrally resolved light passes to a Hamamatsu C4334-01 streak camera where it strikes a photocathode producing photoelectrons, which in turn are deflected in the vertical plane by the electric field of magnitude changing with time at a constant rate. The deflection angle of individual photoelectrons depends on the time of emission of the photoelectron from the photocathode. By the combined action of two detection stages, the input signal of sample luminescence becomes spectrally and temporally resolved and is projected on a 2D CCD matrix forming a streak image. The CCD matrix converts the streak image to a 2D matrix of photon counts vs. wavelength and time.

The excitation part of the apparatus consists of a tunable parametric light source PG 401/SH pumped by the third harmonic of a YAG:Nd laser PL2134 A (EKSPLA) producing 30 ps pulses. All streak images were acquired within a time window of 10 ms after excitation. To perform temperature dependent experiments the samples were held in a closed cycle helium cryostat DE-202 (Advanced Research Systems).

Results

Temperature-dependent emission spectra of Rb$2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$ obtained from the TRES streak image under excitation of 440 nm are presented in Fig. 2a and b, respectively.

In both cases the emission spectra consist of sharp-line luminescence which includes the zero-phonon line(s) indicated by arrows centered at 16 080 cm$^{-1}$ for Rb$2$GeF$_6$:Mn$^{4+}$ and 16 106 cm$^{-1}$ for KNaSiF$_6$:Mn$^{4+}$. At temperatures up to 100 K, apart from the zero-phonon line the Stokes phonon sideband that consists of three phonon repetitions, labeled $\nu_3$, $\nu_4$ and $\nu_5$ is observed. The energies of the respective phonons for Rb$2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$ are listed in Table 1.

As temperature increases, additional anti-Stokes lines with energies higher than the zero-phonon lines appear in the spectra. In addition, a small red shift of all lines with increasing temperature is observed. In Fig. 2a and b the normalized intensities are presented, therefore it looks like the intensities of the Stokes and anti-Stokes line increase at the expense of the zero-phonon line. Actually, it is not the case because an increase of the total intensity of the luminescence with increase of temperature is observed, which is in accordance with the result of previous papers. However, our experimental conditions do not allow for quantitative comparison of the luminescence intensities obtained at different temperatures.

The time resolved emission spectra of Rb$2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$ were measured at different temperatures. Using our apparatus we are able to observe separately the decay of the zero-phonon line, and the Stokes and anti-Stokes phonon sidebands. In all cases luminescence decays are single exponential. For Rb$2$GeF$_6$:Mn$^{4+}$ the decays of the sidebands and the zero-phonon line are almost the same. For KNaSiF$_6$:Mn$^{4+}$ the decay of the zero-phonon line is a little bit faster than the decay of the sidebands. The results obtained for KNaSiF$_6$:Mn$^{4+}$ and Rb$2$GeF$_6$:Mn$^{4+}$ are presented in Fig. 3a and b, respectively.

The experimental results are presented with solid labels, the calculated values are presented with dashed, dotted and solid curves. It is seen in both cases that the increase of intensity of the Stokes and anti-Stokes bands is accompanied by decreasing of the luminescence lifetime.

For quantitative analysis of this effect, the ratio of the integrated intensities of the Stokes and anti-Stokes lines to the zero-phonon line versus temperature were calculated. Fig. 4a–c and Fig. 4d–f present the ratios of the integrated intensity of the sum of the Stokes and anti-Stokes ($I_S + I_a$), the Stokes ($I_S$), and the anti-Stokes ($I_a$) to the zero-phonon line ($I_{zer}$) for Rb$2$GeF$_6$:Mn$^{4+}$ and KNaSiF$_6$:Mn$^{4+}$, respectively. It is seen that the Stokes and anti-Stokes line intensities increase with increasing temperature with respect to the zero-phonon line.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\hbar\nu_o$ (cm$^{-1}$)</th>
<th>$\Omega_{dyn} (=\Omega_{stat})$</th>
<th>$\hbar\nu_o$ (cm$^{-1}$)</th>
<th>$\Omega_{dyn} (=\Omega_{stat})$</th>
</tr>
</thead>
<tbody>
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<td>3</td>
<td>638</td>
<td>0.32</td>
<td>639</td>
<td>0.32</td>
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<tr>
<td>4</td>
<td>344</td>
<td>0.90</td>
<td>345</td>
<td>0.90</td>
</tr>
<tr>
<td>6</td>
<td>240</td>
<td>1.32</td>
<td>230</td>
<td>0.73</td>
</tr>
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</table>

