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Investigation of infrared-to-visible conversion in cubic $\text{Cs}_2\text{NaErCl}_6$ crystals

W Ryba-Romanowski, S Golab and W A Pisarski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-950 Wrocław 2, PO Box 937, Poland

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Abstract. Efficient conversion of infrared radiation centred at $1\ \mu\text{m}$ into visible luminescence has been observed in cubic $\text{Cs}_2\text{NaErCl}_6$ crystals in which electric dipole transitions are forbidden by symmetry selection rules. Luminescence originating from the ${}^4\text{F}_{9/2}$ and ${}^4\text{T}_{9/1}$ levels of Er^{3+} increases strongly with increasing temperature in the 100–300 K region whereas the ${}^4\text{S}_{3/2}$ luminescence appears to be independent of temperature. Experimental results are found to be consistent with non-resonant two-ion mechanisms involved in up-conversion and cross relaxation processes, the multiphonon decay being negligible.

1. Introduction

In our previous paper we demonstrated an efficient Er–Er interaction in cubic $\text{Cs}_2\text{NaErCl}_6$ crystals, resulting in the self-quenching of luminescence originating in the ${}^4\text{S}_{3/2}$ level of Er^{3+} [1]. The self-quenching of luminescence was activated thermally at about 70 K and reduced the ${}^4\text{S}_{3/2}$ lifetime of 8 ms by roughly three orders of magnitude when the sample temperature was raised to 300 K. On the basis of the detailed energy level scheme reported previously [2, 3] the luminescence quenching has been attributed to the non-resonant cross relaxation process in which an excited ion undergoes a ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transition and its unexcited neighbour undergoes a ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{13/2}$ transition. The corresponding cross relaxation rate is surprisingly high in the crystal structure of $\text{Cs}_2\text{NaRECl}_6$ (RE=rare-earth ions) which is uncommon in that the rare-earth ions are situated in the sites of exact O_h symmetry and are well separated by Cl–Na–Cl chains. In centrosymmetric symmetry the electric dipole transitions are forbidden, and considerably weaker magnetic dipole transitions and vibronic transitions occur. Moreover the closest Er–Er distance is as high as 0.77 nm in this structure and one may expect the non-radiative energy transfer by exchange interaction to be suppressed and the multipole interaction to be reduced. Accordingly, very weak concentration quenching of Nd^{3+} luminescence in $\text{Cs}_2\text{NaNdCl}_6$ has been reported and attributed to a long distance between neodymium ions [4]. However, further investigation revealed several examples of efficient interaction between rare-earth ions in $\text{Cs}_2\text{NaRECl}_6$ crystals. Self-quenching of the ${}^5\text{D}_1$ luminescence in $\text{Cs}_2\text{NaEuCl}_6$ crystals was observed and attributed to the phonon-assisted electric dipole–electric dipole mechanism [5]. Recently it has been shown that the resonant magnetic dipole–magnetic dipole interaction, commonly discounted as negligible, accounts well for the self-quenching of the ${}^1\text{G}_4$ luminescence in $\text{Cs}_2\text{NaTmCl}_6$, the calculated non-radiative transfer rate from the donor Tm^{3+} ion being as high as $1.44 \times 10^5\ \text{s}^{-1}$ [6].

The self-quenching of the $^4S_{3/2}$ luminescence of Er^{3+} in $Cs_2NaErCl_6$ appears to be a non-resonant energy transfer process involving coupling between vibronic states of interacting ions. The description of such a mechanism is not easy as the natures of donor and acceptor states should be defined and data relevant to this mechanism are scarce. In the present work we report the non-resonant energy transfer involved in the excitation of visible luminescence in $Cs_2NaErCl_6$ crystal following infrared excitation. The goal of the work is to provide new experimental evidence that the non-resonant energy transfer between rare-earth ions in centrosymmetric systems may be as important as in low-symmetry systems and to point out the cross relaxation schemes which are unusually efficient in these systems. Also, the material may be of technological interest for the design of infrared pumped visible lasers.

