Stark level analysis of the spectral line shape of electronic transitions in rare earth ions embedded in host crystals

H Steinkemper, S Fischer, M Hermle and J C Goldschmidt
Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, D-79110 Freiburg, Germany
E-mail: heiko.steinkemper@ise.fraunhofer.de

New Journal of Physics 15 (2013) 053033 (15pp)
Received 14 January 2013
Published 21 May 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/5/053033

Abstract. Rare earth ions embedded in host crystals are of great interest for many applications. Due to the crystal field of the host material, the energy levels of the rare earth ions split into several Stark levels. The resulting broadening of the spectral line shapes of transitions between those levels determines the upconversion phenomena, especially under broad-spectrum illumination, which are relevant for photovoltaics for instance. In this paper, we present a method to determine the spectral line shape of energy level transitions of rare earth ions from the absorption spectrum of the investigated material. A parameter model is used to describe the structure of the individual energy levels based on a representation of the Stark splitting. The parameters of the model are then determined with an evolutionary optimization algorithm. The described method is applied to the model system of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$. The results indicate that for illumination with a wavelength around 1523 nm, simple upconversion processes such as two-step absorption or direct energy transfer are less efficient than commonly assumed. Hence a sequence of efficient processes is suggested as an explanation for the high upconversion quantum yield of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$, which has not yet been reported in the literature.
1. Introduction

The optical properties of rare earth ions are of great interest for many optical applications such as lasers [1–4], waveguide amplifiers [5, 6] and biological markers [7, 8] and for spectral conversion such as up- and downconversion [9–11]. Upconversion processes generate one high-energy photon out of two or more low-energy photons. Upconversion is of great interest for application in photovoltaics. Semiconductor solar cells cannot utilize photons with energies below the semiconductor’s band gap, because these photons cannot excite an electron into the conduction band. Via upconversion, the otherwise transmitted sub-band-gap photons can be converted into photons that can be utilized by the solar cell. Therefore, upconversion can help in enhancing the efficiency of solar cells.

Up to now, experimental and theoretical investigations of rare-earth-doped materials have been carried out predominantly under monochromatic excitation owing to their application in lasers or waveguide amplifiers [12–14]. For the application in photovoltaics, however, the behavior under broad-spectrum illumination is relevant. Even if only the spectrum transmitted by a silicon solar cell is considered, the spectral distribution of potentially upconvertible photons spans a range of more than 1000 nm. To this point, only a few experimental studies of upconversion under spectral broad excitation have been reported [15–18]. There are also no simulation models describing upconversion under spectral broad excitation, to the best of our knowledge. Up to now, the most comprehensive model of a rare-earth-based upconverter under monochromatic irradiation has been published by Fischer et al [19]. It describes the upconverter material $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_{4}$. This and related models [12, 13, 20] all rely on discrete energy levels of the rare earth ions as determined by Dieke and Crosswhite [21]. Figure 1 shows the lowest eight energy levels of Er$^{3+}$ and the possible transmissions considered in [19] (expanded from six to eight energy levels). Already for the simulation of upconversion under monochromatic excitation, the usefulness of these data is limited. As different transitions that occur in experiments are more or less in resonance with the excitation, weighting factors need to be included for some transitions, which take into account the different degrees of resonance.
Figure 1. Energy level scheme of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ and the most important processes considered in the upconversion rate equation model for illumination at 1523 nm (approximately 6600 cm$^{-1}$). Upconversion can occur by GSA followed by ESA, as well as GSA followed by ETU from one ion (donator) to a second ion (acceptor).

Determining the occurrence and probability of all processes that are possible under broad-spectrum illumination is not possible, based on these data of discrete energy levels.

The transitions, which are possible between the different energy levels of a rare earth ion, have certain spectral line shapes. This spectral line shape represents the energy dependence of the transition probability between two energy levels. It is a probability density function that describes the probability that a given ion will, depending on the transition, emit or absorb a photon with the energy $E_\Delta$ in the interval between $E_\Delta$ and $E_\Delta + dE_\Delta$. If, in an experiment, an ensemble of ions is investigated, the observed spectral line shape will be a result of the spectral line shapes of the individual ions. The spectral line shape of the individual ion is the result of the energetic sub-structure of the involved levels [22], selection rules that may apply to the transition and external factors that influence the transitions, for example the probability for phonon-assisted processes [23].

In this paper, we present a method to determine the spectral line shape of the different transitions, which allows in-depth analysis of processes under broad-spectrum illumination. The method is based on the concept of the ‘shape of an energy level’. This shape of an energy level represents how an energy level contributes to transitions starting from or ending in the observed energy level. Knowing the shapes of two energy levels, it is possible to calculate the spectral line shape for the transition between these two energy levels. Just as in the case of spectral line shape, the shape of the energy level will be determined by the density of states forming the energetic sub-structure, occupation, selection rules and external factors.

