Improvement in the calculation of anti-Stokes energy transfer and experimental justification based on $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal*

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The improvement on the calculation of anti-Stokes energy transfer rate is studied in the present work. The additional proportion coefficient between Stokes and anti-Stokes light intensities of quantum Raman scattering theory as compared with the classical Raman theory is introduced to successfully describe the anti-Stokes energy transfer. The theoretical formula for the improvement on the calculation of anti-Stokes energy transfer rate is derived for the first time in this study. The correctness of introducing coefficient $\exp\{\Delta E/kT\}$ from well-known Raman scatter theory is demonstrated also. Moreover, the experimental lifetime measurement in $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal is performed to justify the validity of our important improvement in the original phonon-assisted energy transfer theory for the first time.

Keywords: improvement of anti-Stokes energy transfer, Raman scattering quantum and classical theory, $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal

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1. Introduction

The wide-used energy transfer theory is a foundation for the whole rare earth ion luminescence, and even the whole photonics,[1,2] in which the rates of Stokes and anti-Stokes phonon assisted energy transfer have the same calculation formula up to now.[3−5] The original energy transfer theory of rare earth ion proposed by Kushida has established a very good basis for the calculation of energy transfer rates. Miyakawa and Dexter[4,5] extended the original energy transfer theory to more practical state by introducing the phonon-assistant energy transfer. The accurate energy transfer rates can be calculated quantitatively based entirely on their theory. It has been basically used up to now continuously and widespreadly. Meanwhile, there are already some further improvements on the above original energy transfer theory for more accurate calculation.[6,7] Auzel has found that an additional coefficient, $\exp\{\Delta E/kT\}$, is essential in discussing the Stokes and anti-Stokes phonon sideband excitation fluorescence.[7] This distinction comes from the different transition probabilities of vibration states of two processes. It was proved also by Tarelho *et al.*[6] that there was still room for the improvement of the original energy transfer theory. Recently we have found for the first time that there is a limitation of the original phonon-assistant energy transfer theory in discussing the energy transfer under the condition of energy mismatch in the study on the fluorescence intensity reverse phenomena.[8,9] It was found for the first time that the traditional phonon-assisted energy transfer theory of rare earth ion energy transfer[3−5] failed to well explain the observed experimental calibrated results as it did not take into account the difference between Stokes and anti-Stokes processes. It is just like the well-known quantum Raman scattering theory[10] which has made an important improvement in the classical Raman scattering theory by sufficiently taking into account the difference between the Stokes and anti-Stokes processes. The additional coefficient, $\exp\{\Delta E/kT\}$, is used not only in quantum Raman scattering theory[10] but also in phonon sideband excitation fluorescence found by Auzel.[7] Thus

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there should be also a difference between Stokes and anti-Stokes phonon-assisted energy transfer rates[7,10] because they are involved in similar emitting and absorbing multiphonon processes.[10−22] Therefore the additional proportion coefficients between Stokes and anti-Stokes light intensities in the quantum Raman scattering theory as compared with the classical Raman theory were introduced into the widely used theory of rare earth ion energy transfer to successfully describe the anti-Stokes energy transfer.[10] This is just like the Stokes and anti-Stokes phonon sideband excitation fluorescences proposed by Auzel.[7] Our improvement in the phonon-assisted energy transfer theory proposed by Dexter and Miyakawa is also the perfection of the whole original energy transfer theory of Kushida *et al.*[3−5] The validity of our important improvement in the original phonon-assisted energy transfer theory is also proved for the first time by experiment in the present work. The improvement in the theory of phonon-assisted energy transfer between rare earth ions is very significant and indispensable when the photonics of nano-materials is probed.[7−25] All the above work on the improvement of energy transfer theory may be just like Feynman's prediction, 'There's plenty of room at the bottom.', for nanomaterial.[14]

