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Anti-Stokes fluorescent cooling by energy transfer

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Abstract

A new model on the mechanism of anti-Stokes fluorescent cooling is proposed, based on which incident laser induces a phonon-assisted energy transfer from one luminescent center to another in an optical medium and causes medium cooling when the energy transfer is an anti-Stokes process and absorbs phonons. Here, we develop the model in two cases: two-phonon-assisted energy transfer for a small energy mismatch and one-phonon-assisted energy transfer for a large energy mismatch. The dependence of relative cooling efficiency on photon energy and temperature is also discussed in evaluating the new mechanism.

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Keywords: Anti-Stokes fluorescence; Laser cooling; Energy transfer

1. Introduction

Pringsheim first proposed anti-Stokes fluorescent cooling in 1929 [1]. Some researchers quarreled over his idea for many years. Later in 1946, Landau proved theoretically that the entropy lost by sample upon cooling is more than compensated for by an increase in the entropy of the light, resulting from the loss of monochromaticity and the loss of the beam's directionality [2]. In 1960s some materials had been suggested or explored as possible-cooling candidates, such as ruby, semiconductor, and Nd^{3+}:YAG [3–5], and in 1981 the first system in which actual cooling was observed involved vibrational transitions of carbon dioxide gas pumped by a CO_2 laser [6]. However, until 1995, there had not been experiment to show this effect in other system. Epstein et al., got net

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cooling in a bulk solid material by this physical principle [7]. Almost in the same time, Clark and Rumbles reported the fluorescent cooling in laser dye solution [8]. Since then, much work has been done in this area [9–16] and optical cooling from room temperature to 208 K has been also reported recently [17].

The mechanism of cooling in previous works was explained by anti-Stokes fluorescence emission within a single luminescent center. Namely, a luminescence center absorbs a low-energy photon, and then emits a high-energy photon. The excess is supplied by the thermal absorption from the optical medium and results in cooling. Both of the absorption and the emission occur in the same luminescence center, so it can be called as anti-Stokes fluorescent cooling in a single center (ASFCSC).

2. Anti-Stokes fluorescent cooling by energy transfer

In this paper, we propose another mechanism for fluorescent cooling in solid or anti-Stokes fluorescent cooling by energy transfer (ASFCET) among the centers within the inhomogeneously broadened spectral profile.

The spectral lines of optically active ions in some solids are inhomogeneously broadened. The inhomogeneous width can be tens or even over one hundred wavenumbers in some mixed crystals and amorphous materials, such as in glasses and polymers. If a narrow band laser is employed to excite centers selectively within the inhomogeneous line, fluorescence line narrowing (FLN) will be observed. For a weak excitation limit, the width of an FLN line would be twice the homogeneous linewidth at the very beginning after the excitation. After that, the energy transfer among the centers will result in a spectral diffusion. In Fig. 1, D is the inhomogeneous profile, and A, B and C are three centers contributed to different parts of D.

There is an energy mismatch between two sites, so any energy transfer among them should be phonon assisted. From Fig. 1 we can see that the excited state of A is higher than that of B in energy, so the energy transfer from A to B will emit phonons. Contrarily, the energy transfer from A to C will absorb phonons. For the later case, the phonon-assisted process will absorb heat from the medium. If the excited C center de-excites by radiative transition the absorbed heat will be brought out of the medium by fluorescence, which results in cooling.

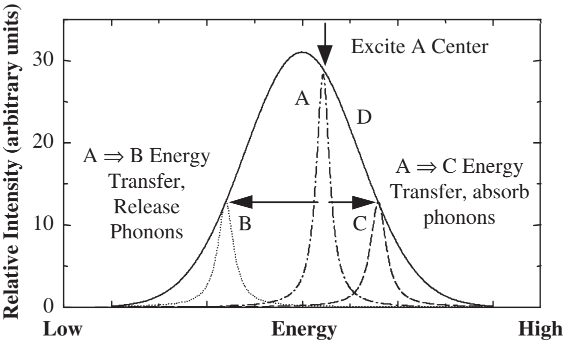

Fig. 1. A, B and C arise from three centers within the inhomogeneously broadened line D. Excitation on A may transfer to B and C. The transfer from A to B releases heat, while the transfer from A to C absorbs heat.