Table 1 Energies and intensities (values of $\Omega_{dyn} = \langle\nu\rangle/\Omega_{stat}$) of individual phonon modes obtained from low temperature luminescence spectra. The intensity of the zero-phonon line was assumed to be equal to 1.
Discussion

For complex consideration of the radiative processes, specifically to analyze the Mn\(^{4+}\) luminescence bandshape and lifetime, we describe the emitting and ground state by the wave functions in the form of the following products:

\[
\psi_s(S) = \psi_s(S) \left( \prod_r Q^{loc}_r(Q^{loc}_r) \right) \psi_s(r) \left( \prod_r Q^{latt}_r(Q^{latt}_r) \right) \]

where \(\psi_s(S)\) and \(\psi_s(r)\) are the spin and orbital part of the wave functions, respectively, and \(\nu\) represents either the \(2E_g\) or \(4A_{2g}\) state. \(Q^{loc}_r(Q^{loc}_r)\) and \(Q^{latt}_r(Q^{latt}_r)\) are vibrational wave functions describing the local and lattice vibrational modes.

The \(2E_g \rightarrow 4A_{2g}\) transition can take place due to the simultaneous occurrence of two effects – the admixture of the spin quartet states to the spin doublet \(2E_g\) emitting state and the admixture of the odd parity states to the even parity \(2E_g/4A_{2g}\) wave functions. The admixture of lowest quartet state \(4T_{2g}\) to the emitting \(2E_g\) state is a result of spin–orbit interaction, which yields in the perturbation approach the following spin wave function representing the emitting state \(2E_g\):

\[
\psi(S)_{2E_g} = \frac{1}{2} + \psi\left(\frac{3}{2}\right) A_{s-o} [E(2E_g), E(4T_{2g}), Q^{loc}_a] \]

Here \(A_{s-o}\) is the integral that represents the spin–orbit interaction, \(E(2E_g)\) and \(E(4T_{2g})\) are energies of the \(2E_g\) and \(4T_{2g}\) states. The admixture of odd parity states is described by odd parity wave functions \(\phi_s(r)\) admixing to the emitting/ground state \((\nu = 2E_g, 4A_{2g})\) which yields the following emitting state orbital wave function:

\[
\phi_s(r) = \phi_{4A_{2g}}(r) + \sum_\nu \phi_s(r) A_{\nu-o} [E_\nu, E_s, Q^{latt}_a] \]

Here \(A_{\nu-o}\) is the integral that represents the interaction with odd parity orbit, and \(E_\nu (\nu = 2E_g, 4A_{2g})\) and \(E_s\) are the energies of the emitting and ground states and the odd parity states, respectively. The product form of the total wave functions allows the spin–orbit effect and the orbital effects to be considered separately and independently.

To describe the temperature dependence of the ratio of intensity of the Stokes and anti-Stokes lines to the zero-phonon line only the effects of odd parity distortion [relation (3)] have to be considered (we assume that the magnitude of spin–orbital interaction is immune to temperature changes). To perform the calculations we have made the following assumptions:

1. All sites of Mn\(^{4+}\) have the same symmetry (single site model) and there is no excitation energy transfer between the individual Mn\(^{4+}\) centres.