2. Theory of improvement on the calculation of anti-Stokes energy transfer rate

Following the classification of Bron and Wagner,[11] triply ionized rare earth ions in usual matrices by laser or photon action through energy transfer appear to fall into the class with small change in mass and spring constant and weak election–lattice coupling. Using the Kubo–Toyozawa–Lax generating function method, the adiabatic approximation and the linear coupling, in the case of small-g coupling constant (low temperature with respect to maximum phonon energy of the lattice), Miyakawa and Dexter have obtained the expression of energy transfer probability[5]

$$W_{\rm ab} = (2\pi/\hbar)\,|H_{\rm ab}|^2 \sum_N {\rm e}^{-(g_{\rm a}+g_{\rm b})}(g_{\rm a}+g_{\rm b})^N/N!\sigma_{\rm ab}\delta(\varepsilon_0 - N\hbar\omega), \tag{1}$$

where $g_{\rm a}$ and $g_{\rm b}$ are the electron–phonon coupling functions of energy donor and accepter related to S_0, the Pekar–Huang–Rhys coupling constant, by $g = S_0(2\bar{n})+1$, with n being the occupation number for the effective phonons of energy $\hbar\omega$ where ω is assumed to be the maximum lattice frequency; $\sigma_{\rm ab}$ is the overlap integral between ions a and b for zero-order process.

We suppose $g = S_0$[7,24] and associate the variation with 'Pekarian' forms at 0°K[13,14] in the phonon-assisted energy transfer process in which phonons are emitted, that is ${\rm e}^{-S_0}S_0^N/N!F_N(T,S_0)$ with

$$F_N(T,S_0) = {\rm e}^{-2S_0\bar{n}} \sum_{l=0}^{\infty} \frac{N!}{l!(l+N)!}(1+\bar{n})^{l+N}(\bar{n}S_0^2)^l. \tag{2}$$

For small $\bar{n}$ and S_0, and large N, Eq. (2) reduces to $(\bar{n}+1)^N$. As a result, for phonon-assisted energy transfer process, assuming that phonons are mainly emitted, the expression of probability can be written as

$$W_{\rm Stokes-ab}(N) = (2\pi/\hbar)\,|H_{\rm ab}|^2\,\sigma_{\rm ab}\frac{{\rm e}^{-(S_{0\rm a}+S_{0\rm b})}(S_{0\rm a}+S_{0\rm b})^N}{N!}(1+\bar{n})^N. \tag{3}$$

For anti-Stokes phonon-assisted energy transfer, where the transferred energy is less than the accepted energy and phonons are mainly absorbed, we have equivalently

$$W_{\rm anti\text{-}Stokes-ab}(N) = (2\pi/\hbar)\,|H_{\rm ab}|^2\,\sigma_{\rm ab}\frac{{\rm e}^{-(S_{0\rm a}+S_{0\rm b})}(S_{0\rm a}+S_{0\rm b})^N}{N!}(\bar{n})^N, \tag{4}$$

where $\bar{n} = ({\rm e}^{\hbar\omega/kT}-1)^{-1}$. By using the Stirling's approximation for $N! \approx (N/{\rm e})^N$ and energy mismatch $\Delta E = N\hbar\omega$, Eqs. (3) and (4) can be rewritten respectively as

$$W_{\rm Stokes-ab}(N) = (2\pi/\hbar)\,|H_{\rm ab}|^2\,\sigma_{\rm ab}{\rm e}^{-(S_{0\rm a}+S_{0\rm b})}{\rm e}^{-\beta\Delta E}, \tag{5}$$

$$W_{\text{anti-Stokes}-\text{ab}}(N) = (2\pi/\hbar)\left|H_{\text{ab}}\right|^2 \sigma_{\text{ab}} \mathrm{e}^{-(S_{0\text{a}}+S_{0\text{b}})} \mathrm{e}^{-(\beta+1/kT)\Delta E}, \tag{6}$$

and

$$W_{\text{Stokes}-\text{ab}}(N)/W_{\text{anti-Stokes}-\text{ab}}(N) = \mathrm{e}^{\Delta E/kT} \tag{7}$$

with β defined as $\beta = (\hbar\omega)^{-1}[\ln(\frac{N}{S_{0\text{a}}(\bar{n}+1)}) - \ln(1+\frac{S_{0\text{b}}}{S_{0\text{a}}}) - 1]$. Considering the definition of α in the multi-phonon relaxation process, $\beta = \alpha - (\hbar\omega)^{-1}\ln(1+\frac{S_{0\text{b}}}{S_{0\text{a}}})$ which is the same as the expression in Ref. [5] under the condition of $g = S_0$.

Note that the expressions of phonon-assisted energy transfers for Stokes process and anti-Stokes process are nearly the same, but different by a factor of $\exp\{\Delta E/kT\}$ which is the ratio between $W_{\text{Stokes}-\text{ab}}$ and $W_{\text{anti-Stokes}-\text{ab}}$. Thus from the formulas (5)–(7), which we obtained for the first time to the best of our knowledge, it is clear that the additional coefficient, $\exp\{\Delta E/kT\}$, must be introduced to describe the difference between the Stokes and anti-Stokes phonon-assisted energy transfers. And a similar phenomenon can be found in the Raman scattering theory.