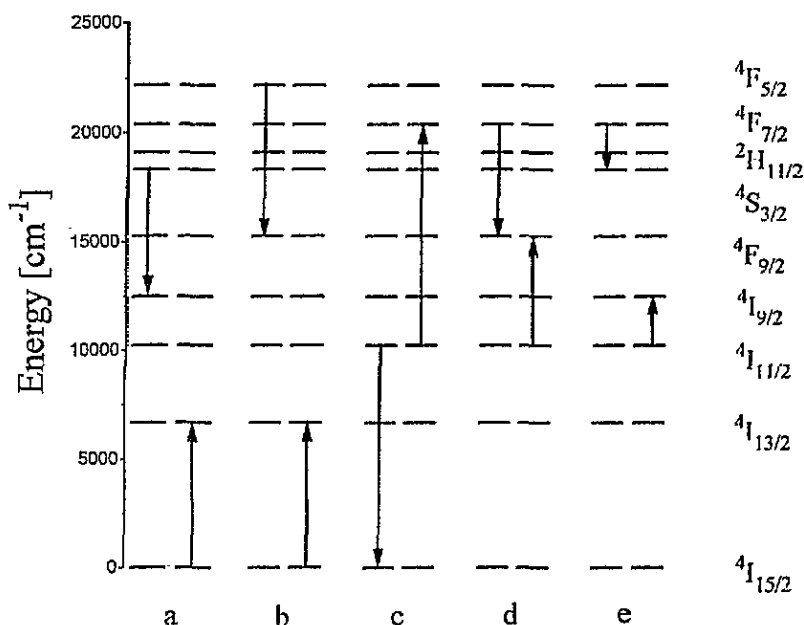


Figure 1. Mechanisms of up-conversion and cross relaxation in a concentrated Er^{3+} system.

2. Background

The complex energy level structure of trivalent erbium ions favours various up-conversion and cross relaxation processes which may control the excitation and relaxation dynamics in concentrated Er^{3+} systems. In figure 1 the well documented two-ion mechanisms are depicted together with the recently proposed relaxation schemes. The cross relaxation process shown in figure 1(a) quenches the luminescence originating in the $^4S_{3/2}$ level in virtually all erbium-doped crystals and glasses. On the other hand the mechanism in figure 1(b) may be evidenced in matrices with reduced phonon energy since it competes with multiphonon relaxation, bridging the relatively small energy gap between the $^4F_{5/2}$ and $^4F_{7/2}$ levels. This mechanism, first observed for an Er^{3+} dimer in CaF_2 [7] and more recently for an Er^{3+} dimer in $CsCdBr_3$ [8], removes the excitation of the $^4F_{5/2}$ level and populates the $^4F_{9/2}$ and $^4I_{13/2}$ levels. It has been inferred from the excitation spectra that it is also efficient in $Cs_2NaErCl_6$ [1]. The up-conversion shown in figure 1(c) is a two-ion

process in which two excitations from the ${}^4\text{I}_{11/2}$ level disappear and one excitation in ${}^4\text{F}_{7/2}$ is created. As the energy gap between the ${}^4\text{F}_{7/2}$ and the next-lower-lying ${}^2\text{H}_{11/2}$ level is not much higher than 1000 cm^{-1} , the ${}^4\text{F}_{7/2}$ excitation decays quickly by multiphonon relaxation to the ${}^4\text{S}_{3/2}$ level in the majority of erbium-doped crystals and glasses. The mechanisms depicted in figures 1(d) and 1(e) may be efficient provided that the multiphonon relaxation from the ${}^4\text{F}_{7/2}$ level is low and the population in the ${}^4\text{I}_{11/2}$ level is high. From the data available we suppose that the two latter mechanisms control the relaxation dynamics of excited states in the $\text{Cs}_2\text{NaErCl}_6$ crystal excited by infrared radiation centred at $1\ \mu\text{m}$. Several other many-body processes may contribute to the excitation and decay of excited states of Er^{3+} ions. The up-conversion from the ${}^4\text{I}_{13/2}$ level plays an essential role in Er^{3+} lasers working at $3\ \mu\text{m}$ [9]. It has been suggested also that three-ion mechanisms are operative at high Er^{3+} concentrations [10]. For these processes to be efficient a high population of the ${}^4\text{T}_{13/3}$ level is required and this condition is not fulfilled in our study.