Based on above discussion, we know that ASFCET can occur in two necessary conditions. (1) Energy transfer happens among the different centers within the inhomogeneous profile. (2) The pump light should be chosen in long wavelength wing of absorption band.

3. Theory

Let us consider two identical luminescence centers 1 and 2 with two-level in each center and ignore any splitting in an individual level. The sublevel is the basis of ASFCSC. We believe that sublevel also influences the ASFCET, but we disregard sublevel for simplifying model and making it clearly in our discussion. The energy difference between the two excited states is denoted as ΔE_{12}. Suppose that energy transfer exists between 1 and 2 centers and the energy gap between ground state and excited state in each center is wide enough. Therefore, the probability of nonradiative transition is approximately zero.

According to the phonon-assisted energy transfer theory [18,19], if the energy mismatch ΔE_{12} is comparable to the phonon energy, one-phonon process will be dominant. The transfer rate W in this case is

$$W = B|\Delta E_{12}|\begin{cases} n(\Delta E_{12}/\eta)+1 & (\Delta E_{12}>0), \\ n(|\Delta E_{12}/\eta) & (\Delta E_{12}<0), \end{cases} \tag{1}$$

where B is a constant and independent of energy mismatch or temperature; $n(x) = [\exp(\eta x/k_{\mathrm{B}}T) - 1]^{-1}$ is the average phonon number in mode x at temperature T. When the energy mismatch is small, the probability of one-phonon-assisted energy transfer will be small because of the low density of low energy phonons and the influence of phonon phase factor. Instead, two-phonon-assisted process is efficient, in which an ω phonon is created and an ω' phonon is annihilated, $\eta(\omega - \omega') = \Delta E_{12}$. Experimental results revealed that two-site nonresonant process (or called one-phonon two-step process) is dominant process for small energy mismatch. The transfer rate becomes

$$W = AT^3, \tag{2}$$

where A is a constant and independent of ΔE_{12} and T.

3.1. Two-phonon-assisted energy transfer for small-energy mismatches

We assume that all luminescence centers in our discussions consist of two-level and the inhomogeneous profile is a Gaussian. The lineshape function is

$$g(\Delta) = \frac{1}{\sqrt{2\pi}\sigma}\mathrm{e}^{-\Delta^2/2\sigma^2}, \tag{3}$$

where $\Delta = \omega - \omega_0$, ω_0 is the central frequency of the inhomogeneous profile, $\sigma = [2\ln 2]^{-1/2}$ HWHM.

If all centers have an identical absorption cross section, the population of the excited states is proportional to $g(\omega - \omega_0)$ upon the excitation of $\eta\omega$. If an excited center at x transfers its energy to an unexcited center at Δ and then the latter de-excited radiatively, the medium will absorb or release heat energy $\eta|x - \Delta|$ from or to the medium, respectively. The energy transfer rate is proportional to the amount of centers at Δ, namely proportional to $g(\Delta)$. For the whole inhomogeneous profile, the heat energy produced in unit time is

$$\int_{-\infty}^{\infty} W_{\Delta\leftarrow x}\, g(\Delta)(x-\Delta)g(x)\,\mathrm{d}\Delta$$
$$= AT^3 g(x)x\int_{-\infty}^{\infty} g(\Delta)\,\mathrm{d}\Delta = \frac{AT^3x}{\sqrt{2\pi}\sigma}\mathrm{e}^{-x^2/2\sigma^2}. \tag{4}$$

Here we use $\int_{-\infty}^{\infty}\Delta g(\Delta)\,\mathrm{d}\Delta = 0$ and $\int_{-\infty}^{\infty} g(\Delta)\,\mathrm{d}\Delta = 1$.