3. Raman scattering theory and introduction of the coefficient

The intensity of Raman scattering in the classical theory can be expressed as

$$I(t) = AE_0^2\left[B_0^2\cos^2(\omega_L t) + B_1^2\cos^2((\omega_L-\omega_q)t) + B_2^2\cos^2((\omega_L+\omega_q)t) + \text{cross}-\text{term} + \ldots\right], \tag{8}$$

where $B_0^2 = \alpha_0^2\omega_L^4$, $B_1^2 = \frac{1}{4}\left(\frac{\partial^2\alpha}{\partial Q^2}\right)_0 Q_0^2(\omega_L-\omega_q)^4$, and $B_2^2 = \frac{1}{4}\left(\frac{\partial^2\alpha}{\partial Q^2}\right)_0 Q_0^2(\omega_L+\omega_q)^4$. Because the average radiation power of the cross-term is zero over a sufficiently long time, the cross-term can be ignored. It is not difficult to see that terms B_0^2, B_1^2 and B_2^2 are related to Rayleigh scattering, Stokes Raman scattering and anti-Stokes Raman scattering respectively. The ratio of B_1^2 to B_2^2 is

$$\frac{B_1^2}{B_2^2} = \frac{\frac{1}{4}\left(\frac{\partial^2\alpha}{\partial Q^2}\right)_0 Q_0^2(\omega_L-\omega_q)^4}{\frac{1}{4}\left(\frac{\partial^2\alpha}{\partial Q^2}\right)_0 Q_0^2(\omega_L+\omega_q)^4} = \frac{I_{\text{Stokes}}}{I_{\text{anti}}} = \frac{(\omega_L-\omega_q)^4}{(\omega_L+\omega_q)^4} < 1. \tag{9}$$

Obviously, the classical electromagnetic theory can explain the physical origins of Raman-shift. But there is a contradiction between the experimental results and the theoretical values of the intensity relationship between Stokes process and anti-Stokes process.

The intensity of Raman scattering in the quantum theory (in the Placzek's approximation) can be expressed as

$$I_{\text{Stokes}} = \text{const}\cdot(\omega_L-\omega_q)^4\frac{\hbar}{2\omega_q}\alpha_{\beta\varphi,q}^2(1+\overline{n_q}), \tag{10}$$

and

$$I_{\text{anti}} = \text{const}\cdot(\omega_L+\omega_q)^4\frac{\hbar}{2\omega_q}\alpha_{\beta\varphi,q}^2\overline{n_q}, \tag{11}$$

where $\alpha_{\beta\varphi,q}$ is the polarization tensor matrix element, and $\overline{n_q}$ is the average population probability of a certain elementary excitation. If the elementary excitation is induced by phonon, which satisfies the Bose–Einstein distribution $\overline{n_q} = [\exp(\hbar\omega_q/k_{\text{B}}T)-1]^{-1}$, substituting it into the above expression we obtain

$$\frac{I_{\text{Stokes}}}{I_{\text{anti}}} = \left(\frac{\omega_L-\omega_q}{\omega_L+\omega_q}\right)^4\exp(\hbar\omega_q/k_{\text{B}}T). \tag{12}$$

From Eq. (12), we note that there is an additional coefficient $\exp(\hbar\omega_q/k_{\text{B}}T)$ compared with Eq. (9). Usually, this coefficient is much larger than 1, so the trouble of the intensity relationship between Stokes process and anti-Stokes process in classical theory is solved.

Thus, the experimental phenomenon of Raman spectroscopy is well explained by quantum Raman theory quantitatively. It is this coefficient that makes the trouble solvable in the relationship between the Stokes and anti-Stokes process intensities in the classical Raman theory. Note that this coefficient comes from the differences among the transitions of vibrational levels. In general, most of the molecules are in

the ground vibrational state, with very few situated at high vibrational states. Therefore the vibrational transitions that start from the ground vibrational level have much larger probabilities, which correspond to the Stokes processes where the electronic system loses energy to the vibrational system. This discussion is also applicable to the phonon-assisted energy transfer process involving energy exchange between the electronic system and vibrational system. Therefore the difference between energy absorption and energy radiation in the vibrational system must be reflected in the phonon-assisted energy transfer.

