

The role of two-step excitation processes in laser cooling experiments: $\text{CaF}_2:\text{Eu}^{2+}$



S.P. Feofilov ^{a,*}, A.B. Kulinkin ^a, V.A. Konyushkin ^b, A.N. Nakladov ^b

^a Ioffe Institute, St. Petersburg, 194021, Russia

^b Prokhorov General Physics Institute, Moscow, 119991, Russia

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ABSTRACT

The fluorescence of CaF_2 single-crystals containing Eu^{2+} ions was studied under the excitation in the long-wavelength tail of the absorption spectrum which is due to electric dipole allowed transitions (“laser cooling regime”). Though no actual cooling was detected, spectra with a dominant anti-Stokes component were observed which demonstrate the possibility to employ electron-phonon bands of Eu^{2+} f-d transitions for optical refrigeration. The absence of observable optical refrigeration is ascribed to Eu^{2+} two-step photoionization processes that are responsible for the excited state absorption. The role of two-step excitation of impurity centers (excited state absorption) in laser cooling experiments is discussed.

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1. Introduction

Finding new kinds of materials where the optical refrigeration or laser cooling employing phonon-assisted anti-Stokes fluorescence may be achieved is a challenging problem. Since the first successful laser cooling results were obtained with Yb^{3+} -doped glass [1], many exciting achievements were reported: laser cooling was observed in different materials including rare earth doped insulating glasses and crystals, organic dye solutions [2], semiconductors [3,4], organic-inorganic perovskites [5]; see Refs. [6–9] for reviews. The most successful results were obtained with ${}^2\text{F}_{7/2}$ – ${}^2\text{F}_{5/2}$ transitions of Yb^{3+} ions in insulating glasses and crystals.

All successful experimental observations of laser cooling in insulating solids containing local fluorescent centers employed 4f–4f transitions of triply-charged rare-earth impurity ions that are parity-forbidden as electric dipole and occur only due to admixture of opposite-parity states of the 4f5d configuration [10]. The low oscillator strength of 4f–4f transitions requires arranging a long optical path of the exciting light inside the laser-cooled samples and limits the possibility to obtain laser cooling of small samples.

In Ref. [11] we reported the results of spectroscopic feasibility

studies of laser cooling via the phonon-assisted anti-Stokes emission in various materials containing local centers of different nature whose electric dipole allowed transitions provide broad electron-phonon bands in the emission spectra. The laser cooling mechanism proposed in Ref. [11] is similar to that studied in experiments with organic dye solutions [2], where the electron-phonon emission of dye molecules was responsible for cooling. On the other hand it differs from an earlier proposal to use an allowed electronic transition free of vibronic coupling in combination with a phonon-coupled step to effect Raman cooling [12].

Among the materials studied in Refs. [11], the Eu^{2+} ions doped insulating crystals (CaF_2 , CaS) look most promising from the point of view of laser cooling experiments. Importantly for these experiments, the Eu^{2+} $4\text{f}^6[{}^7\text{F}_0]5\text{d}^1\text{-f}^7[{}^8\text{S}_{7/2}]$ radiative transitions have a high quantum yield and terminate at the ion ${}^8\text{S}_{7/2}$ ground state only: the transitions to the higher-lying levels would result in Stokes emission and creation of phonons. Indeed, in Ce^{3+} ions, where strong $4\text{f}^05\text{d}^1\text{-4f}^1$ anti-Stokes emission is observed under the excitation below the zero-phonon line energy [13], the transitions to the ${}^2\text{F}_{7/2}$ state located about 2000 cm^{-1} above the ${}^2\text{F}_{5/2}$ ground state result in dominant Stokes contribution to the spectrum. Though no laser cooling was observed in Refs. [11], the experimental results supported the possibility of using broad electron-phonon emission bands of electric dipole allowed radiative f-d transitions for optical refrigeration.

* Corresponding author.

E-mail address: sergey.feofilov@mail.ioffe.ru (S.P. Feofilov).

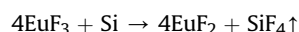
One of the significant problems that prevent achieving laser cooling of Eu^{2+} -doped crystals is the presence of a residual amount of Eu^{3+} whose excitation results in strong f-f Stokes emission which contributes to optical heating of the samples. In order to eliminate this problem the crystals in which the f-d spectrum of Eu^{2+} occurs at wavelengths longer than that of Eu^{2+} f-f transitions may be used. This excludes excitation of Eu^{3+} ions which are usually present in Eu^{2+} doped materials and whose excitation and $^5\text{D}_n$ - $^7\text{F}_m$ fluorescence results in Stokes rather than anti-Stokes emission. The number of crystals in which Eu^{2+} spectra are red-shifted below Eu^{3+} absorption is rather limited [14], CaS being an important example. The detailed studies of CaS:Eu^{2+} optically excited in the long-wavelength tail of the absorption spectrum are reported in Ref. [15]: laser heating (rather than cooling) was observed accompanied by such unexpected results as optical bistability and spontaneous fluorescence and temperature oscillations.

Another approach to eliminate the Stokes emission of Eu^{3+} ions is to select the crystals with really low content of these ions. $\text{CaF}_2:\text{Eu}$ single crystals studied in Ref. [11] in addition to Eu^{2+} contained a residual amount of Eu^{3+} . Under the $\lambda = 457$ nm excitation in the tail of Eu^{2+} absorption, the Eu^{3+} ions 4f-4f fluorescence dominated in the spectrum even though Eu^{3+} relative concentration is lower than that of Eu^{2+} . Here we report the results obtained with $\text{CaF}_2:\text{Eu}$ containing no detectable amount of Eu^{3+} ions.