3. Experimental details

The single crystals of $\text{Cs}_2\text{NaErCl}_6$ and $\text{Cs}_2\text{NaEr}_{0.2}\text{Y}_{0.4}\text{Yb}_{0.4}\text{Cl}_6$ were grown in evacuated quartz ampoules by the Bridgman method. Details of preparation and crystal growth have been described elsewhere [2]. For optical measurements, samples in the form of plane parallel plates have been cut out of the crystal and polished. All luminescence measurements were made using samples 2 mm thick, whereas the thickness of samples for absorption measurements was as high as 11 mm. Visible luminescence was excited by a 80 mW diode laser emitting radiation centred at $1\ \mu\text{m}$. The output laser beam was collimated and focused on the sample with a weakly converging lens in order to keep the beam diameter in the crystal about 1 mm with the corresponding radiation density of the order of 10^4 W m^{-2} . The power incident on the crystal was varied using a set of calibrated neutral density filters. For low-temperature measurements the samples were placed in an Oxford model CF 1204 continuous-flow helium cryostat equipped with a temperature controller. The luminescence was resolved by Zeiss model GDM 1000 double-grating monochromator, detected by a photomultiplier with S-20 or S-11 response depending on the spectral region and the resulting signal was analysed by a SRS 250 boxcar integrator. The Stokes luminescence from excited levels was excited by an argon ion laser or nitrogen laser-pumped dye laser. The latter source was also used for lifetime measurements. The absorption spectra were measured with a Varian model 2300 spectrophotometer.

4. Results

The $\text{Cs}_2\text{NaErCl}_6$ crystal excited by infrared radiation at $1\ \mu\text{m}$ exhibits strong luminescence which is visible as a bright yellow-green light. Dispersed with a monochromator the anti-Stokes luminescence consists of several bands centred at $20\,500\text{ cm}^{-1}$ (487 nm), $18\,300\text{ cm}^{-1}$ (546 nm), $15\,000\text{ cm}^{-1}$ (666 nm) and $12\,400\text{ cm}^{-1}$ (813 nm), the latter band being the strongest. The spectrum recorded with a sample of $\text{Cs}_2\text{NaEr}_{0.2}\text{Y}_{0.4}\text{Yb}_{0.4}\text{Cl}_6$ crystal containing a lower concentration of erbium ions displays the same bands but the distributions of band intensities are different.

The two spectra recorded at room temperature are compared and assigned in figure 2. It can be seen in this figure that the band associated with the ${}^4\text{F}_{9/2}$ - ${}^4\text{I}_{15/2}$ transition at $15\,000\text{ cm}^{-1}$ has a significant intensity in both the samples. The luminescence intensity increases with increasing power of radiation incident on the crystal. In figure 3 the integrated

