CONDENSED-MATTER SPECTROSCOPY

Coherent Cooperative Fluorescence Resonance Energy Transfer[1]

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Abstract—Cooperative fluorescence resonance energy transfer effect is experimentally demonstrated for a few crystals doped with rare-earth ions. We show that, at the liquid helium temperatures in similar crystals, coherent cooperative fluorescence resonance energy transfer, as well as an inverse coherent up-conversion process, could be observed, and briefly discuss possible applications of these effects.

1. INTRODUCTION

Cooperative fluorescence resonance energy transfer (cooperative FRET) has been predicted in 1957 by Dexter [1]. More than forty years after, this same effect has been discovered experimentally first by Basiev et al. for the transitions from Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{15/2}$ (donor) to Ce^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (acceptor) in $La_{1-x}Ce_xF_3 : Nd^{3+}$ crystals [2–4] and later on by Vergeer et al. for the transitions from Tb^{3+} $^5D_4 \rightarrow {}^7F_6$ (donor) to Yb^{3+} $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (acceptor) in $Yb_xY_{1-x}PO_4 : Tb^{3+}$ crystals [5]. The above notation means that an excitation energy, which is initially located at the $^4F_{3/2}$ state of neodymium ion, instead of being irradiated in $^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition, is transferred to two neighboring cerium ions which initially occupied $^2F_{5/2}$ state and occupy the $^2F_{7/2}$ after the transfer, and similarly for the Tb^{3+}–Yb^{3+} system; see Fig. 1. Observation of cooperative fluorescence resonance energy transfer is not only of a purely fundamental interest but such an effect is considered as a practically important case of a quantum cutting phenomenon which exploration can lead to the increase of the efficiency of luminescent materials and solar cells [5–7].

In this paper, we predict that for similar crystals, the *coherent* cooperative fluorescence resonance energy transfer process at low (liquid helium) temperatures could be observed: an electronic excitation,

which is initially localized at one rare-earth ion, in appropriate conditions is fully or partially transferred to two neighboring rare-earth ions without the loss of coherency thus forming entangled quantum state of three ions. An inverse process, that is coherent up-conversion, also could be observed for the same crystals. We believe that, again, these effects are not only of a fundamental interest but that they will find use in a rapidly emerging field of the rare-earth ions-based quantum informatics, where a number of approaches
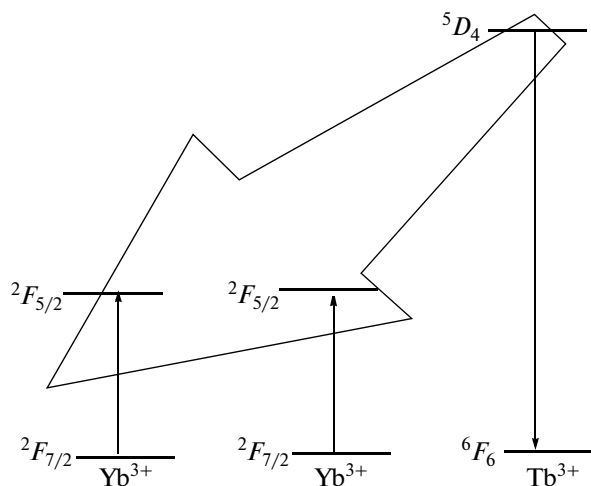

Fig. 1. Schematic diagram of cooperative fluorescence resonance energy transfer for the transitions from one initially excited Tb^{3+} $^5D_4 \rightarrow {}^7F_6$ ion (donor) to two Yb^{3+} ions $^2F_{7/2} \rightarrow {}^2F_{5/2}$ (acceptors).

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were recently proposed, see e.g. [8–17] as just a few important initial papers, which all were followed by numerous subsequent publications.