2. The origin of the emission of the zero-phonon line is related to interaction with the static odd parity crystal field which disturbs the octahedral symmetry of the Mn\(^{4+}\) complex. We do not explicitly take into account the possibility that the zero-phonon line has magnetic dipole character. However, in the proposed model magnetic dipole character of the zero-phonon line luminescence can be included additively to the interaction with the odd parity static field and it does not change the obtained results. The strength of the interactions that yield the zero phonon line is represented by quantity \(\Omega_{stat}^2\).

3. The origins of the Stokes and anti-Stokes lines are related to the interaction with three different odd parity lattice vibrational modes, labeled \(\nu_i, i = 3, 4, 6\). The interaction strength depends on the mode and does not depend on temperature. The strength of the interaction with the \(\nu_i\)th vibrational mode is represented by quantity \(\Omega_{\nu_i}^2\).
Under these assumptions, the quantum mechanical calculations of the temperature dependence of the intensities of the Stokes and anti-Stokes bands and the zero-phonon lines were performed in the Appendix. We have obtained the following relations for the ratio of intensities of the Stokes $I_s$ and anti-Stokes $I_A$ band to the intensity of the zero-phonon line $I_{ZPL}$.

$$
I_s/I_{ZPL} = \sum_\nu \frac{\Omega_{\text{dyn}}^2(\nu)}{\Omega_{\text{stat}}^2} \frac{1}{1 - e^{-\hbar\nu/kT}}
$$

(4)

$$
I_A/I_{ZPL} = \sum_\nu \frac{\Omega_{\text{dyn}}^2(\nu)}{\Omega_{\text{stat}}^2} \frac{e^{-\hbar\nu/kT}}{1 - e^{-\hbar\nu/kT}}
$$

(5)

$$
\frac{(I_s + I_A)}{I_{ZPL}} = \sum_\nu \frac{\Omega_{\text{dyn}}^2(\nu)}{\Omega_{\text{stat}}^2} \coth \left( \frac{\hbar\nu}{2kT} \right)
$$

(6)

In relations (4)-(6) $\hbar\nu/\nu$ is the energy of the $\nu$-th mode, and the quantity $\Omega_{\text{dyn}}^2(\nu)$ is given by eqn (22). The intensity of the zero-phonon line appears to be independent of temperature and is equal to the strength of the interaction with the odd parity lattice distortion. The value of $\Omega_{\text{stat}}^2$ is related to interaction with an odd parity crystal field and is given by relation (21). Relations (4)-(6) show that $I_s/I_{ZPL}$ and $I_A/I_{ZPL}$ increase when temperature increases.

Relations (4)-(6) allow the calculation of the shortening of the radiative lifetime of the luminescence related to the $2E_g \rightarrow 4A_{2g}$ transition:

$$
\tau_E = \frac{1}{1 + \sum_\nu \frac{\Omega_{\text{dyn}}^2(\nu)}{\Omega_{\text{stat}}^2} \coth \left( \frac{\hbar\nu}{2kT} \right)}
$$

(7)

where $\tau_0$ is the radiative lifetime at 0 K.

The values of $\Omega_{\text{dyn}}^2(\nu)/\Omega_{\text{stat}}^2$ can be taken from the experimental spectra at low temperature as the ratio of the integrated intensities of the respective spectral lines. The respective data for phonon modes 3, 4 and 6 in Rb₂GeF₄:Mn⁴⁺ and KNaSiF₆:Mn⁴⁺ are listed in Table 1. The energies of the modes and the values of $\Omega_{\text{dyn}}^2(\nu)/\Omega_{\text{stat}}^2$ were used in formulae (4) and (5) to simulate temperature dependence of the luminescence bands. The results of the calculations are presented by solid curves in Fig. 4. One should keep in mind that since the values of the energies of the phonons and the relative interaction strengths were obtained from independent experiments we did not use any fitting procedure to reproduce the temperature dependence of the luminescence intensity of the Stokes and anti-Stokes lines obtained from the experiment. It is seen that our calculations represent quite well the experimental data for Rb₂GeF₄:Mn⁴⁺. The agreement between theory and experiments in the case of KNaSiF₆:Mn⁴⁺ is not so good. From Fig. 4d–f it is evidently seen that the intensity of the Stokes and anti-Stokes lines increases with temperature to a greater extent than it is predicted by the model.

