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# Phonon coupling of $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystals

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## Abstract

We have studied the influence of the electron-lattice coupling on the luminescence quantum yield for $Cr^{3+}$ ions in a $Cs_2NaAlF_6$ crystal. For this purpose, we analyze the absorption and emission spectra of $Cr^{3+}$ ions by means of the configurational coordinate model in the harmonic approximation. We have found the energy of the breathing phonon associated to $Cr^{3+}$ ions in this host. In our findings we explain the high value of luminescence quantum yield reported previously (near to 70%), if we take into account the uncoupling between the breathing phonon and the normal modes associated to the bulk vibration. The $Cr^{3+}$:$Cs_2NaAlF_6$ crystals promise to be a potential efficiency tunable laser device in the near infrared (700–900 nm) spectral range.

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*Keywords:* A. $Cr^{3+}$ impurities; A. Fluoride crystals; D. Phonon electron interaction; E. Laser spectroscopy

## 1. Introduction

The search for new solid-state tunable laser in the visible spectrum and near infrared has generated, in the last time, strong interest on the study of different type of materials doped with rare earth or transition-metal ions. In order to do so, it is very interesting to know deeply the structure of the potential host material, as well as its optical properties. The research in this field has contributed to develop new photonic devices [1–4].

Transition-metal ions, corresponding to the iron group, can be used as optically active ions. It is well known that its external 3d unfilled shell produces electronic transitions giving rise to intense luminescence. The active 3d-electrons are situated outside the neutral core, reacting strongly to the electric field of the host. Optical transitions originate sharp or broad emission bands depending on the symmetry of the states involved and on the dynamic of the environment surrounding the active ions in the crystal.

Broad bands are formed by the strong coupling between the active ions and the lattice vibrations. In this case, the crystal can be used as a wide spectral tunable emitter. However, there are some situations in which the electronic transitions of the active ions are non-radiative. Crystals that can support large energy phonons ($>1000\ cm^{-1}$) show this characteristic. These phonons can easily couple to ion energetic states, quenching radiative transitions, mainly in the infrared spectral range. This fact limits the laser applications. In order to obtain efficiency an efficient IR luminescent medium, it is important to choose materials with phonon energies much less than the energy gap associated with optical transitions in the active ions. Host materials, as fluoride crystals, are very attractive to use as a light source in the near infrared (NIR) spectral range, since

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they have a cut-off phonon frequency lower than 600 cm$^{-1}$ [5]. It should be pointed out that another limiting factor for laser applications could be the coincidence of the breathing phonon frequency of the active ions with the vibration normal modes. In this case the crystals behave as draining energy from the excite level suppressing radiative transition, as it was suggested by Torchia et al. for $Cr^{3+}$ ions in $LiNbO_3$ crystals [13].

$Cr^{3+}$ ion in fluoride crystals have been investigated by several research groups [6,7] since laser action in $KZnF_3$:$Cr^{3+}$ was obtained for the first time [8].

$Cs_2NaAlF_6$ crystal has an hexagonal perovskite structure ($R3m$ symmetry) with lattice parameters $a = 6.18$ A and $c = 29.87$ Å. $Na^+$ and $Al^{3+}$ cations are alternated in the crystal structure and are surrounded by $F^-$ anions. In this material, $Cr^{3+}$ ions replace substitutionally $Al^{3+}$ ions. In the presented symmetry, $Cr^{3+}$ ions experience a nearly octahedral electric field produced by two planes of $F^-$ ions. As we said above, the crystal field couples strongly to $Cr^{3+}$ $3d^n$ electrons, splitting these energy states. Tanabe and Sugano [9] have calculated the split energy levels for different $d^n$ electron configuration in a rigid environment with octahedral coordination lattice. These energy values are tabulated in terms of the Racah's parameters $A$, $B$ and $C$ and the crystal field Dq [10].

In this work we describe the influence of electron-lattice coupling in the luminescence quantum yield for $Cr^{3+}$ ions in $Cs_2NaAlF_6$. For this purpose we have used the coordinate configurational model in harmonic approximation to describe the $Cr^{3+}$ luminescent features in this host.