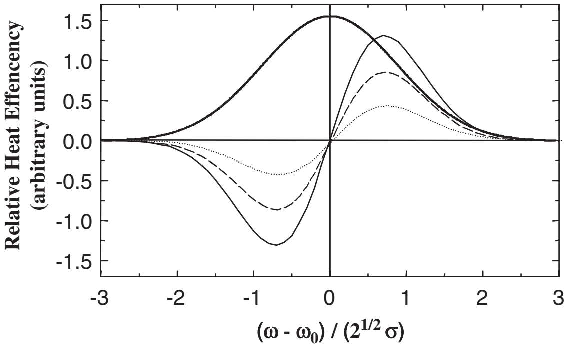

Fig. 2. Relative heating efficiencies at different temperatures in the two-phonon-assisted energy transfer, $T_1 > T_2 > T_3$. The dark line is the inhomogeneous profile.

The curves described by Eq. (4) are shown in Fig. 2. There are two zones in them: the cooling zone where the relative heating efficiency is negative; the heating zone where the relative heating efficiency is positive. When we choose excitation frequency at the cooling zone, the higher the temperature, the higher the fluorescent cooling efficiency.

3.2. One-phonon-assisted energy transfer for large-energy mismatches

When energy transfer happens within a wide inhomogeneous line, generally, the energy mismatches are large. One-phonon-assisted energy transfer process is preferable.

For the energy transfer from x to Δ, if $x > \Delta$, the process will emit phonon(s); oppositely, if $x < \Delta$, it will occur with phonon annihilation. Since the transfer rate is dependent of x, we should consider both the cases separately.

According to Eq. (1), the energy transfer rates for them are

$$W_1 = B\frac{e^{(x-\Delta)/k_BT}}{e^{(x-\Delta)/k_BT}-1}(x-\Delta), \quad x>\Delta, \tag{5}$$

$$W_2 = B\frac{1}{e^{(\Delta-x)/k_BT}-1}(\Delta-x), \quad x<\Delta, \tag{6}$$

respectively. The number of initially excited centers is proportional to $g(x)$, and the number of the centers within $[\Delta, \Delta + d\Delta]$ is proportional to $g(\Delta)\,d(\Delta)$. The energy changes by

$$\begin{aligned} & g(x)\left[\int_{-\infty}^{x} W_1 g(\Delta)(x-\Delta)\,d\Delta \right. \\ & \left. \quad + \int_{x}^{\infty} W_2 g(\Delta)(x-\Delta)\,d\Delta\right] \\ & \quad = Bg(x)\left[\int_{-\infty}^{x}(x-\Delta)^2 g(\Delta)\frac{e^{(x-\Delta)/k_BT}}{e^{(x-\Delta)/k_BT}-1}\,d\Delta \right. \\ & \left. \qquad - \int_{x}^{\infty}(x-\Delta)^2 g(\Delta)\frac{1}{e^{(\Delta-x)/k_BT}-1}\,d\Delta\right] \\ & \quad = Bg(x)\int_{0}^{\infty}\frac{\mu^2}{e^{\mu/k_BT}-1} \\ & \qquad \times \left[e^{\mu/k_BT}g(\mu-x) - g(\mu+x)\right]d\mu, \end{aligned} \tag{7}$$

where $\mu = (x - \Delta)$. Fig. 3 shows the result of (7) by a numerical integration. (The two curves in it were obtained at two temperature, $k_BT_1/(2^{1/2}\sigma) = 2$ and 0.5.) The dark line is the inhomogeneous profile. Also, there are two zones in them: the cooling zone and the heating zone. The higher the temperature is, the bigger the cooling zone is. When the temperature gets lower, the cooling zone will shift toward long wavelength and the cooling efficiency will decrease. It is because of that the mean phonon number $\langle n\rangle$ reduces with the decrease of temperature.