2. COHERENT COOPERATIVE FLUORESCENCE RESONANCE ENERGY TRANSFER

A necessary prerequisite for existence of the coherent cooperative fluorescence resonance energy transfer effect is the really long decoherence times observed for different rare-earth ions in crystals at the liquid helium temperatures. In the most favorable cases such times can attain a few milliseconds as this was shown, for example, for $^7F_0 \to \,^5D_0$ transition of Eu^{3+} ion in Y_2SiO_5 crystal [18], while the decoherence times lying in the microsecond range are quite common for the different crystals, especially in the presence of magnetic field. Numerous examples can be found in the literature, see e.g. [19, 20] and [21] where a kind of a mini-review what optical transitions in rare earth ions look especially attractive for quantum computing can be found. For our purposes, here this is enough to cite the 27 μs decoherence time measured for the $^4F_{3/2}$ excited state of Nd^{3+} ion in YVO_4 crystal [22], the value of the true homogeneous width of 28 kHz, that is the decoherence time around 10 μs, observed for the transition $^5D_4 \to \,^7F_6$ in Tb^{3+} ion in $LiYF_4$ crystal in the presence of 42 kG magnetic field [23], and so on. Due to the long decoherence times coherent FRET has not only been observed for rare-earth ions in crystals (pair- and quartet- centers of Nd^{3+} ions in fluoride crystals [24]) but has been already used to prepare different quantum states interesting for the quantum informatics [25].

From now on, we will restrict our consideration with the transition from Tb^{3+} $^5D_4 \to \,^7F_6$ (donor) to Yb^{3+} $^2F_{7/2} \to \,^2F_{5/2}$ (acceptor) in $Yb_xY_{1-x}PO_4 : Tb^{3+}$ crystals. As has been indicated above, incoherent cooperative FRET as well as an inverse up-conversion process (for the latter excitations from two Yb ions sum up onto one Tb ion) were observed for this system earlier, see [5] and references cited therein. We failed to find in the literature the decoherence data pertaining exactly to such crystal but its similarity with many other analyzed systems enables to propose comparable, that is of the order of a few microseconds, decoherence times for it.

The theory of non-coherent cooperative FRET is relatively well established (its foundations have been laid out already by Dexter [1], and important refinements were done lately; see [5, 26, 27]). For our current purposes the exposition given by Kushida [26] seems the most appropriate, hence below we follow the main lines and notation of his papers, whose straightforward modification enables to analyze the case of coherent cooperative FRET.

Let us consider an electromagnetic interaction involving three particles A, B, C whose initial state $|abc\rangle$ changes to $|a'b'c'\rangle$. If, say, particle A is initially excited while particles B and C are not, we have a case of coherent cooperative FRET. For the case of an exact energy resonance between the transitions involved (see below for the discussion of this assumption), the transfer rate can be written as

$$P = \frac{1}{\hbar}\langle abc | H | a'b'c'\rangle. \tag{1}$$

Here, H is a three-particle interaction Hamiltonian which can be expressed as a sum of appropriate combinations of two-particle interaction Hamiltonians H_{AB}, H_{AC}, H_{BC} thus giving in the second order of the perturbation theory the following general expression suitable to be used for both coherent cooperative FRET and coherent up-conversion:

$$
\begin{aligned}
\langle abc | H | a'b'c'\rangle = \sum_\mu &\left(\frac{1}{E_{a'c'} - E_{\mu c}} + \frac{1}{E_{ab} - E_{\mu b'}} \right) \\
&\times \langle ab | H_{AB} | \mu b'\rangle\langle \mu c | H_{AC} | a'c'\rangle \\
+ \sum_\mu &\left(\frac{1}{E_{a'b'} - E_{\mu b}} + \frac{1}{E_{ac} - E_{\mu c'}} \right) \\
&\times \langle ac | H_{AC} | \mu c'\rangle\langle \mu b | H_{AB} | a'b'\rangle \\
&+ [H_{AB}][H_{BC}] + [H_{BC}][H_{AB}] \\
&+ [H_{AC}][H_{BC}] + [H_{BC}][H_{AC}].
\end{aligned}
\tag{2}
$$

Here the notation $E_{a'c'}$, etc. means the energy of the state $|a'c'\rangle$ and μ designates some energy level of an appropriate particle (for example, particle A for the case of the term $\langle ab | H_{AB} | \mu b'\rangle\langle \mu c | H_{AC} | a'c'\rangle$ above), and the expressions in square brackets abbreviate the terms similar to those two which are explicitly written. Hamiltonians H_{AB}, H_{AC}, H_{BC} are "standard" Hamiltonians describing the two-particle multipolar electromagnetic interaction. Kushida performed the detailed analysis of the contributions to the matrix element (2) coming from dipole−dipole (dd), dipole−quadrupole (dq), and quadrupole−quadrupole (qq) two-particle interactions, and one of examples given by him deals exactly with the interactions between ions of Yb^{3+} an Tb^{3+} which are of interest now. In particular, he demonstrated that the main contribution to the value of $\left|\langle abc | H | a'b'c'\rangle^2\right|$ comes from the lowest-order parity-allowed dq−dq process. (Note, that for this dq−dq process an intermediate level μ should be located in the d-zone of either donor or acceptor ions; correspondingly one can speak about a cooperative energy transfer pathway for the former case and an accrective energy transfer pathway for the latter case; cf. [5, 27, 28]). Kushida also found that the dq−dd (or dd−dq)

and *dd–dd* processes give contributions which are respectively one and two orders of magnitude smaller than that due to the *dq–dq* mechanism, and hence they can be neglected for our current purposes.