This discrepancy should be discussed in context with the luminescence kinetics results. It is seen that in the case of KNaSiF₆:Mn⁴⁺ the zero-phonon line luminescence decays faster than the Stokes and anti-Stokes lines. Such effect is possible only when we have at least two different Mn⁴⁺ sites – one which yields a strong zero-phonon line and weak sidebands and decays with time $\tau_0$ and another which yields a weak zero-phonon line and strong sidebands and decays with time $\tau_1 > \tau_0$. This phenomenon can explain the effect of longer decay time of the phonon sidebands in the sample. The fact, that the temperature increases the intensity of the phonon sidebands faster than predicted by relations (4)-(6) can be explained by temperature-induced excitation energy migration between Mn⁴⁺ centers.

To analyze the temperature dependence of the luminescence lifetime of Mn⁴⁺ emission in fluorides one should take into account simultaneously the interaction with an odd parity crystal field and phonons as well as the spin–orbit coupling that allows the $2E_g \rightarrow 4A_{2g}$ transition. Relations (1)-(3) allow the calculation of the spin–orbit effect separately from the interaction with odd parity crystal field. The discussion presented in a previous paper shows that the contribution of the spin quartet to the emitting $E_g$ state is approximately equal to

$$
\psi(3/2)_g = \psi(3/2)_T \frac{V_{s-o}}{A'}
$$

(8)

The review of the different approaches that consider the spin-orbit admixture of the $^4T_{2g}$ to the emitting $^2E_g$ and the most complete model that includes all excited states and coupling to the symmetrical local vibrational mode is presented in ref. 30 and 13. In the case of Mn⁴⁺ in fluorides, the probability of the radiative transition per unit of time was calculated for the $2E_g \rightarrow 4A_{2g}$ luminescence. Since the lifetime $\tau_E$ is equal to the inverse transition probability, one obtains:

$$
\tau_E = \frac{1 + 3 \exp \left( \frac{-A}{kT} \right)}{\left( \frac{V_{s-o}}{A'} \right)^2 + 3 \exp \left( \frac{-A}{kT} \right)}
$$

(9)

where $1/\tau_T$ is the probability of the spin allowed $^4T_{2g} \rightarrow 4A_{2g}$ transition, $\tau_T$ is the $^4T_{2g}$ lifetime and $V_{s-o}$ is the effective spin–orbit coupling constant. Quantity $A$ is the energy separation between the $^4T_{2g}$ and the $^2E_g$ states. The value of $A$ is considered as a thermal activation energy of the $^4T_{2g}$ state. The quantity $A'$ is the difference between the energies of the $^4T_{2g}$ and $^2E_g$ states obtained from the excitation spectrum (i.e. the difference between the peak of the excitation band related to the $^4T_{2g}$ and energy of $^2E_g \rightarrow 4A_{2g}$ zero-phonon transition). This is the energy of the vibrational state related to the $^4T_{2g}$ electronic manifold which most effectively mixes with the emitting vibrational state of the $^2E_g$ electronic manifold.