In section 2, we show how the structure of the individual energy levels can be deduced from experimental data. We introduce a physically motivated parameter model that generates the structure of the energy levels based on the Stark splitting of the considered energy level. With this parameter model one can determine the spectral line shape functions of all possible transitions between the different energy levels. In section 3, we apply the presented method to
the upconverter material $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$. These data could be subsequently used in simulations of upconversion under broad-spectrum illumination. In this work, we focus on the discussion of which processes are affected by the determined spectral line shape and identify new possible upconversion mechanisms, which have been neglected or underestimated in previous analyses that had been based on the discrete energy level data only. A sequence of efficient processes is discussed as an explanation for the high upconversion quantum yield of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ under illumination with wavelengths around 1523 nm. This discussion is presented in section 4.

2. Method to determine the spectral line shapes

2.1. Energy levels of rare earth ions, Stark splitting and nomenclature

Commonly, each discrete energy level of a considered rare earth ion is assigned the identification $2S + 1L_J$, where $S$, $L$ and $J$ are the quantum numbers of spin, angular momentum and total angular momentum, respectively. In this paper, $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ is used as a model system, on which the presented method is applied. In the following, we will denote the energy levels of the trivalent erbium with $i = 1–8$ beginning with the ground state $^4I_{15/2}$ (see also figure 1).

In the case of optical transitions in rare earth ions, the shape of the energy levels and consequently the spectral line shape are dominated by Stark splitting. The Stark splitting of the energy levels is a result of the Stark effect, which describes the shifting and splitting of spectral lines due to the presence of an external static electric field. In the case of a rare earth ion embedded in a host, the energy levels of the ion split owing to the crystal field of the host material. The number of possible Stark levels of each energy level depends on the quantum number of the total angular momentum $J$ of the energy level and the number of electrons of the considered ion [21]. Following Kramer’s theorem [24], each energy level $i$ splits into a maximum number $s_{i,\text{max}}$ of Stark levels, with

$$s_{i,\text{max}} = \begin{cases} 2J + 1 & \text{for an even number of electrons,} \\ \dfrac{2J+1}{2} & \text{for an odd number of electrons.} \end{cases} \quad (1)$$

The precise number and width of the Stark levels, however, depend on the symmetry and the intensity of the crystal field [21]. For trivalent erbium (Er$^{3+}$) the ground state $^4I_{15/2}$ splits into a maximum of eight Stark levels owing to an odd electron number, for instance. For the identification of each level, the Stark levels of an energy level $i$ are named by $s_i = 1, 2, \ldots, s_{i,\text{max}}$, beginning with the lowest Stark level, throughout this paper. For Er$^{3+}$, the energetically highest Stark level of the ground state is therefore labeled with $i = 1$ and $s_1 = 8$, for example.

Each Stark level has a distinct energy and a distinct width [25, 26]. The width of a Stark level measured for an ensemble of ions is increased by the fact that different ions might experience different crystal fields, resulting in a different Stark splitting. In microcrystalline $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ for example, there are two possible crystal sites for the Er$^{3+}$ resulting in two different Stark splittings [27]. Additionally, the crystal field is changed due to crystal defects and on the surface of the microcrystals. In consequence, the Stark splitting results in a broadening of the discrete energy levels. Therefore, various transition energies correspond to the same transition between two broad energy levels.
2.2. Parameter model for the shape of the energy levels based on the Stark splitting

As the structure of the Stark levels dominates the shape of the energy levels of the embedded rare earth ions, a parameter model describing these shapes should consider the Stark levels. The location of the peaks in the shape of the energy level will coincide with the Stark level, while the relative height and width will be influenced by selection rules and external factors.

We chose a parameterization, in which a Gaussian distribution is assigned to each Stark level $s_i$:

$$f_{is}(E) = x_{is,\text{scale}} \frac{1}{\sqrt{2\pi} x_{is,\text{width}}} \exp\left(-\frac{1}{2} \left(\frac{E - E_{i,\text{center}} + x_{is,\text{splitting}}}{x_{is,\text{width}}}^2\right)\right).$$

(2)

Here $x_{is,\text{scale}}$ is a scaling factor determining the relative height, $x_{is,\text{width}}$ the width and $x_{is,\text{splitting}}$ the deviation of the Stark level from the energy $E_{i,\text{center}}$ of the discrete energy level $i(\frac{2S+1}{2})$ without Stark splitting. The parameters $x_{is,\text{scale}}, x_{is,\text{width}}$ and $x_{is,\text{splitting}}$ are the free parameters of the model.