It is worth noting that the additional proportion coefficient for anti-Stokes process in the quantum theory of Raman scattering

$$\frac{1+\overline{n_q}}{\overline{n_q}} = \exp\left(\hbar\omega_q/k_{\rm B}T\right) \tag{13}$$

comes from the difference in transition between vibrational levels. In the quantum theory of Raman spectroscopy,[10] considering the first order Raman scattering, the change in vibrational quantum number is $\Delta n_q = \pm 1$, where $\Delta n_q = +1$ corresponds to Stokes scattering, while $\Delta n_q = -1$ corresponds to anti-Stokes scattering. In general, most of the molecules are in the ground vibrational state, with very few situated at high vibrational states. Therefore the vibrational transitions from the ground vibrational level have much larger probabilities, which correspond to the Stokes process where electronic system loses energy to the vibrational system. This discussion is also applicable to the phonon assisted energy transfer process which is discussed in this paper, because all of these processes involve the energy exchange between the electronic system and the vibrational system. So the difference between energy absorption and energy radiation in vibrational system must be reflected in the phonon assisted energy transfer process. Thus by analogy, it can be expected that there must be a similar coefficient $\exp\left(\hbar\omega_q/k_{\rm B}T\right)$ to that in Eq. (12) in the relationship between the rates of Stokes energy transfer and anti-Stokes energy transfer. Therefore it is required to introduce the coefficient $\exp\{hc\tilde{\upsilon}_k/kT\}$ to improve the traditional energy transfer theory,[3−5] in which the original Kushida theory remains unchanged and the original phonon-assistant Miyakawa and Dexter theory is improved by the coefficient $\exp\{hc\tilde{\upsilon}_k/kT\}$. The original theory is considered reasonable only for discussing Stokes process, whereas the rate of anti-Stokes energy transfer should be divided by the introduced coefficient $\exp\{hc\tilde{\upsilon}_k/kT\}$, where $\tilde{\upsilon}_k$ is the energy mismatch of the transfer process.

4. Stokes and anti-Stokes phonon sideband excitation fluorescence

A similar result was achieved by Auzel in discussing the Stokes and anti-Stokes phonon sideband excitation fluorescence.[7] Assuming the same variation with temperature as the one proposed for decay, with any 'Pekarian' form at 0°K ($\mathrm{e}^{-S_0}S_0^N/n!$) in the processes, and considering the case of small $\overline{n}$ and S_0 and large N, where $\overline{n}$ is the occupation number for the effective phonons, S_0 is the Pekar–Huang–Rhys coupling constant and N is the order of the multiphonon process involved, the probabilities for multiphonon Stokes and anti-Stokes excitation are

$$W_{\rm Stokes}(N) = \frac{I(N)}{c}\frac{8\pi^3}{3h^2}\left|M\right|^2\frac{\mathrm{e}^{-S_0}S_0^N}{N!}(1+\overline{n})^N, \tag{14}$$

and

$$W_{\text{anti-Stokes}}(N) = \frac{I(N)}{c}\frac{8\pi^3}{3h^2}\left|M\right|^2\frac{\mathrm{e}^{-S_0}S_0^N}{N!}(\overline{n})^N, \tag{15}$$

respectively.

By using Stirling's approximation, Eqs. (14) and (15) are written, respectively, as

$$W_{\rm Stokes}(\Delta E) = \frac{I}{c}\frac{8\pi^3}{3h^2}\left|M\right|^2\mathrm{e}^{-S_0}\mathrm{e}^{-\alpha_{\rm S}\Delta E}, \tag{16}$$

and

$$W_{\text{anti-Stokes}}(\Delta E) = \frac{I}{c}\frac{8\pi^3}{3h^2}\left|M\right|^2\mathrm{e}^{-S_0}\mathrm{e}^{-(\alpha_{\rm S}+1/kT)\Delta E}, \tag{17}$$

where $\alpha_{\rm S} = (\hbar\omega_m)^{-1}\{\ln[N/S_0(\overline{n}+1)]-1\}$, and $\hbar\omega_m$ is the effective phonon energy.

We find that Stokes process and anti-Stokes process are also different by factor $\exp\{\Delta E/kT\}$, where ΔE is the energy gap between the excitation and the electronic level. Thus in the energy transfer process which exhibits energy mismatch and multiphonon phenomenon, the rates for Stokes energy transfer and anti-Stokes energy transfers should be different, too, by factor $\exp\{\Delta E/kT\}$.