## 2. Experimental procedure

Fluoride crystals were synthesized by a direct temperature-gradient method as a result of the reaction of aqueous solutions of CsF (30–35 mol%) and NaF. The mole ratio CsF/NaF was changed from 4.8 to 5.2 and mixed with appropriate oxide mixtures of $Al_2O_3$ and $Cr_2O_3$ (99.995% pure). The growth conditions carried out were: a temperature of about 750 K, a temperature gradient of about 2 K/cm and pressures of 100–150 Mpa [11]. The $Cr^{3+}$ added in the mixture was 0.5%.

Optical absorption was conducted at room temperature by means of a Beckman DU-65 spectrophotometer while luminescence emission was measured after excitation with an OPO from GWU (Germany) by using a cross-dispersion spectrograph with a CCD camera multichannel (Mechelle 900).

The source of excitement was an OPO pumped by the third harmonic (355 nm) of a Q-Switch Nd:YAG laser (Surelite II, Continuum) yielding 8 ns of pulse wide and output energy higher than 20 mJ in the visible region.

## 3. Results and discussion

Fig. 1 shows the absorption and emission spectra corresponding to $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystal. The absorption spectrum (open circles) presents two broad bands centered at 22900 cm$^{-1}$ (~450 nm) and 15,600 cm$^{-1}$ (~620 nm) corresponding to $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$ vibronic transitions, respectively. The wide shape of these bands reveals a strong lattice coupling between the active ions and the host. The emission spectrum (open square) shows a unique wide band centered at 12934 cm$^{-1}$ (~770 nm) corresponding to $^4T_2 \rightarrow {}^4A_2$ vibronic transition. This emission band is independent of the excitation band reached. The emission and absorption bands are fitted using gaussian functions (solid lines) and the centered values are shown on head of the spectra.

The absorption spectrum shown in Fig. 1 is used to calculate the strength of the octahedral crystal field (Dq) and the spectroscopic Racah's parameters $B$ and $C$. It is known [12] that Dq is obtained directly from the energy associated to the peak of the $^4A_2 \rightarrow {}^4T_2$ absorption band, following this relation:

$$\mathrm{Dq} = [E(^4T_2) - E(^4A_2)]/10 = 1616\ \mathrm{cm}^{-1}. \tag{1}$$

The $B$ value can be calculated by means of this expression:

$$\frac{B}{\mathrm{Dq}} = \frac{\left(\frac{\Delta E}{\mathrm{Dq}}\right)^2 - 10\left(\frac{\Delta E}{\mathrm{Dq}}\right)}{15\left(\frac{\Delta E}{\mathrm{Dq}} - 8\right)}, \tag{2}$$

where $\Delta E = 7127$ cm$^{-1}$ is the energetic difference between $^4T_2$ and $^4T_1$ states (strong absorption bands in Fig. 1). We obtain the value $B = 740$ cm$^{-1}$.

The last Racah's parameter ($C$) can be calculated from an approximate expression given by Henderson e Imbusch [12].

$$C = [E(^2\mathrm{E}) - 7.9B + 1.8B^2/\mathrm{Dq}]/3.05; \tag{3}$$

Using the experimental value $E(^2\mathrm{E}) = 14,900$ cm$^{-1}$ from Ref. [7] and the values found previously for Dq and $B$, the result $C = 3168$ cm$^{-1}$ is obtained. Exact determination of $C$ requires the diagonalization of the $4 \times 4$ matrix associated to $^2$E states [10]. The lowest eingenvalue is a transcendental equation, which solution gives the exact value of $C = 3174$ cm$^{-1}$. $C/B = 4.29$ found in this work supports the validity of the model used to calculate the Racah's parameters [12].