The shape of each energy level $i$ is determined by calculating the sum over the corresponding Stark levels $s_i$:

$$f_i(E) = \sum_s f_{is}(E).$$

(3)

Figure 2 illustrates the shape of two fictional energy levels consisting of four and two Stark levels, respectively.
2.3. Shape of the energy level and line shape function

For two given shapes $f_i(E)$ and $f_j(E)$ of the energy levels $i$ and $j$, the line shape function $g_{ij}(E_\Delta)$ of a transition between the energy levels $i$ and $j$ can be calculated via

$$g_{ij}(E_\Delta) = \frac{\int f_i(E) f_j(E + E_\Delta) \, dE}{\int \int f_i(E) f_j(E + E_\Delta) \, dE \, dE_\Delta}.$$  

(4)

The integral in the denominator is the normalization, which ensures that

$$\int g_{ij}(E_\Delta) \, dE_\Delta = 1$$

(5)

is valid. The integral in the numerator can be understood as first shifting the shape of the higher energy level $f_j(E)$ by $E_\Delta$, and subsequently determining the area under the product of the shape of the lower energy level and the shifted shape of the higher energy level. This corresponds to an evaluation of the transition strength from the higher to the lower energy level with the exact transition energy $E_\Delta$. Figure 3 visualizes this explanation.

By a subsequent integration over $E_\Delta$, a measure can be obtained of how likely the transition between certain energy levels is.

2.4. Determination of the Stark level parameters

The shape of the energy levels can be obtained in a reverse optimization process from experimentally observed spectral line shapes. For this purpose, we generated a set of shapes for

\[\text{Figure 3.} \text{ Shifting the shape of the energy level } f_j(E) \text{ by } E_\Delta \text{ allows determining the transition strength from the higher level } j \text{ to the lower energy level } i \text{ with the exact transition energy } E_\Delta. \text{ The area under the product of the shape of the energy level of level } i \text{ and the shifted shape of level } j \text{ gives the probability for the transition energy } E_\Delta. \text{ Repeating this evaluation for each value of } E_\Delta \text{ yields the spectral line shape } g_{ij}(E_\Delta).\]
the different energy levels. Subsequently, the spectral line shape of all ground state transitions is calculated and compared with the experimentally determined spectrum of the absorption coefficients of the ground state absorption (GSA) of the examined material. The parameters of the Stark level model are varied, and consequently the shape of the energy levels, until the calculated line shape functions and the absorption spectrum are in good agreement. For this purpose an evolutionary algorithm is used.

At first, for all transitions between the ground state \((i = 1)\) and any considered excited state \((2 \leq j \leq j_{\text{max}})\) the transition probabilities \(P_{ij}(E_{\Delta})\) are calculated. A spectrum \(P_1(E_{\Delta})\) is determined by the sum over all \(P_{ij}(E_{\Delta})\) which represents a theoretically determined GSA spectrum:

\[
P_1(E_{\Delta}) = \sum_{j=2}^{j_{\text{max}}} P_{1j}(E_{\Delta}).
\]

The spectrum \(P_1(E_{\Delta})\) is compared with the experimentally determined absorption spectrum \(P_{\text{GSA}}(E_{\Delta})\). We calculate the quantity \(q\) representing the quality of the agreement of the calculated spectrum \(P_1(E_{\Delta})\) and the experimental spectrum \(P_{\text{GSA}}(E_{\Delta})\):

\[
q = \sum_{E_{\Delta}} (P_1(E_{\Delta}) - P_{\text{GSA}}(E_{\Delta}))^2 w(E_{\Delta}).
\]

In principle, \(q\) is the sum over the square deviation of \(P_1(E_{\Delta})\) and \(P_{\text{GSA}}\) for any transition energy \(E_{\Delta}\). A smaller value of \(q\) represents better agreement of the calculated and the experimentally determined data. We introduced an additional weighting function \(w(E_{\Delta})\) that allows eliminating measurement artifacts in the absorption spectrum from the calculation of \(q\).

To find the global minimum of \(q\) an evolutionary algorithm is used. An evolutionary algorithm was chosen due to the large number of free parameters of the model. Considering the eight lowest energy levels of \(\beta\)-NaEr\(_{0.2}\)Y\(_{0.8}\)F\(_4\), there are 43 Stark levels. Each of these Stark levels has three free parameters: the width \(x_{1s,\text{width}}\), the scale \(x_{1s,\text{scale}}\) and the energetic position \(x_{1s,\text{splitting}}\). In total there are 129 variation parameters. The algorithm starts with 20 randomly created parameter sets. Each of these parameter sets mutates 50 times, which means that each parameter of the set is varied with a certain probability. As a result, the next generation has 1000 new individuals. The strength of the mutation is chosen randomly, as well. Weaker mutations are more probable than strong ones. The occasional strong mutations are needed to escape local minima of \(q\). Only the 20 fittest individuals of each generation survive, which are those with the smallest values of \(q\). These survivors are used as the basis for the next generation. An optimal set of parameters is found if the global minimum of \(q\) is reached.