Moreover, plenty of upconversion research, which was a frontier, over the past decades, found the experimental fact that the Stokes upconversion process resulting from Stokes energy transfer was obviously stronger than the anti-Stokes upconversion process

resulting from anti-Stokes energy transfer. Our improved anti-Stokes energy transfer theory can also help the original theory to explain the above upconversion phenomena very well.[14−21]

5. Experimental sample

Since the 1990s, YVO_4 crystal has been studied widely and found very good applications. YVO_4 crystal is tetragonal, belongs to a uniaxial crystal, and has very good light transmission properties. In the range of 40–5000nm, it has a high optical transmittance, and can be used as fluorescent agent, polarizer and laser matrix material. YVO_4 crystal, with high laser damage threshold, good mechanical properties, chemical stability, low pump threshold, and large laser emission cross section, is one of the most popular new laser crystal materials.[15] The Er^{3+}:YVO_4 crystal used in the present study is grown by the Czochralski method. The concentration of Er^{3+} in the crystal is 0.5mol% as measured through inductively coupled plasma atomic emission spectrum (ICP: JY:ULTIMA). The size of the crystal is 5 mm × 7 mm × 10 mm. The mass density of the sample is 4.22 g/cm^3. The a-axis is in the direction of the 5 mm side, and c-axis is in the direction of the 7 mm side.

6. Experimental justification based on $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal for the improvement on calculating anti-Stokes energy transfer

Our interesting investigations[18] for the improvement on calculating the anti-Stokes energy transfer are confirmed by our further experiment, which supports our investigation on the introduction of a coefficient $\exp\{ch\tilde{\upsilon}_k/kT\}$ to characterize the difference between Stokes energy transfer and anti-Stokes energy transfer.[18,19]

The YVO_4 crystals doped with Er^{3+} and Yb^{3+} ions at different concentrations are considered, which are Er(1%)Yb(30%):YVO_4, Er(1%)Yb(70%):YVO_4 and Er(1%)Yb(99%):YVO_4. The pulse laser equipment, i.e. Nd:YAG pulse laser (EKSPLA Company, NL303), is used to measure the lifetimes of $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} ion in this series of materials. The monochromator employed is SpectraPro-500i (Acton Research Corporation). The pulse laser energy is about 0.7 mJ/per pulse with the duration about 5 ns. The laser spot is about 5 mm in diameter. The sample is irradiated by the pumping laser. The fluorescence in a vertical angle is collected into the monochromater. Then the lifetime signal is measured by PMT. Figure 1 gives the schematic diagram of energy level structure of the Er^{3+} Yb^{3+} codoped sample. Figures 2 and 3 show the experimental results of $^4S_{3/2}$ and $^4F_{9/2}$ energy levels for Er(1%)Yb(30%):YVO_4 sample. All the results are listed in Table 1.

We focus on the lifetime changes of two levels in the Er^{3+} and Yb^{3+} ions co-doped materials. Note that as the concentration of Yb^{3+} ion increases, the lifetime of $^4S_{3/2}$ decreases rapidly, but the lifetime of $^4F_{9/2}$ is nearly unchanged. The depopulating channels of rare earth ions include induced absorption, induced emission, spontaneous emission, multi-phonon relaxation and energy transfer. We know that the change in Yb^{3+} concentration has little influence on these processes except for the energy transfer. Because of the same experimental condition and the same matrices in which the rare earth ions locate, the environment factors that determine the rates of these single ion processes are nearly the same. But the change in Yb^{3+} concentration has a significant influence on the energy transfer through changing the distance between the rare earth ions. The rates of energy transfer will increase greatly as concentration increases. And we can conclude that the change of lifetime results from the change in energy transfer rate.

Table 1. Lifetime results (in units of s) of $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} ion in the series of $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal materials.