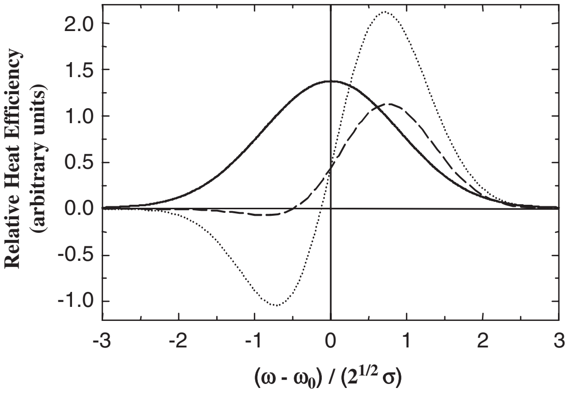

Fig. 3. Relative heating efficiencies at different temperatures in the one-phonon-assisted energy transfer process, $k_BT/(2^{1/2}\sigma) = 0.5$ and 2. The dark line is the inhomogeneous profile.

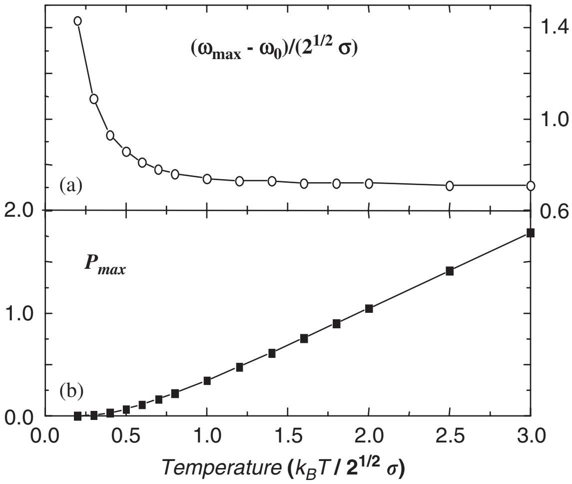

Fig. 4. Dependencies of ω_{max} (a) and P_{max} (b) on temperature.

The best excitation frequency for cooling and the corresponding relative cooling efficiency are denoted by ω_{max} and P_{max}, respectively. The dependencies of ω_{max} and P_{max} on temperature are shown in Fig. 4. They are similar to those in ASFCSC [12,20].

4. Conclusion and discussion

Here, we have presented a theoretical model, which shows that ASFCET can occur in some special materials. Two necessary conditions are needed to produce ASFCET effect. (1) There is nonradiative energy transfer among different centers within an inhomogeneously broadened spectral profile. (2) The wavelength of exciting light should be chosen at the long-wavelength wing of the absorption spectrum. Both of one-phonon-assisted energy transfer and two-phonon-assisted energy transfer can produce ASFCET effect.

All the papers reported in the past considered only the mechanism of ASFCSC. Doubtless, ASFCSC is important and dominant in the fluorescent cooling of solid; however, ASFCET also can exist in the same time. Actually, the excitation transfers for rare-earth ions have been studied a lot even for ytterbium ions in fluoride glasses. Ageava et al. [21] found that the luminescence spectra of Yb^{+3} in fluoride glasses deformed and shifted toward longer wavelength and the deformation and shift getting greatest for large activator concentrations or low temperature. Additionally, the time evolution of laser-induced resonant line-narrowed spectra was studied in Yb^{3+} by Paisner [22]. The time-resolved spectra of 0.5% Yb in a silicate glass showed that energy transfer occurred among Yb^{3+} ions. On the other hand, Weber et al. [23] observed a luminescence spectra shift to higher energies with the time evolution of the $\mathrm{Mo}^{3+}\,{}^2E \rightarrow {}^4A_2$ emission in phosphate glasses. All of these experiments declared that energy transfer processes are important in some photoluminescence materials especially for high concentration, and they may take part in fluorescent cooling and influence cooling efficiency.

Acknowledgments

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