Based on this optimal set of variation parameters and the resulting shapes of the energy levels \(f_i(E)\), it is possible to calculate the spectral line shape functions \(g_{ij}(E_{\Delta})\) of any possible transition between the energy levels \(i\) and \(j\) using equation (4).

In order to achieve physically reasonable results, certain restrictions to the Stark level parameters have been made. Obviously, negative scaling factors and widths of the Stark levels are not reasonable. But also too high values for the width and the Stark splitting have to be forbidden. For example, a Stark splitting of the magnitude of the energy gap between two energy levels could lead to mixing of energy levels. The limits for the variation parameters of the model are listed in table 1.

The upper limit for \(x_{1s,\text{width}}\) and both limits for \(x_{1s,\text{splitting}}\) were estimated from the literature, where the Stark splitting of Er\(^{3+}\) in different host materials was investigated [25, 26, 28].
Table 1. Limitations of the variation parameters $x_{is,\text{scale}}$, $x_{is,\text{width}}$ and $x_{is,\text{splitting}}$ for the scaling, width and splitting of the investigated Stark levels.

| Parameter          | Lower limit | Upper limit   |
|--------------------|-------------|---------------|
| $x_{is,\text{scale}}$ | $> 0$       | No limit      |
| $x_{is,\text{width}}$ | $> 0 \text{ cm}^{-1}$ | $< 110 \text{ cm}^{-1}$ |
| $x_{is,\text{splitting}}$ | $> -170 \text{ cm}^{-1}$ | $< 170 \text{ cm}^{-1}$ |

Figure 4. The spectrum of the absorption coefficient $P_1$ of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ was calculated based on the Stark level parameterization of the shape of the individual energy levels. The parameters of the model have been optimized using an evolutionary algorithm. $P_1$ is in good agreement with the experimentally determined spectrum of the absorption coefficient $P_{\text{GSA}}$. The inset gives exemplarily a detailed view of the nontrivial structure of the energy transition from the ground state into the first excited state ($1 \rightarrow 2$). Measurement artifacts around 7200 and 11 400 cm$^{-1}$ were purposely neglected and therefore not fitted by $P_1$.

An upper limit for $x_{is,\text{scale}}$ is not necessary since $x_{is,\text{scale}}$ is directly restricted by the fitting quality $q$.

3. Results

3.1. Spectral line shapes of ground state absorption and the shape of the energy levels for $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$

We applied the method presented in the previous section to the upconverter material $\beta$-NaY$_{0.3}$Er$_{0.2}$F$_4$. As reference spectrum $P_{\text{GSA}}$ the experimentally determined absorption coefficient of $\beta$-NaY$_{0.3}$Er$_{0.2}$F$_4$ was used [19]. Figure 4 shows that for the considered transitions...
Figure 5. Energy level scheme of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ with the corresponding shape of the energy levels. The widths of the energy levels are enlarged and not related to the left energy axis. The relative widths of the energy levels compared with each other are illustrated correctly.

between the eight lowest energy levels, good agreement between the calculated spectrum $P_1$ and the reference spectrum $P_{GSA}$ is achieved.

The experimental data show some measurement artifacts due to light source and detector changes in the measurement setup at around 7200 and 11 400 cm$^{-1}$. To exclude these from the parameter optimization, the weighting function $w(E_{\Delta})$ in equation (7) was used.

The shapes of the energy levels leading to the best agreement between the calculated spectrum $P_1$ and the measured absorption spectrum $P_{GSA}$ (compare figure 4) are shown in figure 5.

3.2. Spectral line shapes of other transitions

Based on the shape of the energy levels, the spectral line shape functions $g_{ij}(E_{\Delta})$ of any possible transition between the eight considered energy levels can be calculated. As already discussed in section 2.2, the shape of the energy levels is determined by several parameters. In particular, the parameters for the relative height of the Stark levels do not represent one single physical magnitude but are dependent on several effects such as, for example, the occupation of the Stark level. The higher the considered energy levels, the smaller their occupation. It is not necessarily the case that all these parameters are the same for any possible transition. Therefore, the obtained spectral line shapes are more a qualitative indicator, which transitions can occur at which transition energy, rather than a quantitative measure of how likely these transitions are.

