Spectral Intensities for the $Cs_2NaDyCl_6$ and $Cs_2NaHoCl_6$ Systems

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Abstract. The main goal of this research work is to rationalize the rich vibronic structure of two lanthanide type crystals, such as $Cs_2NaDyCl_6$ and $Cs_2NaHoCl_6$, which belongs to the space group $Fm3m(O_5^h)$. These systems are known to be highly relativistic and as a consequence, major corrections to previous calculation models, are due to be taken into account so as to rationalize the observed spectral intensities. Our emphasis has been placed upon both the origin and nature of the physical model to be employed as well as on the strategy to be followed in order to improve our current understanding of the intensity mechanism with reference to general radiative transitions for complex systems, in the solid state physics.

1. Preliminary Remarks
It is well recognized that the lanthanide type crystals are relevant for a series of studies in broad areas of linear and non linear optics. The previous and current efforts have been focused to the identification and assignments of new electronic transitions, in both absorption and emission, at low temperature. This operational conditions are chosen so as to avoid to the maximum extend phase transitions, the presence of some unwanted impurities and to enhance some optical properties and their associated resolution of the associated spectra. Much attention has also been placed upon energy transfer phenomena, such as resonant energy transfer, diagonal and non diagonal processes assisted by phonons, experimental studies, concentration quenching in stoichiometric crystals, cross relaxation involving different donor and acceptor species, energy transfer in transition metal-lanthanide systems and the photon avalanche. All of these areas have been the target of the research efforts of many groups and several physical models and calculation methods have been described in the literature. This work was inspired in our understanding which indicates the real need of more comprehensive and detailed studies of the fundamental principles governing these processes. We have decided to generalize our theoretical model so as to test the validity of various approximations against the available experimental data. It is has always been one of our target to gain understanding in semi empirical methods relevant to this kind of research, by including a minimum set of parameters to be fitted from a rather scarce and incomplete databasis of experimental data. A special care is taken about not including additional any parameters to be adjusted. In this work, we deal with some complicated
excitations for the $Cs_2NaDyCl_6$ and $Cs_2NaHoCl_6$ systems, knowing than almost none of these excitations is pure and most likely are observed as superposition of several transitions which occur roughly at the same energy.

In this study, we have chosen crystals of the lanthanide types since there are obvious advantages such as: (a) single site symmetry for the lanthanide ions, (b) pure octahedral coordination at room temperature, (c) isostuctural for all lanthanide and halide combinations ($F, Cl, Br$) at room temperature, (d) only a very small perturbation from octahedral site symmetry in the event of a phase transition, (e) pure electronic two-photon transitions are potentially electric dipole allowed and (f) large lanthanide-lanthanide separation in the crystal, equal to $\frac{a}{\sqrt{2}}$, through space (or a through bonds) which reduces lanthanide-lanthanide interactions relative to simpler systems, e.g. $LaBr_3$. Low temperature phase transitions from cubic to tetragonal symmetry have been observed in the $Cs_2NaLnX_6$ elpasolites and have been studied with most detail in the chloride and bromide type systems.

Some experimental findings indicate for systems such as: $A_2BLnX_6$, phase transitions may be avoided by maximizing the size of the $A^+$ and minimizing the size of $B^+$, $Ln^{3+}$ and $X^-$ ions.

2. Model

Our model calculation and strategy to be considered is as follows: (a) a ten atom system model is considered as representative of a sub cell for the crystal, see Figure 1, (b) as a result, 24 vibrational degrees of freedom should be included as well as a $t_{1g}$-rotatory mode (the latter inactive both in Raman and in IR). Thus, the vibrational representation of the normal modes for the crystal may be partitioned as follows:

$$\Gamma_{\text{vib}} = \alpha_{t_{1g}} (S_1) + \varepsilon_{g} (S_2) + t_{1g} (S_3) + 2t_{2g} (S_4, S_5) + 4t_{1u} (S_6, S_7, S_8, S_9) + t_{2u} (S_{10})$$