The energy for the most relevant states, taking the energy of the $^4A_2$ state equal to zero, can be calculated from

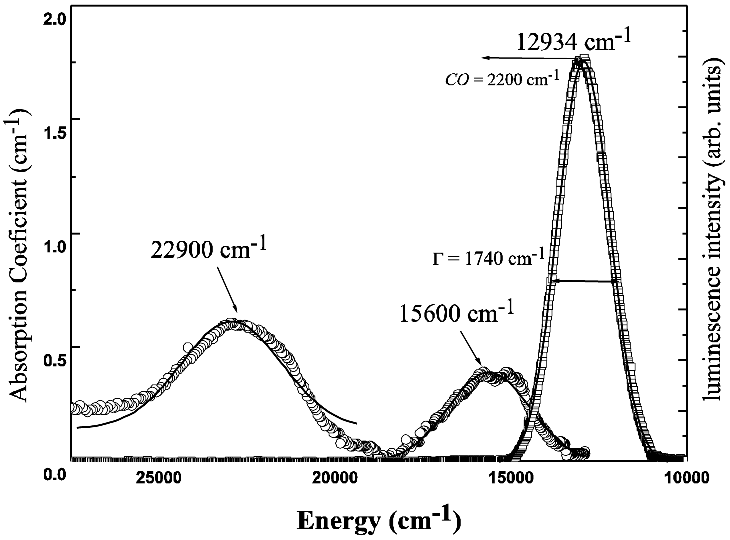

Fig. 1. Absorption and luminescence spectra of $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystal at room temperature. Energy values of relevant levels, Stokes shift (CO) and FWHM bandwidth ($\Gamma$) of emission band are indicated.

Eqs. (1)–(3) using the Racah's parameter found above:

$$\left.\begin{aligned} &E(^4A_2)/B = 0,\\ &E(^4T_2)/B = 10/a,\\ &E(^4T_1)/B = \{20 + 15a - [(10+15a)^2 - 480a]^{1/2}\}/2a,\\ &E(^2E)/B = 3.05C/B + 7.90 - 1.80a,\\ &\text{where } a = B/\mathrm{Dq}. \end{aligned}\right\} \tag{4}$$

The Tanabe–Sugano diagram for the main spectroscopic states of $Cr^{3+}$ ions in fluorite crystals is presented in Fig. 2. The vertical broken line represents the appropriate value for Dq/$B$ (2.18) found for this particular crystal. From the diagram it is not clear which of the $^4T_2$ or $^2E$ states corresponds to the lowest energy level. This fact can be interpreted as both levels could be emitter in contradiction with the emission spectrum shown in this paper. The emission broad band observed is associated to the $^4T_2 \rightarrow {}^4A_2$ transition, very different in shape from those originated by the $^2E$ emission level (narrow bands [12]).

To solve this controversy in a satisfactory way, it is necessary to consider a more complex model which takes into account the $Cr^{3+}$ electron-lattice coupling. The vibrating environment can be represented by the configurational coordinate model in the harmonic approximation

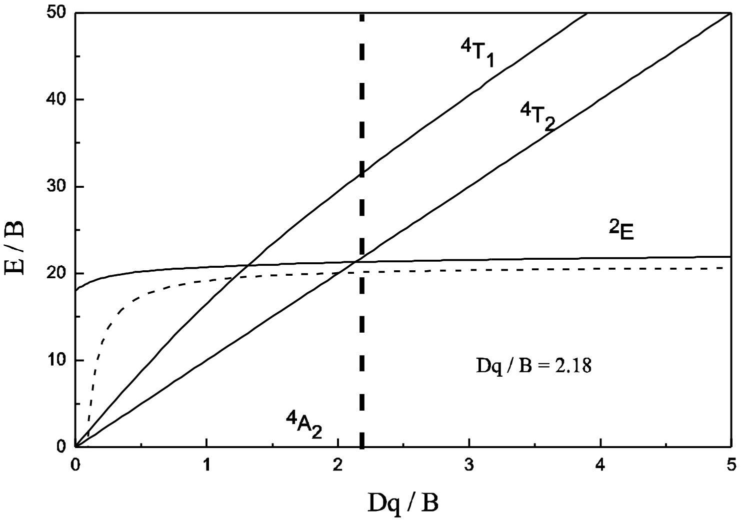

Fig. 2. Tanabe–Sugano's diagram for $Cr^{3+}$ ions in $Cs_2NaAlF_6$. The solid line for $^2E$ level corresponds to the exact resolution of the matrix from Ref. [13], while the broken line is the approximation given by Eq. (3).