Figure 6 shows the obtained spectral line shapes for transition energies from 5500 to 7500 cm$^{-1}$ and from 9500 to 11 000 cm$^{-1}$. The first energy range corresponds to wavelengths...
Figure 6. Spectral line shape functions \( g_{ij}(E_{\Delta}) \) for transition energies from 5500 to 7500 cm\(^{-1}\) and from 9500 to 11 000 cm\(^{-1}\). In these energy ranges, GSA into the second and third energy level is possible. Furthermore, large overlap between several different spectral line shapes is visible (R, S and T), indicating the possibility for efficient energy transfer processes. The gray areas indicate the spectral ranges of the corresponding transitions determined by Dieke and Crosswhite [21].

from 1820 to 1330 nm, which includes the relevant wavelength range (e.g. GSA to \(^4\)I\(_{13/2}\)) for erbium-based upconverters for the application with silicon solar cells [29, 30]. The second energy range corresponds to wavelengths from 1050 to 910 nm. Erbium-doped upconverters, also co-doped with ytterbium, show good upconversion quantum yield in this wavelength range as well [31]. Therefore GSA should be significantly strong in this energy range or in the case of the co-doped material at least significantly resonant with the corresponding transition of ytterbium around 10 300 cm\(^{-1}\). As figure 6 indicates, GSA into the second and third energy level is possible in the presented energy ranges. Excited state absorption (ESA) from the second into the fourth level and from the fourth into the sixth and seventh level appears likely as well. It has to be mentioned, however, that these excitations do not occur at exactly the same energy range. Another route for GSA followed by ESA is the direct excitation of the third level, followed by a transition into the eighth level.

Furthermore, large overlap between several different spectral line shapes is visible, pointing to the possibility for efficient energy transfer processes. Energy transfer is considered to be the most efficient upconversion process in rare earth ions [32], for materials with comparatively high doping concentration as commonly used in many host crystals, including the here investigated \(\beta\)-NaYF\(_4\). Energy is transferred from one ion, the donor (D), to another ion, the acceptor (A). This transfer can also be regarded as simultaneous deactivation of D and activation of A. The transition probability due to energy transfer \(W_{DA}\) can be expressed by the oscillator strengths of the radiative transitions [33] which are proportional to the Einstein coefficients of donator \(A_{ij,D}\) and acceptor \(A_{ij',A}\). Additionally, \(W_{DA}\) is proportional to the overlap integral of the spectral line
shapes of the considered transitions of D and A [33, 34]:

\[ W_{DA} \propto A_{ij,D}A_{i'j',A} \int g_{ij,D}(E_\Delta)g_{i'j',A}(E_\Delta) \, dE_\Delta. \] (8)

Therefore, a large overlap between the spectral line shapes indicates that there is a high probability for energy transfer processes, given the case that the involved transitions are reasonably strong by themselves.

4. Discussion

The obtained results, especially the identified possible further transitions, need to be carefully examined and the findings need to be matched to experimental data. A high upconversion quantum yield of erbium-doped NaYF₄ (and co-doped with ytterbium) has been reported under illumination with excitation energies of 10 238 cm⁻¹, which is equivalent to a wavelength of about 980 nm [31]. Regarding the large overlap of the calculated spectral line shapes \( g_{13}(E_\Delta) \) and \( g_{38}(E_\Delta) \) located at this transition energy, which are labeled with (T) in figure 6, this result is in very good agreement with our findings. Both GSA followed by ESA and energy transfer upconversion can occur for these wavelengths based on the calculated spectral line shapes.

Erbium-doped upconverters show a high upconversion quantum yield under excitation around 6600 cm⁻¹ (≈1520 nm) as well [29, 30, 35]. This finding is not directly supported from the presented results. Upconversion via GSA (1 → 2) followed by ESA (2 → 4) should not be very efficient under monochromatic irradiation at 6600 cm⁻¹ since the ESA (2 → 4) is resonant at lower transition energies below 6600 cm⁻¹. Furthermore, the spectral line shapes of both transitions \( g_{12}(E_\Delta) \) and \( g_{24}(E_\Delta) \) show nearly no overlap, making resonant energy transfer unlikely. That these transitions are off resonance is also suggested from the data of Dieke and Crosswhite published for the material system LaCl₃ [21]. The derived transition energies are also shown in figure 6. As one can see, they coincide well with the peaks of the determined spectral line shape functions. Nevertheless, considering the data of Dieke and Crosswhite there is no distinct evidence for resonant energy transfer which could explain the high upconversion quantum yield under excitation around 6600 cm⁻¹ (≈1520 nm) mentioned before.