It is well recognized though that to make some progress in the understanding of the electronic spectra of this type of systems, it is crucial to model a sensible and plausible vibrational interacting force field so as to get a proper description of the normal modes. This study has been undertaken in our laboratory with reference to the lanthanide type crystals, using a number of seventy two internal coordinates and ninety eight internal Hooke type force constants. These results will be published in detail somewhere else. An obvious approximate model would be to neglect the coupling between the internal and the external vibrations for the whole crystal. Thus, we may attempt the following assignments and identifications for the frequencies of the crystal (when passing from the 10 to the 7 – atoms system models).

$$\nu_4(10) \Leftrightarrow \nu_4(7, \text{stretching} - t_{1u}), \nu_7(10) \Leftrightarrow \nu_7(7, \text{bending} - t_{1u}),$$

$$\nu_{10}(10) \Leftrightarrow \nu_6(7, \text{bending} - t_{2u}).$$

For the $Cs_2NaLnCl_6$, $Ln = Pr, Eu, Tb, Dy, Ho, Er, Tm$, the ten fundamental vibrational frequencies $\nu_i (i = 1-10)$ have been collected and reported by Tanner et al. A full discussion of the approximation used in the vibronic model, when neglecting this is well documented in the literature and does not need to be repeated here.
2.1. Vibronic Intensities for the Cs$_2$NaDyCl$_6$ system.

A vast amount of spectroscopic experimental data is available from Tanner et al$^5$, and references there in, from emission and absorption, for systems such as: (a) dilute and doped Cs$_2$NaGdCl$_6$:DyCl$_6^{-3}$ and (b) pure stoichiometric Cs$_2$NaDyCl$_6$, in the temperature range: 5−300 K. With reference to the emissions, the following excitations have been considered: $^4F_{9/2} \rightarrow ^6H_{J}$ ($J = 15/2, 13/2, 11/2, 9/2, 7/2$). We have diagonalized the energy matrix and obtained a set of representative symmetry adapted wave functions in the group-sub group chain: $SO_4 \supset O_4$, so as to estimate both the total and the relative vibronic distributions for the excitation quoted above. The details of the calculations are not given for the sake of brevity, though could be obtained by request to RA.

A nice emission spectrum at 20 K has been reported for the doped Cs$_2$NaGdCl$_6$:DyCl$_6^{-3}$ system$^6$, where the assignment is given and the various peaks labelled from 1-41. Also the vibronic origins for the $\Gamma_6 \rightarrow a\Gamma_7, b\Gamma_7, \Gamma_6$ were located at 17,376, 17,295 and 17,213 in wave numbers. Next, we list the estimated values for the oscillator strengths and relative vibronic intensities for a number of excitations, using a 7-atoms system and a truncated expansion for the Hamiltonian of the system, see Table 1. The excitations are labelled for the sake of brevity as follows: (1) $\Gamma_6 \rightarrow \Gamma_6$, (2) $\Gamma_6 \rightarrow \Gamma_7$, (3) $\Gamma_6 \rightarrow a\Gamma_8$, (4) $\Gamma_6 \rightarrow b\Gamma_8$, (5) $\Gamma_6 \rightarrow c\Gamma_8$, (6) $a\Gamma_8 \rightarrow \Gamma_6$, (7) $a\Gamma_8 \rightarrow \Gamma_7$, (8) $a\Gamma_8 \rightarrow a\Gamma_8$, (9) $a\Gamma_8 \rightarrow b\Gamma_8$ and (10) $a\Gamma_8 \rightarrow c\Gamma_8$. The values for the oscillator strengths for each false origin in a given transition is labelled as $f^\ast(\nu_\lambda)$ and are given in units of $2(C_4/e)^2 = 4.832.10^{-3}$, where $C_4 = 2e^2 \langle r^4 \rangle / (\Delta E R_0)^{k+1}$.