As it is shown in ref. 18, relation (8) leads to the relation (9) for the temperature dependence of the lifetime of the $2E_g \rightarrow 4A_{2g}$ transition. Relation (9) does not take into account the thermal population of and radiative transition from the $2T_{1g}$ state. This is due the fact that the spin–orbit coupling of the $^4T_{1g}$ state and
$2^2T_{2g}$ state is much weaker than that of the $2^2E_g$ state and $2^2T_{2g}$ and can be omitted. On the other hand, temperature diminishing of the lifetime related to activation of the Stokes and anti-Stokes transitions should be taken into account. When this effect is included one obtains the following formula for the $2^2E_g \rightarrow 4^2A_{2g}$ transition lifetime:

$$\tau_E = \frac{\tau_T \left( 1 + 3 \exp \left( \frac{-\Delta}{kT} \right) \right)}{\left[ 1 + \sum \frac{Q_{\text{dyn}}^2(\nu)}{Q_{\text{stat}}^2} \coth \left( \frac{-\hbar \nu}{2kT} \right) \right] \left( \frac{V_{\text{x-o}}}{\Delta} \right)^2 + 3 \exp \left( \frac{-\Delta}{kT} \right)}$$

In Fig. 3a, the temperature dependence of the luminescence lifetime calculated using relation (7) is presented by the short dashed curve. One notices that the experimental data and calculated lifetime are in agreement for temperatures lower than 200 K. The diminishing of the lifetime not predicted by relation (7) is observed for higher temperatures. In Fig. 3a and b the dotted curves were obtained using the relation (9), where only the spin–orbit interaction and the thermal population of the $4^2T_{2g}$ state is considered. The values of $\Delta$ and $\Delta'$ were obtained from the excitation and emission spectra and the spin–orbit coupling constant obtained from the excitation and emission spectra 13,18 and are presented in Table 2. The spin–orbit coupling constant and the $4^2T_{2g}$ luminescence lifetime were treated as fitting parameters (the respective values are listed in Table 2).

It is seen that calculated dependence of the luminescence lifetime on temperature does not follow the experimental results in the temperature range from 100 to 400 K for Rb$_2$GeF$_6$:Mn$^{4+}$ and from 100 to 350 K for KNaSiF$_6$:Mn$^{4+}$. The results obtained using relation (10) are presented by dotted curves. Here, parameters describing the coupling with the odd parity crystal field and phonon modes as well as the energies of the phonons were independent input constants, and the spin–orbit coupling and values of the $4^2T_{2g}$ lifetime, $\tau_T$ were the fitting parameters. It is seen that the calculated dependence that includes both the interaction with odd parity distortions and spin orbit coupling reproduces quite well the experimental results for KNaSiF$_6$:Mn$^{4+}$, whereas the coincidence is weaker for Rb$_2$GeF$_6$:Mn$^{4+}$. In particular, it is seen that for Rb$_2$GeF$_6$:Mn$^{4+}$ the experimental lifetime diminishes faster than the calculated lifetime in the temperature range of 150–400 K.

One should consider this effect in the context of quantum efficiency of the system. At 300 K the quantum efficiency of Rb$_2$GeF$_6$:Mn$^{4+}$ is equal to 0.73, 16 whereas the quantum efficiency of KNaSiF$_6$:Mn$^{4+}$ is equal to 0.90. In a typical situation diminishing of the quantum efficiency takes place due to nonradiative processes, which are activated at increased temperature and this effect is accompanied by diminishing of the luminescence lifetime.

One can include such process of diminishing the luminescence lifetime with increasing temperature in the case of the Rb$_2$GeF$_6$:Mn$^{4+}$ system. Let us assume that the Mn$^{4+}$ in Rb$_2$GeF$_6$ can decay nonradiatively with probability $p_{nr}$ and activation energy $E_{nr}$. The non-radiative process affects the lifetime in a similar way (according to Arrhenius law) as the radiative transition from the $4^2T_{2g}$ state to the ground state activated with energy $\Delta$, and therefore it can be easily included additively, modifying relation (10). In this way the dependence of the $2^2E_g \rightarrow 4^2A_{2g}$ transition lifetime on temperature is described by the following relation:

$$\tau_{E'} = \frac{\tau_T \left( 1 + 3 \exp \left( \frac{-\Delta}{kT} + \exp \left( \frac{E_{nr}}{kT} \right) \right) \right)}{\left[ 1 + \sum \frac{Q_{\text{dyn}}^2(\nu)}{Q_{\text{stat}}^2} \coth \left( \frac{-\hbar \nu}{2kT} \right) \right] \left( \frac{V_{\text{x-o}}}{\Delta'} \right)^2 + 3 \exp \left( \frac{-\Delta}{kT} \right) + p_{nr} \cdot \tau_T \cdot \exp \left( \frac{-E_{nr}}{kT} \right)}$$