On the other hand, besides resonant energy transfer, there is also the possibility of (nonresonant) phonon-assisted energy transfer [33]. The energy mismatch between donator and acceptor can be bridged by the emission or absorption of one or more phonons. Hence the transition probability due to phonon-assisted energy transfer depends on the size of the energy mismatch and the phonon energy of the host crystal [23, 36]. In turn the phonon energy depends on the temperature, making energy transfer a rather complex process. The fact that high upconversion quantum yield in the considered spectral range around 1520 nm is also reported for host materials with low phonon energies, such as ZBLAN glass ceramics [37], makes it unlikely, however, that phonon-assisted energy transfer is the only explanation for the observed high upconversion quantum yield.

Therefore, we propose an additional efficient upconversion process that has not yet been reported in the literature. We consider the case of two erbium ions—one already excited in the fourth energy level and one in the ground state (figure 7). In a first step, ion (b), or any other ion in the vicinity and in the ground state, is excited into the second energy level via GSA (1 → 2). Since the pumping energy of about 6600 cm⁻¹ (≈1520 nm) is located close to the maximum of the spectral line shape function \( g_{12}(E_\Delta) \), this transition is very likely. In the next step (II)
Figure 7. Possible sequence of efficient energy transitions, starting from the case of one ion (a) excited to the fourth energy level and another ion (b) in the ground state. The sequence (I–VI) features a complete upconversion process, converting two low-energy photons (1520 nm) into one high-energy photon (980 nm) and returning both ions in their initial states.

energy is transferred from ion (b) (2 → 1) to ion (a) (4 → 7). Regarding the large overlap of the corresponding spectral line shape functions $g_{12}(E_{\Delta})$ and $g_{47}(E_{\Delta})$, this is a highly resonant energy transfer process (see (S) in figure 6). Due to the small energy gap between the energy levels 6 and 7, ion (a) relaxes almost instantly due to multi-phonon relaxation (MPR) into the next lower energy level (III.a). Meanwhile ion (b), or any other ion in the vicinity and in the ground state, can be re-excited into the second energy level (III.b). Ion (a) is now in energy level 6 and ion (b) in energy level 2. Cross relaxation between the two ions (IV) can lead to a state with both ions in the fourth energy level. This cross relaxation process again is resonant (compare (R) in figure 6). Ion (b) can now relax under emission of one high-energy photon back into the ground state. The most likely process is MPR followed by spontaneous emission at 980 nm, as illustrated in figure 7 (V.b and VI.b). Summarized, the sequence of steps I–VI transfers two low-energy photons (1520 nm) into one high-energy photon (980 nm) returning both ions into their initial states, which represents one complete upconversion process.

For this upconversion process to take place in an ensemble of Er$^{3+}$ ions, a significant population of the fourth energy level is necessary. Under illumination with an excitation energy of about 6600 cm$^{-1}$ (~1520 nm), this population can be achieved by GSA followed by phonon-assisted energy transfer, for example. If no immediate relaxation occurs from the fourth level, the described process sequence (I–VI) could lead to an avalanche-like population increase of the fourth level, until a steady state of excitation and the different relaxation processes, including the emission of higher energy photons, is reached.

The population of the fourth energy level ($^4I_{9/2}$) and consequently the proposed upconversion process depends significantly on the phonon energy of the host crystal. Fluorides, such as the investigated $\beta$-NaYF$_4$, show lower phonon energies as oxides but higher ones as
chlorides, bromides and iodides [38]. As stated before, phonon-assisted processes are needed to populate the fourth energy level in the first place. For these processes higher phonon energies are beneficial. But higher phonon energies also result in increased MPR rates [38, 39] and consequently in the depopulation of the fourth energy level via MPR into the third energy level. Nevertheless, since we have shown that resonant direct upconversion processes may have been overestimated in the past, the presented process is one possible explanation for the high upconversion quantum yield of $\beta$-Na$_{0.8}$Er$_{0.2}$F$_4$.

To support our thesis we can take a look at some former investigations of the upconverter $\beta$-Na$_{0.8}$Er$_{0.2}$F$_4$. The maximum of the monochromatic upconversion quantum yield of $\beta$-Na$_{0.8}$Er$_{0.2}$F$_4$ was reported at a wavelength of 1523 nm [29, 30]. This wavelength coincides with the maximum of the absorption peak of the transition from the ground state $^4I_{15/2}$ to the first excited state $^4I_{13/2}$ [19], compare also figure 4. If there was a significant overlap of the absorption peaks of the transitions from $^4I_{15/2}$ to $^4I_{13/2}$ (1 → 2) and from $^4I_{13/2}$ to $^4I_{9/2}$ (2 → 4), the maximum of the monochromatic upconversion quantum yield should be consequently located at a wavelength in between the maxima of the two absorption peaks, as reported for erbium-doped LaCl$_3$ under excitation around 980 nm [40]. The possibility that both absorption maxima are located at exactly the same wavelength of 1523 nm is very unlikely and should result in much higher upconversion quantum yield than reported so far, since ESA should be much stronger as well. But as mentioned before, energy transfer upconversion (ETU) was identified as the most efficient upconversion process. These results support our thesis that there are no direct resonant upconversion processes.