Some remarks from the results quoted in Table 1 are as follows: Transitions: (1) the estimated intensities are too small and no experimental data is available, (2) this excitation is most likely to be not pure and therefore it could be obscure by a magnetic dipole excitation corresponding to $a\Gamma_6 \rightarrow b\Gamma_8$, (3) only the $\Gamma_6 \rightarrow a\Gamma_8 + \nu_3$ transition is reported, (4) the vibronic transition $\Gamma_6 \rightarrow a\Gamma_8 + \nu_6$ shows a similar intensity with respect to the $a\Gamma_8 \rightarrow c\Gamma_8$ magnetic dipole transition and it is rather intense, therefore the $\Gamma_6 \rightarrow a\Gamma_8 + \nu_6$ is likely to be obscured in this energy region, (5) this corresponds to a situation in which only the $\Gamma_6 \rightarrow c\Gamma_8 + \nu_3$ can be observed, (6) here, the transition $a\Gamma_8 \rightarrow \Gamma_6 + \nu_3$ appears as a shoulder, imbedded in a very intense transition, (7) there is no experimental evidence, (8) in this case, the intensities associated with the $a\Gamma_8 \rightarrow a\Gamma_8 + \nu_4$ for $k = 4, 6$ appear rather overestimated by this model, (9) this is a magnificent example, where the estimated intensities agree fairly well with experiment and (10) this is also a good test for the model.

2.2. Vibronic Intensities for the Cs$_2$NaHoCl$_6$ system.

For this system, there is a number of experimental studies$^7$−$^{12}$ and a number of interesting transitions, which deserve to be studied. We have, though chosen the excitation at about 488 nm corresponding to the $^5F_2 \rightarrow ^5I_{15}$ emission, since the terminal electronic states have the same spin multiplicity and one may expect a rather clean and well resolved spectrum. We have found that the vibronic transitions corresponding to these excitations may roughly be located as given in Table 2. As it is seen, the lines
labelled as 12, 13 and 14 match perfectly well with excitations of \( \Gamma_1 \rightarrow \Gamma_\nu + \nu \) and this should be taken into account when the theoretical predictions are discussed. We may argue that the observed total oscillator strengths are, indeed a measure of the surface under each curve associated with a peak of the transition and therefore, a kind of summation of these surfaces should be carried out when dealing with theoretical and experimental studies. For the sake of completeness and brevity, we list a crude estimate of the vibronic intensity distributions; associated with these excitations, see Table 3.

The notations is as follows: (1) \( a\Gamma_1 \rightarrow \Gamma_2 \), (2) \( a\Gamma_4 \rightarrow \Gamma_3 \), (3) \( a\Gamma_4 \rightarrow a\Gamma_4, a\Gamma_2 \), (4) \( a\Gamma_4 \rightarrow b\Gamma_4 \) and (5) \( a\Gamma_4 \rightarrow b\Gamma_5 \). The experimental values are given in square brackets and the summation corresponding to each of the vibronic transitions should be handled with care and we need to carried out this procedure taken into account at the very least the orbital degeneracy of the electronic states involved in the overall transition. A complete review for this system will be discussed somewhere else and we have only made a single point about the superposition of vibronic transitions and a suggestion about how to handle it. We could improve this calculation by taking into account a more expanded basis set and some other small refinements in the model. Although the intrinsic limitations of our current approach, we may argue that the scheme is flexible and has some utility. Further improvements are also needed and work in this direction is in progress in our research group (a generalized lattice dynamic vibronic model).