The results of the calculations are represented by the solid curve in Fig. 4a. One notices that good fit has been obtained for activation energy equal to 443 cm$^{-1}$ and the probability of non-radiative deexcitation is equal to 1.3 $\times 10^5$ s$^{-1}$. Considering the data presented in Fig. 4a one can estimate the quantum efficiency of the system at different temperatures using the relation

$$\eta = \frac{\tau_{E'}(T)}{\tau_E(T)}$$

At 300 K, relation (12) yields $\eta = \frac{\tau_{E'}(300)}{\tau_E(300)} = 0.72$. This result is very close to the value estimated from other experiments. The values of $p_{nr}$ and $E_{nr}$ obtained for Rb$_2$GeF$_6$:Mn$^{4+}$, specifically small excitation energy and very small frequency factor (nonradiative transition probability) suggest that the non-radiative deexcitation responsible for diminishing the quantum efficiency is not related to the auto ionization of electrons from the Mn$^{4+}$ excited level to the conduction band. The more probable effect is the tunneling of electrons to a nonradiative deexcitation center of unknown nature.

### Conclusions

We have presented a comprehensive quantum mechanical approach that takes into account the spin–orbit coupling and interaction with odd parity crystal fields and odd parity

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta$ (cm$^{-1}$)</th>
<th>$\Delta'$ (cm$^{-1}$)</th>
<th>$V_{\text{x-o}}$ (cm$^{-1}$)</th>
<th>$\tau_T$ (μs)</th>
<th>$p_{nr}$ (s$^{-1}$)</th>
<th>$E_{nr}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_2$GeF$_6$:Mn$^{4+}$</td>
<td>2900$^{18}$</td>
<td>5500$^{18}$</td>
<td>48</td>
<td>0.44</td>
<td>70</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>2.76</td>
<td>1300</td>
<td>443</td>
</tr>
<tr>
<td>KNaSiF$_6$:Mn$^{4+}$</td>
<td>3060$^{13}$</td>
<td>5700$^{13}$</td>
<td>20</td>
<td>0.12</td>
<td>45</td>
<td>0.88</td>
</tr>
</tbody>
</table>
KNaSiF₆:⁴⁺⁺⁺⁺ this effect is thermally excited, but its origin still small zero-phonon line (and large phonon sidebands). In Fig. 1b, which modifies the spin–orbit coupling of the ⁴T₂g and with the symmetrical local modes described by the diagram in ⁴A₂g states, and allows the ²E₉ — ⁴A₂g transition which in the first approximation is spin-forbidden.

The obtained results are applicable not only to Mn⁴⁺⁺⁺⁺ doped hosts but also any narrow line emitting system where the forbidden optical transitions are determined by interaction of the optical centre with an odd-parity static crystal field and odd-parity phonon modes – such as in the case of Cr³⁺ or trivalent lanthanides. As such, these results are relevant to the current scientific effort to develop novel narrow band emitting phosphors for LED based lighting and backlighting applications.

Conflicts of interest
There are no conflicts to declare.