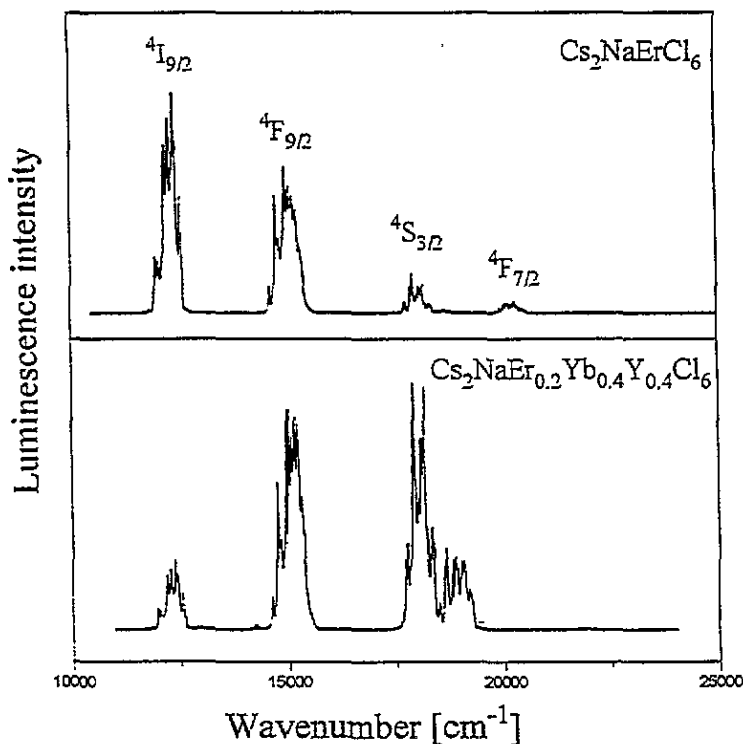


Figure 2. Anti-Stokes luminescence of $\text{Cs}_2\text{NaErCl}_6$ (upper curve) and $\text{Cs}_2\text{NaEr}_{0.2}\text{Yb}_{0.4}\text{Y}_{0.4}\text{Cl}_6$ (lower curve) excited at $1\ \mu\text{m}$ and recorded at room temperature.

intensities of transitions originating in the ${}^4\text{S}_{3/2}$, ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{9/2}$ levels of Er^{3+} in $\text{Cs}_2\text{NaErCl}_6$ are plotted versus excitation power. Experimental data are denoted by full symbols and the straight lines follow a power n increase with the n value indicated. Whereas the increase in intensity of the ${}^4\text{S}_{3/2}$ luminescence may be well approximated by a squared function of the excitation power, the value of n for the luminescence originating in the ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{9/2}$ levels is less than 2, indicating the presence of a power-dependent loss mechanism. The influence of the sample temperature on luminescence intensities is shown in figure 4. At low temperatures up to about 100 K the intensity of the ${}^4\text{F}_{9/2}$ luminescence is negligibly small; next it increases by roughly three orders of magnitude when the sample temperature is raised to 300 K. In contrast with this behaviour the ${}^4\text{S}_{3/2}$ luminescence is almost constant in the 100–300 K temperature region.

5. Discussion

The remarkable feature of the anti-Stokes luminescence in $\text{Cs}_2\text{NaErCl}_6$ crystal is the strong emission originating in the ${}^4\text{F}_{9/2}$ level of Er^{3+} . The mechanism of the ${}^4\text{F}_{9/2}$ population build-up appears to be different from that involved in the commonly known up-converters containing erbium ions. The up-conversion process in which an excited ion makes the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ transition and its unexcited neighbour makes the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{F}_{9/2}$ transition may be excluded because the energy mismatch for this process exceeds $1000\ \text{cm}^{-1}$. As the highest energy of the ErCl_6^{3-} vibrational modes is $260\ \text{cm}^{-1}$ [2], at least four phonons should be created in order to conserve the energy. The ${}^4\text{F}_{9/2}$ level is not populated by multiphonon