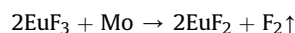
2. Experiment

The experiments were performed with CaF_2 single crystals containing Eu ions. The samples containing various additional impurities were prepared in General Physics Institute.

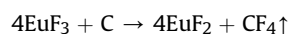
The crystals were grown by vertical unidirectional crystallization method in graphite multi-cell crucibles. Under normal conditions Eu is trivalent (Eu^{3+}) and in order to change its valence the reduction-oxidation reaction needs to be carried out. To achieve this, polycrystalline silicon (Si) and molybdenum (Mo) in a form of powder were used. The growth was performed in seven-cell graphite crucible. The concentration of EuF_3 varied from 0,2% to 2,0% molar. The concentration of Si varied from 0,6% to 1,0% molar and concentration of Mo varied from 1,0% to 3,0% molar. During the growth an inert atmosphere was formed by filling the operation chamber with argon; the chamber was preliminary evacuated to 10^{-3} mm/Hg. Reduction-oxidation of Eu^{3+} with silicon is performed as follows:



Reduction-oxidation of Eu^{3+} in the presence of molybdenum (Mo) acting as a catalyst at high temperature is performed as follows:



In addition, graphite is a deoxidant (reducing agent) of Eu^{3+} :



Most of the optical measurements were performed at room temperature. For measurements with thermally-isolated crystals the samples were mounted in vacuum in the sample chamber evacuated with a turbo vacuum pump (cold finger liquid helium refrigerator chamber was used).

The samples were excited with semiconductor lasers ($\lambda = 405$, 440 nm). The fluorescence was detected with a grating spectrometer equipped with a CCD camera or with a double-grating

monochromator and a photomultiplier operating in a photon-counting regime.

The temperature changes of thermally-isolated samples were detected by two methods: (i) monitoring the changes of fluorescence intensity and comparing with the calibration temperature dependences of corresponding fluorescence measured under the weak (few milliwatts) excitation with the samples placed in air inside a variable temperature optical chamber (see section 3) and (ii) with a chromel-alumel (Type K) thermocouple glued onto the sample (and by which the sample was suspended in the vacuum chamber) and a digital voltmeter with 0.1 μV accuracy.

3. Experimental results and discussion

The fluorescence spectra of a series of $\text{CaF}_2:\text{Eu}$ samples excited at 405 nm (close to the absorption spectrum maximum) at ambient conditions are shown in Fig. 1. It may be seen that the relative content of Eu^{2+} ions (broad fluorescence band in the blue) and Eu^{3+} ions (sharp lines in the red) dramatically varies from sample to sample. These variations are due to crystal growth conditions and co-doping with different ions. The concentration of EuF_3 in initial mixture varied from 0.2% to 2.0% molar. The concentration of Si varied from 0,6% to 1,0% molar and concentration of Mo varied from 1,0% to 3,0% molar. The samples with the lowest content of Eu^{3+} ions (IV and VII) were selected for laser cooling experiments. The 0.5% Eu-doped samples IV and VII contained 3.0% of Mo and 1.0% Si respectively. In these samples no Eu^{3+} ions fluorescence could be observed in any excitation conditions.

In Fig. 2 the fluorescence spectra of $\text{CaF}_2:\text{Eu}$ crystals (samples IV and VII) under the excitation at $\lambda_{\text{exc}} = 440$ nm are shown; the spectrum excited at $\lambda = 405$ nm (identical for samples IV and VII) is also displayed. The Eu^{2+} absorption is also displayed showing that the 440 nm excitation occurs in the extreme long-wavelength tail

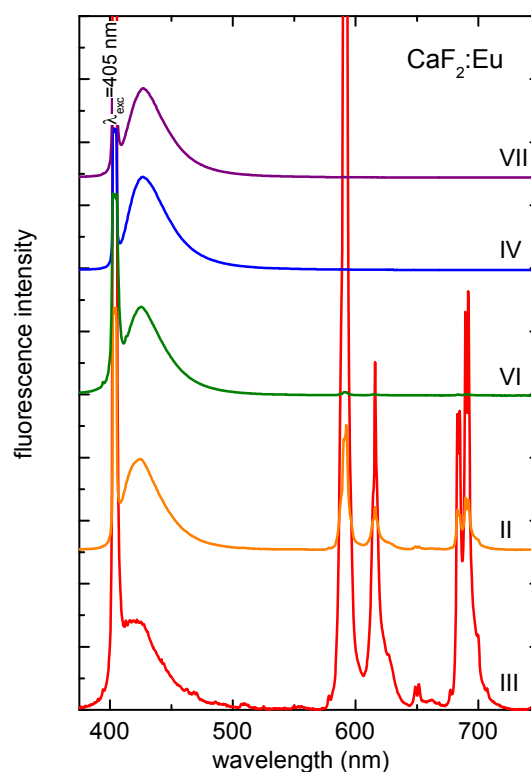


Fig. 1. Fluorescence spectra of a series of $\text{CaF}_2:\text{Eu}$ samples excited at $\lambda_{\text{exc}} = 405$ nm, $T = 295$ K. Broad band in the blue - Eu^{2+} , sharp lines in the red - Eu^{3+} .

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