Table 1: Vibronic Intensities for \( \text{Cs}_2\text{NaDyCl}_6 \).

| \( f(\nu_1) \) | \( f(\nu_2) \) | \( f(\nu_3) \) | \( f(\nu_4) \) |
|---|---|---|---|
| 1 | \( 6.38 \cdot 10^{-3} \) | \( 1.36 \cdot 10^{-4} \) | \( 1.52 \cdot 10^{-2} \) | \( 7.61 \cdot 10^{-1} \) |
| 2 | \( 1.06 \cdot 10^{-4} \) | \( 1.38 \cdot 10^{-5} \) | \( 6.23 \cdot 10^{-3} \) | \( 1.48 \cdot 10^{-2} \) |
| 3 | \( 3.49 \cdot 10^{-6} \) | \( 2.98 \cdot 10^{-6} \) | \( 2.78 \cdot 10^{-4} \) | \( 1.82 \cdot 10^{-3} \) |
| 4 | \( 3.15 \cdot 10^{-6} \) | \( 7.21 \cdot 10^{-7} \) | \( 2.38 \cdot 10^{-5} \) | \( 3.02 \cdot 10^{-4} \) |
| 5 | \( 2.94 \cdot 10^{-6} \) | \( 6.60 \cdot 10^{-7} \) | \( 3.61 \cdot 10^{-5} \) | \( 6.55 \cdot 10^{-4} \) |
| 6 | \( 3.39 \cdot 10^{-6} \) | \( 2.20 \cdot 10^{-6} \) | \( 4.32 \cdot 10^{-5} \) | \( 2.39 \cdot 10^{-4} \) |
| 7 | \( 2.23 \cdot 10^{-6} \) | \( 6.33 \cdot 10^{-7} \) | \( 3.89 \cdot 10^{-5} \) | \( 6.02 \cdot 10^{-4} \) |
| 8 | \( 2.60 \cdot 10^{-6} \) | \( 1.92 \cdot 10^{-4} \) | \( 1.40 \cdot 10^{-2} \) | \( 9.47 \cdot 10^{-1} \) |
| 9 | \( 1.04 \cdot 10^{-5} \) | \( 4.65 \cdot 10^{-6} \) | \( 4.12 \cdot 10^{-4} \) | \( 9.27 \cdot 10^{-3} \) |
| 10 | \( 2.60 \cdot 10^{-5} \) | \( 5.60 \cdot 10^{-5} \) | \( 4.70 \cdot 10^{-3} \) | \( 6.42 \cdot 10^{-2} \) |

Table 2: The \( \text{Cs}_2\text{NaHoCl}_6 \) System.

| \( a\Gamma_4 \rightarrow \Gamma_2 \) | \( 9890(18) \) | \( 10036(11) \) | \( 10059(9) \) |
| \( a\Gamma_4 \rightarrow \Gamma_3 \) | \( 9857(20) \) | \( 10003(13)^I \) | \( 10026(12)^I \) |
| \( a\Gamma_4 \rightarrow a\Gamma_4 \) | \( 9981(14)^I \) | \( 10127(5) \) | \( 10150(4)^I \) |
| \( a\Gamma_4 \rightarrow a\Gamma_3 \) | \( 9981(14)^I \) | \( 10127(5) \) | \( 10150(4)^I \) |
| \( a\Gamma_4 \rightarrow b\Gamma_3 \) | \( 9829(21) \) | \( 9975(14)^I \) | \( 9981(13)^I \) |
\[ a\Gamma_4 \rightarrow b\Gamma_2 \quad \begin{array}{ccc}
9877(19) & 10023(12)^2 & 10046(10)
\end{array} \]

Table 3: Vibronic Intensity Distributions. The \( \text{Cs}_2 \text{NaHoCl}_6 \) System.

| \( \nu_3 \) | \( \nu_4 \) | \( \nu_6 \) |
|-----------|-----------|-----------|
| 1         | 1.00 : 10.00 : 23.00 | [1.00 : 5.00 : 6.00] |
| 2         | 1.00 : 1.00 : 0.80  | [1.00 : 4.00 : 4.00] |
| 3         | 1.00 : 1.80 : 1.50  | [1.00 : 0.60 : 1.50] |
| 4         | 1.00 : 63.00 : 150.00 | [1.00 : 7.00 : 3.50] |
| 5         | 1.00 : 1.70 : 0.60  | [1.00 : 2.50 : 4.00] |

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