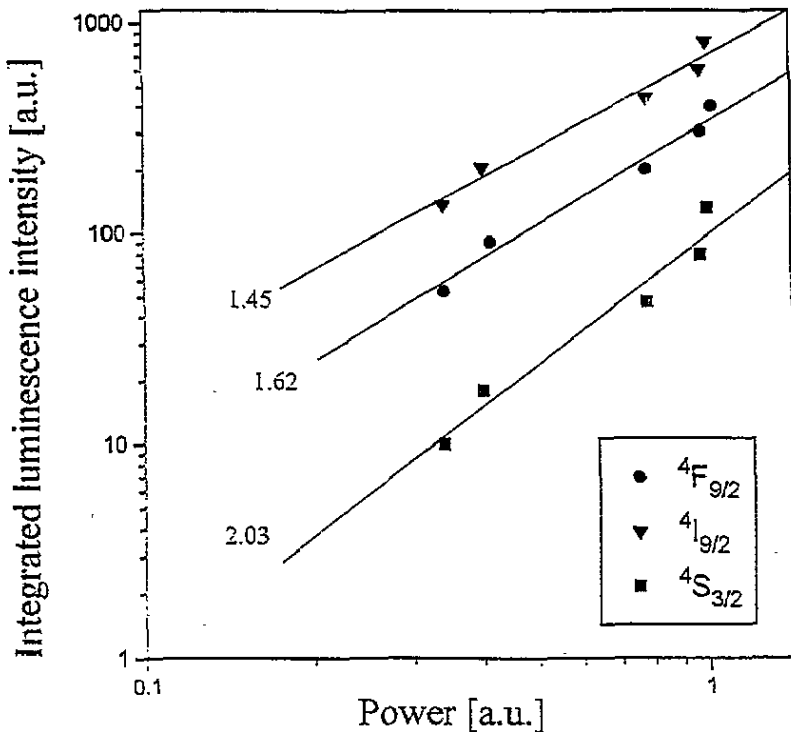


Figure 3. Integrated luminescence intensity for transitions originating from the ${}^4\text{S}_{3/2}$, ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{9/2}$ levels of Er^{3+} in $\text{Cs}_2\text{NaErCl}_6$ versus the power of infrared excitation (a.u., arbitrary units). The straight lines follow a power n dependence with the n -values indicated.

relaxation from the higher energy levels since the ${}^4\text{F}_{7/2}$, ${}^2\text{H}_{11/2}$ and ${}^4\text{S}_{3/2}$ levels are absent in the excitation spectrum of the ${}^4\text{F}_{9/2}$ luminescence [1]. In $\text{Cs}_2\text{NaErCl}_6$ the Stokes ${}^4\text{F}_{9/2}$ emission may be excited directly into this level or by the cross relaxation process shown in figure 1(b) which follows the excitation of the ${}^4\text{F}_{5/2}$ level. Therefore we suppose that the ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels of Er^{3+} in the $\text{Cs}_2\text{NaErCl}_6$ crystal excited at $1\ \mu\text{m}$ are not populated by multiphonon relaxation from higher-lying levels. Instead, the ${}^4\text{F}_{7/2}$ level which is excited by an up-conversion process from ${}^4\text{I}_{11/2}$ (figure 1(c)) may relax by two simultaneous cross relaxation processes depicted in figures 1(d) and 1(e). The energy level scheme indicates that these transitions are close to resonant and can provide an efficient excitation of the ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels in the temperature region investigated. Considering all relaxation pathways the rate equation system for the levels from ${}^4\text{I}_{15/2}$ to ${}^4\text{F}_{7/2}$ may be written as:

$$\frac{dN_1}{dt} = w_5 N_5 N_0 - \frac{N_1}{\tau_1} \quad ({}^4\text{I}_{13/2})$$

$$\frac{dN_2}{dt} = x - 2w_2 N_2^2 - w_6 N_6 N_2 - w'_6 N_6 N_2 - \frac{N_2}{\tau_2} \quad ({}^4\text{I}_{11/2})$$

$$\frac{dN_3}{dt} = w_5 N_5 N_0 + w'_6 N_6 N_2 - \frac{N_3}{\tau_3} \quad ({}^4\text{I}_{9/2})$$

$$\frac{dN_4}{dt} = w_6 N_6 N_2 - \frac{N_4}{\tau_4} \quad ({}^4\text{F}_{9/2})$$