5. Conclusion and outlook

In this paper, we presented a method to calculate the spectral line shapes of electronic transitions in rare earth ions. These calculations are based on a parameter model of the shape of the individual energy levels that ultimately result in the observed spectral line shapes of the transitions. For rare earth ions in host crystals, this shape of the energy levels is essentially generated by the Stark splitting. Due to the crystal field of the host material, the energy levels of the embedded rare earth ion split into several Stark levels depending on the total angular momentum of the energy level. The parameterization of the resulting shape of the energy levels is therefore based on a representation of the different Stark levels.

We determined the parameters of the Stark level model by an evolutionary algorithm. By variation of the underlying parameters describing the Stark levels, and the comparison of the resulting spectral line shapes of transitions starting from the ground state, with the absorption spectrum of the investigated material, an optimum set of parameters can be found. These parameters and the deduced shapes of the individual energy levels can then be used to determine the spectral line shapes of all possible transitions between the energy levels.

The presented method was applied to calculate the shape of the energy levels and the spectral line shapes of the electronic transitions of trivalent erbium in the material system $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$. The calculated absorption spectrum showed very good agreement with the experimentally determined absorption coefficient of the material. Furthermore, we discussed in detail the calculated spectral line shapes for the spectral ranges from 5500 to 7500 cm$^{-1}$ (1820 to 1330 nm) and from 9500 to 11 000 cm$^{-1}$ (1050 to 910 nm), which are relevant for the application of the investigated material for upconversion of near-infrared photons. On the one hand, we could identify efficient resonant energy transfer for upconversion in the spectral
range from 9500 to 11 000 cm$^{-1}$, which is in good agreement with experimental results for the upconversion quantum yield of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$. On the other hand, no such obvious upconversion mechanism can be identified for the spectral range from 5500 to 7500 cm$^{-1}$, as there is nearly no overlap between the corresponding spectral line shapes. This means that both resonant energy transfer including these transitions and resonant GSA followed by ESA are very unlikely under monochromatic excitation in this spectral range. This result stands in contrast to experimentally observed high upconversion quantum yields for this spectral range. We therefore proposed an unreported sequence of resonant transitions that could explain the high upconversion quantum yield of $\beta$-NaEr$_{0.2}$Y$_{0.8}$F$_4$ under illumination with wavelengths around 1520 nm.

In this paper, we have shown that the presented method allows for the determination of the spectrally resolved transition properties from the absorption spectrum of rare-earth-doped materials and enables a qualitative discussion of energy transition processes. To increase the quantitative accuracy of the data, ESA data derived from pump and probe techniques [41–43] could be used as input parameters as well.

The generated data could also be used as input parameters in rate equation models, thus enabling the simulation of broad-spectrum phenomena involving the rare earth ions. This is especially relevant for the description of upconversion under spectral broad illumination, which is relevant for photovoltaics. However, the presented method is completely independent of any upconversion model and is not restricted to any special application. Any rare earth or transition metal ion embedded in a host material can be investigated as long as the determination of the absorption spectrum is possible.

Acknowledgments

We thank Dr K W Krämer from the University of Bern for helpful discussions and for providing the upconverter samples. The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 246200. Stefan Fischer gratefully acknowledges scholarship support from the Deutsche Bundesstiftung Umwelt DBU.

References

[1] Weber M J 1979 Handbook of the Physics and Chemistry of Rare Earths (New York: North-Holland)
[2] Barnes N P, Allen R E, Esterowitz L, Chicklis E P, Knights M G and Jenssen H P 1986 IEEE J. Quantum Electron. QE-22 337–43
[3] Pollack S A and Chang D B 1988 J. Appl. Phys. 64 2885–93
[4] Pollnau M and Jackson S D 2002 IEEE J. Quantum Electron. 38 162–9
[5] van den Hoven G N, Koper R J I M, Polman A, van Dam C, van Uffelen J W M and Smit M K 1996 Appl. Phys. Lett. 68 1886–8
[6] Slooff L H, van Blaaderen A, Polman A, Hebbink G A, Klink S I, Van Veggel F C J M, Reinhoudt D N and Hofstraat J W 2002 J. Appl. Phys. 91 3955–80
[7] Niedbala R S, Feindt H, Kardos K, Vail T, Burton J, Bielska B, Li S, Milunic D, Bourdelle P and Vallejo R 2001 Anal. Biochem. 293 22–30
[8] Chatterjee D K, Rufaiahah A J and Zhang Y 2008 Biomaterials 29 937–43
[9] Gibart P, Auzel F, Guillaume J C and Zahraman K 1996 Japan. J. Appl. Phys. 35 4401–2
[10] Trupke T, Green M A and Würfel P 2002 J. Appl. Phys. 92 4117–22