Based essentially on the theoretical estimations of different parameters important for the problem at hand, in paper [26] Kushida presented numerical estimations for the rate of the non-coherent cooperative FRET process for the system of Tb–Yb–Yb ions for the interionic distances $R_{AB} = R_{AC} = R_{BC} = 7$ a.u. = 3.7 Å, that is for the value very close to 3.8 Å which corresponds to the ion positions found in the meridian plane of an elementary cell of YPO_4 crystal containing four yttrium ions; see Fig. 2 in [29], cf. also [5]. From his estimations, the following contribution of the *dq–dq* process to the squared matrix element can be straightforwardly inferred:

$$\left| \left\langle {}^2F_{7/2}(Yb^{3+}), {}^2F_{7/2}(Yb^{3+}), {}^5D_4(Tb^{3+}) \middle| H \middle| {}^2F_{5/2}(Yb^{3+}), {}^2F_{54/2}(Yb^{3+}), {}^7F_6(Tb^{3+}) \right\rangle \right|^2 / \hbar^2 = 7.2 \times 10^{12} \text{ s}^{-2}. \tag{3}$$

As for the pure intraconfiguration *qq–qq* processes, their consideration is evidently difficult due to the large number of levels of the $4f^N$ electron configuration participating in such a process as an intermediate state μ, hence the precision of the relevant estimations is limiting. Nevertheless, Kushida succeeded to demonstrate that both the interconfigurational and intraconfigurational contributions are of the same order of magnitude.

Using the aforementioned results of Kushida and taking into account the dependence of the parameters of the problem on the characteristics of the concrete crystal as well as the uncertainty with the contribution of the *qq–qq* process, from (1–3) one can give reasonably reliable estimation of the coherent cooperative FRET rate as about $P \cong 3 \times 10^6$ s^{-1}. This means that the characteristic time necessary, for example, for the complete entanglement of three interacting ions, $T = \pi/2P$, is around 500 ns (or better to say that this time lies in the range 450–1000 ns) and hence reasonably shorter than decoherence time characteristic for similar systems.

An inverse process, that is the coherent up-conversion where the excitation energy of two acceptor centers is resonantly summed up on one donor center, can be analyzed for the transitions involved along the same lines. Such an analysis readily demonstrates the feasibility of this process for the same crystals and experimental conditions.

3. DISCUSSION AND CONCLUSIONS

Thus our analysis shows that the coherent cooperative FRET and coherent up-conversion processes could be realized for appropriate crystals doped with rare earth ions. If necessary, the expressions given above can be easily generalized. For example, one can easily take into account the case of an inexact resonance for the system donor—two neighboring acceptors. This situation is also quite common with the standard case of two interacting two-level systems when the resonance condition is only approximately hold (see e.g. [30]), of which the inexact resonance for the coherently interacting donor and acceptor(s) is a particular example, see also [12, 31, 32].

However, apparently such a generalization is not timely at the current stage where coherent cooperative FRET has not yet been observed. For this, the main issue to overcome is, of course, the necessity to obtain a spectral resonance (overlapping) of rather narrow spectral lines, as implied by large decoherence times; this condition is, of course, much more stringent that it takes place for usual incoherent cooperative FRET. However, two circumstances should be taken into account when speaking about this issue. The first is a very broad, and constantly enlarging, scope of crystals
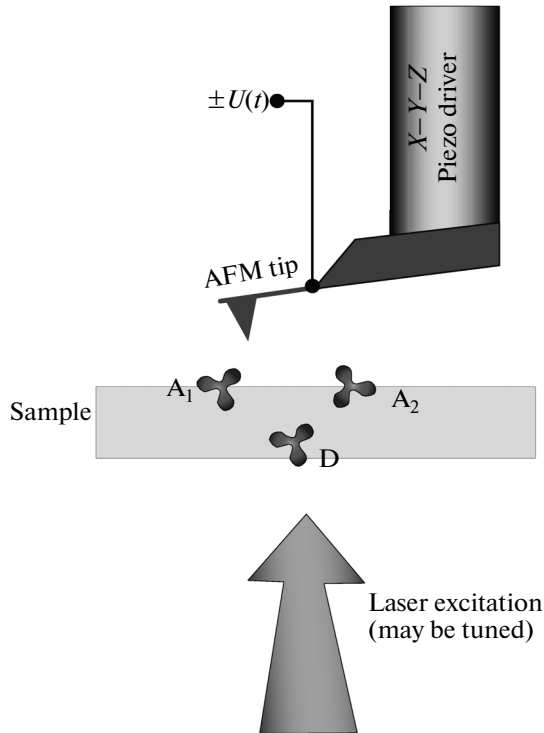