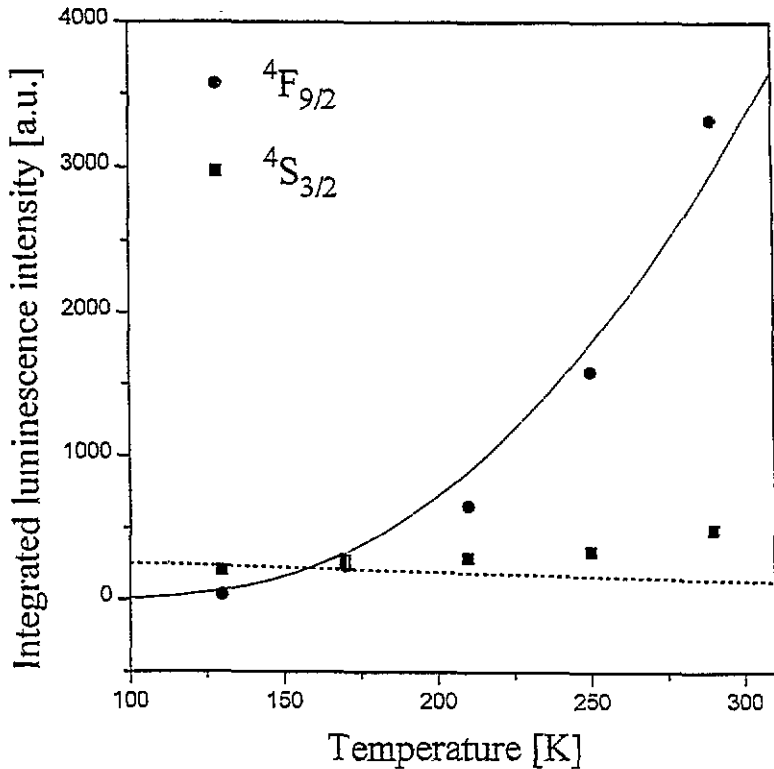


Figure 4. Influence of temperature on the integrated luminescence intensity for transitions originating in the ${}^4F_{9/2}$ and ${}^4S_{3/2}$ levels of Er^{3+} in $\text{Cs}_2\text{NaErCl}_6$ (a.u., arbitrary units): ●, ■, experimental data. See text for explanation of theoretical lines.

$$\frac{dN_5}{dt} = w'_6 N_6 N_2 - w_5 N_0 - \frac{N_5}{\tau_5} \quad ({}^4S_{3/2})$$

$$\frac{dN_6}{dt} = w_2 N_2^2 - w_6 N_6 N_2 - w'_6 N_6 N_2 - \frac{N_6}{\tau_6} \quad ({}^4F_{7/2}). \quad (1)$$

In these expressions the populations of the levels are denoted by N_i , the corresponding lifetimes by τ_i and the coupling coefficients between the transitions for two ions processes by w_i . The coupling parameters for cross relaxations depicted in figures 1(d) and 1(e) which involve the same initial levels but different terminal levels are denoted by w_6 and w'_6 , respectively. x denotes the excitation rate in units of reciprocal cubic centimetre seconds and is given by $x = (P/S)\alpha/h\nu$, where P is the incident power, S is the cross section of the laser beam in the crystal, α is an absorption coefficient at the excitation wavelength and $h\nu$ is the photon energy. The system (1) preserves the notation of earlier work [9, 10], the only difference being the absence of multiphonon relaxation processes. Thus the excited levels except for the ${}^4I_{11/2}$ level are fed exclusively by two-ion processes, the downward vibronic transitions ending on the ground level as observed in experiments. The absorption coefficient at the excitation wavelength is 0.03 cm^{-1} at room temperature; accordingly the excitation rate amounts to $0.8 \times 10^{19} \text{ cm}^{-3} \text{ s}^{-1}$ and we may conclude that the excitation is weak, i.e. $N_i \ll N_0$. Considering low rates of vibronic decay in comparison with the observed cross relaxation rates we neglect the term N_6/τ_6 in the last equation of the equation system (1). Thus in the steady-state regime ($dN_i/dt = 0$; $x = \text{constant}$) the populations of

the ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels are expressed in terms of the ${}^4\text{I}_{11/2}$ population:

$$N_5 = \frac{w'_6 N_6 N_2}{w_5 N_0} = \frac{w'_6 w_2 N_2^2}{w_5 N_0 (w_6 + w'_6)} \quad (2)$$