	Er(1%)Yb(30%):YVO_4	Er(1%)Yb(70%):YVO_4	Er(1%)Yb(99%):YVO_4
$^4S_{3/2}$	4.97988×10^{-6}	1.56038×10^{-6}	7.10064×10^{-7}
$^4F_{9/2}$	1.66593×10^{-7}	1.60081×10^{-7}	1.58753×10^{-7}

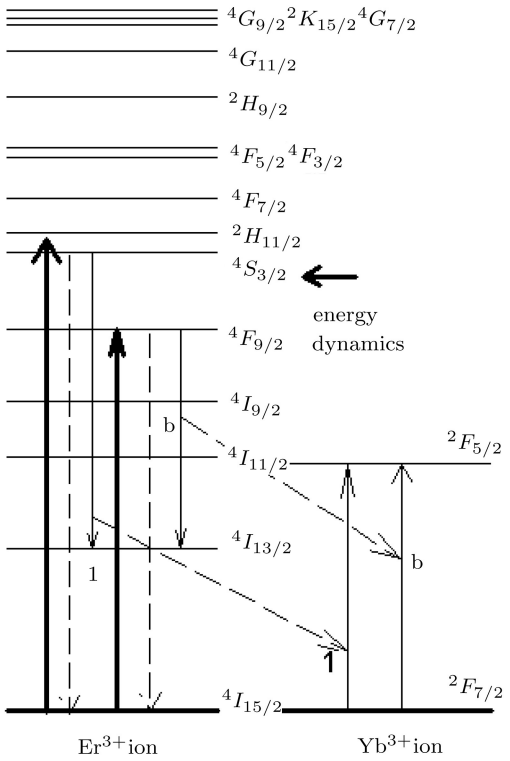


Fig. 1. Schematic diagram of energy level structure of Er^{3+} Yb^{3+} codoped sample.

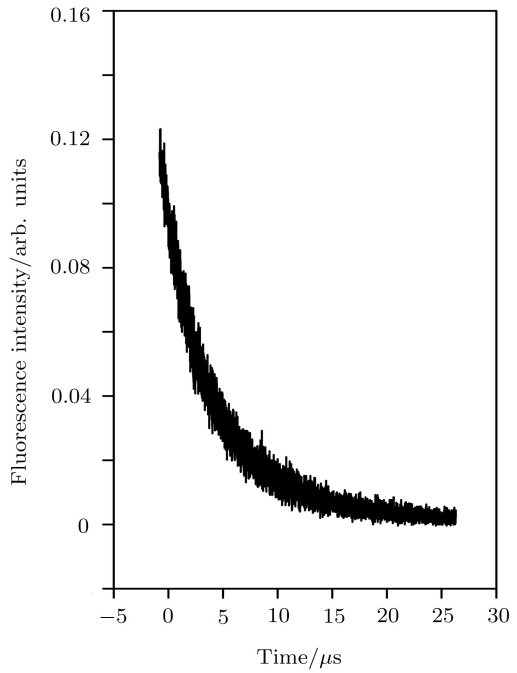


Fig. 2. Experimentally measured lifetime results (units is μs) of $^4S_{3/2}$ energy level when excited by 522 nm pulse laser for Er(1%)Yb(30%):YVO_4 sample.

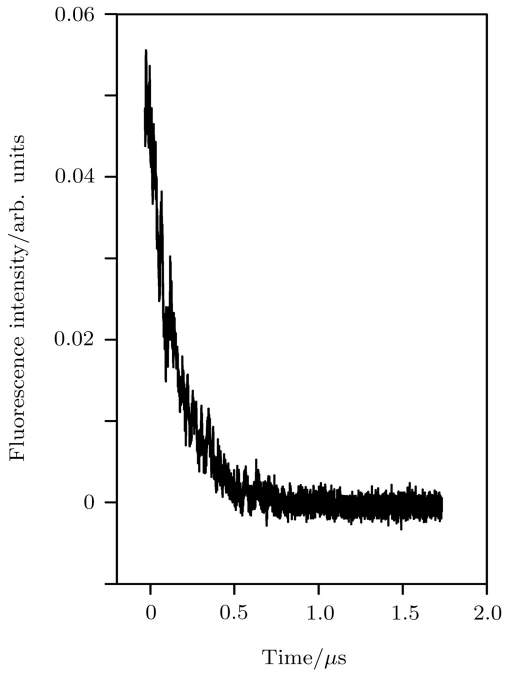


Fig. 3. Experimentally measured lifetime results (units is μs) of $^4F_{9/2}$ energy level when excited by 652 nm pulse laser for Er(1%)Yb(30%):YVO_4 sample.