Appendix: static and dynamic interactions with odd parity crystal fields
In adiabatic approximation, the emitting “e” and the ground “g” state wave function are represented by a product of the electronic part depending on electronic coordinate r and the vibrational wave functions depending on ionic configuration coordinates, representing the vibration modes (phonons)

\[ |\psi_{\text{eq}}(Q_1, \ldots Q_z, r)\rangle = \prod_{\nu=1}^{3} \chi^{\nu}(Q_\nu) \varphi_{\text{eq}}(r) = \prod_{\nu=1}^{3} |n_\nu\rangle \varphi_{\text{eq}}(r) \]  \hspace{1cm} (13)

In formula (13) \( n_\nu \) is the vibrational excitation number and \( \nu \) labels the vibrational mode (phonons), and \( Q_\nu \) is the respective configurational coordinate. The electric dipole transitions within the 3d⁴ electronic configuration of Mn⁴⁺⁺⁺⁺ are forbidden (because the orbital wave functions of electrons in the emitting and the ground state are characterized by the same orbital number \( l = 2 \) — and hence have the same, even parity) unless the interaction with odd parity crystal field \( V^{\text{odd}}(r) \) and odd parity phonons admixtures wave functions of opposite parity described by wave functions \( \phi^\text{odd}(r) \) with energies \( E^\text{odd}_\nu \). The total perturbation
Considering relations (14) and (15) one obtains the emitting state and the ground electronic state and

\[
\varphi_{eg}(r) = \varphi_{eg}^{d}(r) + \frac{1}{\sqrt{2}} \sum_{\nu} \varphi_{eg}^{\nu}(r) \frac{d^{\nu\nu}H_{eg}(Q_{1}, \ldots, Q_{2}, r) \varphi_{eg}^{d}(r) dr}{dQ_{\nu}}
\]

(15)

where

\[
\Theta_{eg}^{\nu}(r) = \sum_{j} \varphi_{eg}^{\nu}(r) \frac{d^{\nu\nu}H_{eg}(Q_{1}, \ldots, Q_{2}, r) \varphi_{eg}^{d}(r) dr}{dQ_{\nu}}
\]

(16)

and

\[
\Theta_{eg}^{d}(r, \nu) = \frac{1}{\sqrt{2}} \sum_{i} \varphi_{eg}^{i}(r) \frac{d^{i\nu}H_{eg}(Q_{1}, \ldots, Q_{2}, r) \varphi_{eg}^{d}(r) dr}{dQ_{\nu}}
\]

(17)

The effective dipole transition moment for transition between the emitting state \(\varphi_{eg}(r)\) and final state \(\varphi_{eg}(r)\) is given by:

\[
M_{eg} = \int dQ_{1} \ldots dQ_{2} dr \varphi_{eg}^{d}(r) \frac{d^{i\nu}H_{eg}(Q_{1}, \ldots, Q_{2}, r) \varphi_{eg}^{d}(r) dr}{dQ_{\nu}}
\]

(19)

where \(\hat{m}(r)\) is the dipole moment operator. Relations (13), (15)–(18) allow relation (19) to be transformed into the form:

\[
M_{eg}^{n_{\nu}, n'_{\nu}} = \left[ \Omega_{\text{stat}}^{\nu}(r) \delta_{n_{\nu}, n'_{\nu}} + \Omega_{\text{dyn}}^{\nu}(r) \right] \frac{n_{\nu} \left( a_{\nu} + a_{\nu} \right)}{n_{\nu}}
\]

(20)

where \(\delta_{n_{\nu}, n'_{\nu}}\) is the Dirac function and the integrals \(\Omega_{\text{stat}}(\nu)\) and \(\Omega_{\text{dyn}}(\nu)\), given by

\[
\Omega_{\text{stat}} = \int \Theta_{eg}^{\text{stat}}(r) \hat{m}(r) \varphi_{eg}^{d}(r) dr
\]

(21)

\[
\Omega_{\text{dyn}}(\nu) = \int \Theta_{eg}^{\text{dyn}}(r, \nu) \hat{m}(r) \varphi_{eg}^{d}(r) dr
\]

(22)

are the effective electric dipole transition moments, which depend on the particular odd parity vibrational mode \(\nu\) but are independent of the vibrational excitation numbers \(n_{\nu}\). The values of \(\Omega_{\text{dyn}}^{\nu}(r)\) are considered to be constants and are estimated from low temperature spectra. Quantities \(\Omega_{\text{dyn}}^{\nu}(r)\) for respective phonon modes \(\nu = 3, 4, 6\) in Rb_{2}GeF_{2}:Mn^{2+} and KNaSiF_{4}:Mn^{2+} were obtained from low temperature spectra and are listed in Table 1.