[12]. Applying this model it is possible to represent correctly the energy levels of $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystals.

The configurational coordinate model assumes that the first shell of neighboring ions, formed by an octahedron of $F^-$ anions, pulsates harmonically about its equilibrium position. This displacement is represented by the Q coordinate. As a further approximation, we consider the same breathing frequency for all the electronic potentials. This assumption can be represented graphically as identical parabolas associated to each $Cr^{3+}$ energy level (Fig. 3). This diagram shows that, by considering the lattice vibration, the lowest minimum of the excited states corresponds to $^4T_2$, in accordance with the experimental results shown in this work

The parabolas minimum corresponds to the equilibrium position for each $Cr^{3+}$ energy level. The $Q$ difference between the minima associated to the ground and excited levels is proportional to the number of coupling phonons in the electronic transitions. For large difference it is observed wide bands in the absorption and emission spectrum [12].

Usually electron-lattice coupling is characterized by a dimensionless constant, the Huang–Rhys parameter $S$. It is defined as the number of vibrating quanta excited in the absorption transition:

$$S = E_{\mathrm{dis}}/\hbar\omega,$$

where $E_{\mathrm{dis}}$ is the energy difference between the excited level reached in the transition and the minimum associated to the same parabola. This situation is obtained after acceding to the excite level by means of a vertical line from the ground state (Frack–Condon's law), as it is sketched in Fig. 3.

In order to determine the breathing phonon energy corresponding to $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystals we use the spectroscopic data from Fig. 1. The absorption and emission bands associated to the transitions $^4A_2 \rightarrow {}^4T_2$, are approximately Gaussians. In this case, the difference in energy between the absorption and emission band peaks (Stokes shift, CO), is related with $S$ by the following expression [12],

$$\mathrm{CO} = (2S - 1)\hbar\omega, \qquad (5)$$

Other equation necessary to calculate the phonon energy and the Huang–Rhys parameter is given by the expression of the spectrum bandwidth

$$\Gamma(T) = 2.35h\omega(S\coth(h\omega/kT))^{1/2}. \qquad (6)$$

$\Gamma(T)$ represents the FWHM of the emission band and $k = 0.695\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$ is the Boltzman's constant. Using Eqs. (5) and (6), the values found experimentally for the Stokes shift ($\mathrm{CO} = 2200\ \mathrm{cm}^{-}1$) and the bandwidth ($\Gamma(T) = 1740\ \mathrm{cm}^{-1}$), we finally obtain $\hbar\omega = 260\ \mathrm{cm}^{-1}$ and $S = 4.5$ for $T = 295$ K.

Table 1 summarizes the values found for $Cr^{3+}$ ions in $Cs_2NaAlF_6$ crystals. The certainty in the Racah's parameters and the breathing phonon value is estimated around 5%. We compare these results with those found for $Cr^{3+}$ ions in $LiNbO_3$ crystals [13]. As it can be seen, the main difference relies over the Dq/$B$ that indicates higher crystal field intensity over $Cr^{3+}$ ions in $LiNbO_3$ than in $Cs_2NaAlF_6$ crystals. This result, together with the values found for the $S$ parameter let us conclude that $Cr^{3+}$ ions in fluoride crystals have a weaker coupling to the lattice than in $LiNbO_3$ crystals.

On the other hand, we notice that the energy of $Cr^{3+}$ breathing phonon ($260\ \mathrm{cm}^{-1}$) does not coincide with the