Fig. 2. Illustrating the possibility to control the system with the local Stark effect induced by the sharp tip of Atomic Force Microscope with a variable electric potential $U(t)$ applied scanning close to the donor–acceptor system.

containing dopant ions at question, as well as the recent progress in synthesis of nanocrystals, crystals embedded into different matrices, crystals characterized by certain permanent strain, and so on. This does enable to hope to achieve the overlapping of inhomogeneous spectral lines at question. Second circumstance is the broad possibilities of further fine spectral tuning by applying local magnetic and (especially) electric fields to the crystals. The difference of the permanent dipole moments of rare-earth ions in the ground and excited states [33, 34] makes the optical transitions in these ions very sensitive to the local electric field, and in the typical case the application of an electric field of the magnitude 20–200 kV/cm enables to "scan" the frequency of a transition of some particular ion throughout the whole inhomogeneous spectral line [12]. Situation is indeed the same as with our recent proposal concerning coherent FRET quantum computing controlled by Scanning Probe Microscope [12] as well as with some other proposals of similar kind [8, 10], and we illustrate this point in Fig. 2. For the radius of the curvature of an AFM tip around 10 nm and the tip—ion distance of 10 nm (these are the values quite standard for the field), an application of a potential $U = 5$ V results in the electric field magnitude of the order of 300 kV/cm.

We would like to conclude our exposition with the following remark aiming to stress the potential applicability of the considered effect for the quantum informatics. Exploiting the Scanning Probe Microscope—based control of the system at hand as this is outlined in Fig. 2, one is able, at least in principle, not only to "adjust" passively the donor/acceptor spectra thus realizing the coherent cooperative FRET, but also to perform controllable manipulations upon this three particle system. Using the basis $|0_{D,A1,A2}\rangle$, $|1_{D,A1,A2}\rangle$ to describe either donor D or acceptor A1, A2 centers are excited (1) or not (0), any quantum state of the donor—acceptor system subject to coherent cooperative FRET can be written as an appropriate combination of the states of the type

$$|\Psi\rangle = a|0_D\rangle|0_{A1}\rangle|0_{A2}\rangle + b|0_D\rangle|0_{A1}\rangle|1_{A2}\rangle + c|0_{A1}\rangle|1_{A1}\rangle|0_{A2}\rangle + \ldots + d|1_D\rangle|1_{A1}\rangle|1_{A2}\rangle. \qquad (4)$$

(For example, an initial state of the system is $|\Psi\rangle_{in} = |1_D\rangle|0_{A1}\rangle|0_{A2}\rangle$ while the fully entangled three particle state created in the process of the coherent cooperative energy transfer corresponds to $|\Psi\rangle_{entang} = \frac{1}{\sqrt{2}}(|0_D\rangle(|1_{A1}\rangle + |1_{A2}\rangle) + |1_D\rangle(|0_{A1}\rangle + |0_{A2}\rangle)))$. Such a notation clearly reveals rich and complicated nature of entangled quantum states in this three-particle system. Of course, the symmetry of the problem (excitation can be transferred only at one and the same rate to *both* acceptors) imposes a number of constrains on the coefficients *a, b, c... d* and their achievable time evolution, but by varying the conditions changing the local electric or magnetic fields imposed, a broad variety of the states (4) can be prepared and used, especially when clusters of interacting FRET particles are involved, cf. [35, 36]. Note also that the hyperfine structure of the spectral transitions considered here very essentially enlarges the number of available quantum states, and exciting new possibilities to control the quantum system appear if, in addition to the optical excitation, appropriate RF pulses resonance with the hyperfine structure are applied, cf. [16, 17]. Generalization of the present approach to allow for this hyperfine structure into account is straightforward but we will postpone this for the future papers.

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