New Journal of Physics 15 (2013) 053033 (http://www.njp.org/)
[11] Trupke T, Green M A and Würfel P 2002 J. Appl. Phys. 92 1668–74
[12] Weber M J 1967 Phys. Rev. 156 231–41
[13] Blixt P, Nilsson J, Carlnas T and Jaskorzynska B 1991 IEEE Photon. Technol. Lett. 3 996–8
[14] Suyver J F, Aebischer A, Garcia-Revilla S, Gerner P and Güdel H U 2005 Phys. Rev. B 71 125123
[15] Baluschev S, Miteva T, Yakutkin V, Nelles G, Yasuda A and Wegner G 2006 Phys. Rev. Lett. 97 143903
[16] Goldschmidt J C, Fischer S, Löper P, Krämer K W, Biner D, Hermle M and Glunz S W 2011 Sol. Energy Mater. Sol. Cells 95 1960–3
[17] MacDougall S K W, Ivaturi A, Marques-Hueso J, Krämer K W and Richards B S 2012 Opt. Express 20 A879–87
[18] Fischer S, Fröhlich B, Steinkemper H, Krämer K W and Goldschmidt J C 2013 in preparation
[19] Fischer S, Steinkemper H, Loper P, Hermle M and Goldschmidt J C 2012 J. Appl. Phys. 111 013109
[20] Tkachuk A M, Razumova I K, Mirzaeva A A, Malyshev A V and Gapontsev V P 2002 Opt. Spectrosc. 92 67–82
[21] Dieke G H and Crosswhite H M 1963 Appl. Opt. 2 675–86
[22] Gruber J B, Sardar D K, Zandi B, Hutchinson J A and Trussell C W 2003 J. Appl. Phys. 93 3137–40
[23] Miyakawa T and Dexter D L 1970 Phys. Rev. B 1 2961–9
[24] Kramers H A 1930 Proc. R. Acad. Amsterdam 33 959
[25] Huang Y D, Mortier M and Auzel F 2001 Opt. Mater. 15 243–60
[26] Huang Y D, Mortier M and Auzel F 2001 Opt. Mater. 17 501–11
[27] Aebischer A, Hostettler M, Hauser J, Krämer K, Weber T, Güdel H U and Bürgi H-B 2006 Angew. Chem. 118 2869–73
[28] Krämer K W and Güdel H U 1997 Phys. Rev. B 56 13830–40
[29] Richards B S and Shalav A 2007 IEEE Trans. Electron. Devices 54 2679–84
[30] Fischer S, Goldschmidt J C, Löper P, Bauer G H, Brüggemann R, Krämer K, Biner D, Hermle M and Glunz S W 2010 J. Appl. Phys. 108 044912
[31] Suyver J F, Aebischer A, Biner D, Gerner P, Grimm J, Heer S, Krämer K W, Reinhard C and Güdel H U 2005 Opt. Mater. 27 1111–30
[32] Auzel F 2004 Chem. Rev. 104 139–73
[33] Henderson B and Imbusch G F 1989 Optical Spectroscopy of Inorganic Solids (Monographs on the Physics and Chemistry of Materials) (Oxford: Clarendon Press)
[34] García Solé J, Bausá L E and Jaque D 2005 An Introduction to the Optical Spectroscopy of Inorganic Solids (Madrid: Wiley)
[35] Ivanova S and Pellé F 2009 J. Opt. Soc. Am. B 26 1930–8
[36] Yamada N, Shionoya S and Kushida T 1972 J. Phys. Soc. Japan 32 1577
[37] Henke B, Pientka F, Johnson J A, Ahrens B, Miclea P T and Schweizer S 2010 J. Phys.: Condens. Matter 22 155107
[38] Lüthi S R, Pollnau M, Güdel H U and Hehlen M P 1999 Phys. Rev. B 60 162–78
[39] Weber M J 1968 Phys. Rev. 171 283–91
[40] Krämer K W, Güdel H U and Schwartz R N 1998 J. Alloys Compounds 275–277 191–5
[41] Pollnau M, Lüthy W, Weber H P, Krämer K, Güdel H U and McFarlane R A 1996 Appl. Phys. B 62 339–44
[42] Boulanger P L, Doualan J L, Girard S, Margerie J and Moncorgé R 1999 Phys. Rev. B 60 11380–90
[43] Boulanger P L, Doualan J L, Girard S, Margerie J, Moncorgé R and Viana B 2000 J. Lumin. 86 15–21