Relations (20) and (21) allow the calculation of the intensity of the transition between the vibrational emitting state described by \(\varphi_{eg}(r) \int n_{\nu} / n_{\nu}'\) and the ground vibrational state \(\varphi_{eg}(r) \int n_{\nu} / n_{\nu}'\)

\[
I_{\nu}^{n_{\nu}, n'_{\nu}} = \frac{\Omega_{\text{stat}}^{\nu} \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu}' + \Omega_{\text{dyn}}^{\nu}(r) \left( n_{\nu} + 1 \right) \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu}' \left[ \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu}' \right] \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu}' \right)
\]

(23)

The relations (20) and (23) show that the transitions between the vibrational states that have the same quantum numbers \(n_{\nu} = n_{\nu}'\) or numbers different by one \(n_{\nu} = n_{\nu}' \pm 1\) are allowed. The former transitions are responsible for the intensity of the zero-phonon line, whereas the latter are responsible for the intensity of the phonon sidebands.

At low temperature \(kT \ll \hbar \omega_{l} n_{\nu} = 0\) and \(n_{\nu} = 1\). In Fig. 5 this transition is indicated by a red arrow that joins the vibrational levels 0 in the emitting state and 1 in the ground state \((0 \to 1)\). The transitions of this type are responsible for the Stokes lines in sharp-line phonon sidebands.

When the temperature increases to the point that \(kT \sim \hbar \omega_{l}\) also the higher vibrational levels of the emitting state with \(n_{\nu} = 1, 2, 3 \ldots\) become partially occupied. In such cases, additional channels for radiative transition are open. The first channel is the transition to \(n_{\nu} = 0, 1, 2 \ldots\) which corresponds to the anti-Stokes lines in the sharp-line phonon sideband. The second channel is related to the transition to \(n_{\nu} = 2, 3, 4 \ldots\) which adds up to the intensity of the Stokes lines.

Relation (23) allows the calculation of the probability of radiative transitions responsible for zero-phonon lines and the Stokes and anti-Stokes bands as follows:

\[
I_{\nu}^{ZPL} = \frac{\Omega_{\text{stat}}^{\nu} \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu} \cdot e^{-\hbar \omega_{l} / kT}}{\sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu} \cdot e^{-\hbar \omega_{l} / kT}} = \Omega_{\text{stat}}^{\nu}
\]

(24)

\[
I_{\nu} = \frac{\Omega_{\text{dyn}}(\nu) \sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu} \cdot e^{-\hbar \omega_{l} / kT}}{\sum_{n_{\nu}=0} n_{\nu} \cdot n_{\nu} \cdot e^{-\hbar \omega_{l} / kT}}
\]

(25)
\[
I_A = \sum_{n_1} \Omega_{\text{dyn}}^2(\nu) e^{-\frac{\nu h \omega_0}{kT}} \prod_{\nu' \neq \nu} e^{-\frac{n_{\nu'} h \omega_0}{kT}} \\
\prod_{\nu} e^{-\frac{n_\nu h \omega_0}{kT}}
\]

\[
= \sum_{\nu} \Omega_{\text{dyn}}^2(\nu) e^{-\frac{h \omega_0}{kT}} \\
1 - e^{-\frac{h \omega_0}{kT}}
\]

One notices that both quantities \( I_S \) and \( I_A \) depend on the vibrational quantum number \((n_\nu + 1) \) and \( n_\nu \) and therefore increase when higher excited states are thermally occupied, whereas \( I_{ZPE} \) does not depend on temperature.

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