$$N_4 = \frac{w_2 N_2^2}{\tau_4} \quad (3)$$

With these relations we may examine the temperature dependence of the luminescence intensity for the ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels. Four crystal-field components of the ${}^4\text{I}_{11/2}$ level have been located at 9976, 10 036, 10 163 and 10 199 cm^{-1} whereas three crystal-field components of the ${}^4\text{F}_{7/2}$ level have been located at 20 388, 20 437 and 20 460 cm^{-1} [3]. The absorption of the exciting light with energy centred at 10 010 cm^{-1} populates the ${}^4\text{I}_{11/2}$ level by vibronic transition whose intensity weakly depends on temperature in the 100–300 K region since it involves the emission of phonons. However, in the up-conversion process leading to the population of ${}^4\text{F}_{7/2}$, the transitions must originate from the highest components of the ${}^4\text{I}_{11/2}$ level, and additionally they have to be assisted by phonon absorption in order to cover the energy gap between the ${}^4\text{I}_{11/2}$ and ${}^4\text{F}_{7/2}$ levels. On the assumption that the coupling parameter in equation (3) depends on temperature through the phonon occupation number and the population N_2 of the highest crystal-field component of the ${}^4\text{I}_{11/2}$ level is given by the Boltzmann distribution, equation (3) will be of the form

$$N_4(T) = A \left[\exp\left(-\frac{\Delta E}{kT}\right) / \sum_i \exp\left(-\frac{\Delta E_i}{kT}\right) \right]^2 \frac{1}{\exp(\hbar\omega/kT) - 1} \quad (4)$$

since the lifetime τ_4 weakly depends on temperature [1]. In this expression, A contains all factors independent of temperature; the squared factor determines the population of the crystal-field level at 10 199 cm^{-1} and the sum is performed over four crystal-field levels split out of the ${}^4\text{I}_{11/2}$ multiplet; the last factor determines the temperature dependence of absorption of the highest-energy vibrational mode. Putting $\Delta E = 207 \text{ cm}^{-1}$, $\hbar\omega = 260 \text{ cm}^{-1}$ and assuming $A = 432\,100$ to fit the experimentally measured intensity at 90 K we obtain the dependence indicated by the solid curve in figure 4. In contrast with this behaviour the temperature dependence of the ${}^4\text{S}_{3/2}$ population will be different because the rate of the cross relaxation denoted by $w_5 N_0$ in equation (2) depends strongly on temperature, too. It has been shown that the variation in the rate $w_5 N_0$ of the cross relaxation from the ${}^4\text{S}_{3/2}$ level in $\text{Cs}_2\text{NaErCl}_6$ may be reasonably well approximated by the expression [1]

$$w_5 N_0(T) = k \left[\exp\left(-\frac{\Delta E'}{kT}\right) / \sum_i \exp\left(-\frac{\Delta E'_i}{kT}\right) \right]^2 \frac{1}{\exp(\hbar\omega/kT) - 1} \quad (5)$$

where $\Delta E'$ denotes the energy of the highest crystal-field components of the ground ${}^4\text{T}_{15,2}$ level, the sum is performed over five crystal-field levels split out of the ground state and the last factor determines the temperature dependence of the phonon absorption. Thus, the increase in the ${}^4\text{S}_{3/2}$ population is counterbalanced by the increasing rate of the cross relaxation when the sample temperature is raised. On substitution of $w_5 N_0$ in equation (4) by equation (5) and on the assumption that the coupling parameters w_6 and w'_6 for resonant cross relaxations from the ${}^4\text{F}_{7/2}$ level are independent of temperature, equation (3) was fitted to the experimental temperature dependence of the ${}^4\text{S}_{3/2}$ emission in a similar way to the ${}^4\text{F}_{9/2}$ emission discussed above. The result is indicated by the dotted line in figure 4. It can be seen that the simplified approach supposing the non-resonant two-ion mechanism which involves the absorption of a single vibrational mode of highest energy accounts qualitatively

for experimental results. In this approach the excited-state absorption has been neglected but it may contribute to the depletion of long-lived levels such as $^4F_{9/2}$ and $^4I_{9/2}$, giving rise to the power-dependent losses evidenced in figure 3.

6. Conclusions

Efficient conversion of infrared radiation into visible luminescence in a cubic $Cs_2NaErCl_6$ crystal has been observed at room temperature. It appears that the multiphonon relaxation does not contribute to the excitation and decay of excited states which are supposed to be populated solely by ion-ion interaction. The proposed non-resonant up-conversion and cross relaxation mechanisms involving phonon-assisted dipole-dipole interaction account well for the experimental data and are consistent with previously reported results.

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