When $^4S_{3/2}$ is excited, the main energy transfer channel is $\{^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ because its energy mismatch is +1200 cm^{-1}, much smaller than that in any other energy transfer channel which depopulates the level. Similarly, when $^4F_{9/2}$ is excited, the main energy transfer channel is $\{^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ because its energy mismatch is −2000 cm^{-1}, much smaller than that in any other energy transfer channel which depopulates this level. According to the original energy transfer theories proposed by Kushida, Miyakawa and Dexter, we can estimate the rates of these two channels. The reduced matrix elements of the unit tensor operator U^2 for $^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+})$ are (0.0, 0.0 and 0.3419). The U^2 for $^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+})$ are (0.0109, 0.1533 and 0.0870). Considering the Judd–Ofelt intensity parameters of Er:YVO_4 which are calculated from the absorption spectrum: $\Omega_2 = 11.675 \times 10^{-20}$, $\Omega_4 = 2.910 \times 10^{-20}$ and $\Omega_6 = 1.923 \times 10^{-20}$, we find that the energy transfer rates of the two channels are not much different. The rate of $\{^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ is a little larger than that of $\{^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ only because it possesses a slightly smaller energy mismatch.

Thus through the original theories, we find that as Yb^{3+} concentration increases, the rates of $\{^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ and $\{^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ increase synchronously and they are not much different. For the $^4S_{3/2}$ level, these estimated results are in agreement with the experimental results. As the energy transfer rate increases, the lifetime decreases clearly. But for the $^4F_{9/2}$ level, the estimates are inconsistent the measurements. The lifetime obtained from the experiment is changeless.

This contradiction problem is solved if we take into account the improved coefficient for anti-Stokes energy transfer, $\exp\{\Delta E/kT\}$, which portrays the difference between Stokes energy transfer and anti-Stokes energy transfer. As shown in the schematic of Er^{3+}, Yb^{3+} ion' energy levels in Fig. 1, $\{^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ is a Stokes process, whereas $\{^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ is an anti-Stokes process. If we do not distinguish these two styles of energy transfer, the transfer rates of the two channels are not much different. But if we introduce the coefficient $\exp(hc\tilde{\upsilon}_k/kT)$ into the anti-Stokes process, the rate of $\{^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$ will be much smaller than the rate of $\{^4S_{3/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}), {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^2F_{5/2}(Yb^{3+})\}$. It is clear that the change in energy transfer rate of $^4F_{9/2}$ level is negligible because of the small value of the channel rate. That is the explanation of why the lifetime of $^4F_{9/2}$ level is basically unchanged with the rare earth ion concentration increasing. In conclusion, the experimental results are justificative as it is necessary to introduce the improved anti-Stokes energy transfer coefficient $\exp\{\Delta E/kT\}$ in order to distinguish and calculate Stokes energy transfer rate and anti-Stokes energy transfer rate.

7. Conclusion

The original energy transfer theory of rare earth ion proposed by Kushida[3] has established a very good basis for the calculation of energy transfer rates. Miyakawa and Dexter[4,5] extended the original energy transfer theory to a more practical state by introducing the phonon-assisted energy transfer. However, the Miyakawa and Dexter theory cannot distinguish the Stokes and anti-Stokes energy transfers. The calculation of Stokes and anti-Stokes energy transfer rates in Miyakawa and Dexter theory has the same formula. Meanwhile, plenty of research on upconversion and so on has found the experimental fact that Stokes upconversion process resulting from Stokes energy transfer is obviously larger than anti-Stokes upconversion process resulting from anti-Stokes energy transfer.[17−25] In our recent work,[18] it was found that, in the unchanged good Kushida theory,[3] the original phonon-assisted rare earth ion energy transfer theory[4,5] cannot well explain the observed experimental results as it does not take into account the difference between Stokes and anti-Stokes process. It is just like the well-known quantum Raman scattering theory with the important improvement on classical Raman scattering theory as it takes into account the difference between Stokes and anti-Stokes process sufficiently. The additional proportion coefficient for anti-Stokes light intensity in the quantum Raman scattering theory[10] as compared with the classical Raman theory was introduced to successfully describe the anti-Stokes energy transfer. In the present article, we derive the theoretical formula for improving the calculation of anti-Stokes energy transfer for the first time. The correctness of introducing the coefficient, $\exp\{\Delta E/kT\}$, from the well-known Raman scattering theory is demonstrated also. Moreover, the lifetime measurement experiments for the $Er_{0.01}Yb_xY_{1-0.01-x}VO_4$ crystal are also conducted to verify the validity of our important improvement in the original phonon-assisted energy transfer theory for the first time.

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