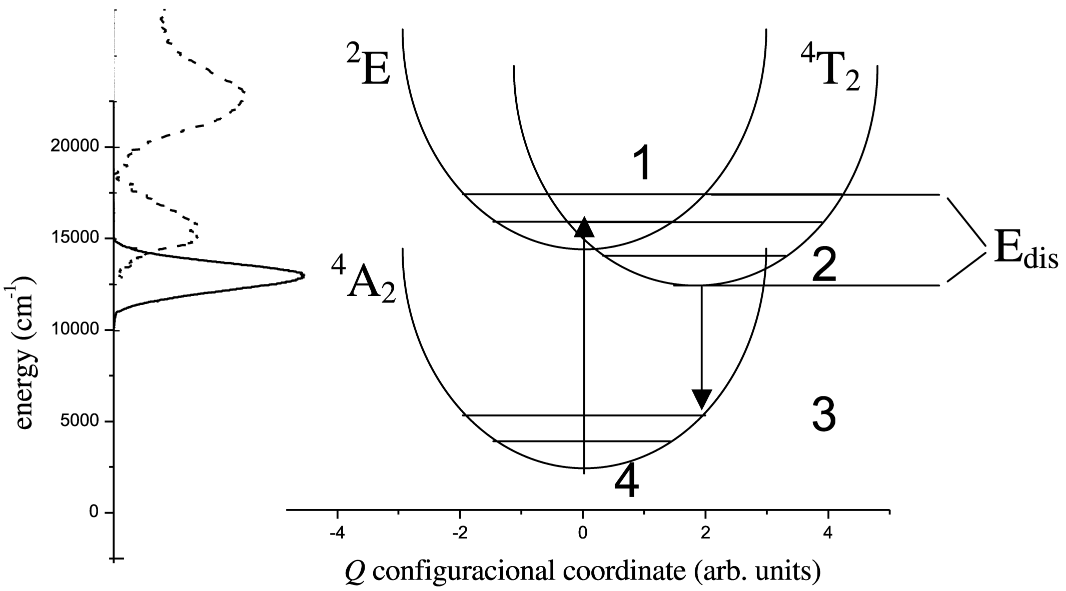

Fig. 3. Coordinate configurational diagram of $Cr^{3+}$ ions in $Cs_2$ $NaAlF_6$ crystals. The numbers indicate the four level system to get laser oscillation in this material.

Table 1
Racah parameters *B* and *C*, crystals field intensity (Dq) and Hung–Rhys parameter (*S*) associated to $Cr^{3+}$ ions in $Cs_2AlNaF_6$ and in $LiNbO_3$ crystals [13]

| | $Cr^{3+}$ in $CsNaAF_6$ (this work) | $Cr^{3+}$ in $LiNbO_3$ [13] |
|---|---|---|
| Dq ($cm^{-1}$) | 1613 | 1527 |
| *B* ($cm^{-1}$) | 740 | 533 |
| *C* ($cm^{-1}$) | 3174 | 3244 |
| Dq/*B* | 2.18 | 2.9 |
| $\hbar\omega$ ($cm^{-1}$) | 260 | 343 |
| *S* | 4.5 | 6.86 |

vibration normal modes for $Cs_2NaAlF_6$ crystals (307, 316, 364, 310 and 520 $cm^{-1}$ [5]). We conclude that the non-radiative transition associated to $^4T_2 \rightarrow {}^4A_2$ is not increased by energy transfer to bulk modes, as it was suggested for $Cr^{3+}$ ions in $LiNbO_3$ crystals [13]. For this reason, $Cr^{3+}$ ions in $Cs_2NaAlF_6$ present a high luminescence quantum yield [14] and it can be a potential material for the development of new tunable light source for the NIR spectral range. Also we have considered the possibility that $Cr^{3+}$ ions in Cs2NaAlF$_6$ crystals can be operated as a four level laser system. This situation is represented in Fig. 3 with the numbers 1–4.

## 4. Conclusions

We have shown the important role that plays the electron-lattice coupling to represent correctly the energy levels of $Cr^{3+}$ ions in $Cs_2NaAlF_6$. We have determined the breathing phonon energy associated to $Cr^{3+}$ ions in this crystal (260 $cm^{-1}$) using the Coordinate Configurational Model in the harmonic approximation. From the spectroscopic data (absorption and emission spectrum) we calculated the Racah parameter, the crystal field and the Huang–Rhys value. The decoupling between the breathing phonon and normal vibration modes of the bulk [5] is in accordance with the high quantum efficiency yield reported [14] (near to 70%). This high value, together with the large lifetime of the excited energy level (330 μs at room temperature) of $Cr^{3+}$ ions in $Cs_2AlNaF_6$ crystal, promises to be an excellent candidate to develop a new tunable laser device in the near IR spectral range.

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