Spectral intensities in trivalent lanthanide systems
Applications to the Cs₂NaDyCl₆ and Cs₂NaHoCl₆ crystals

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abstract

The main goal of this research work is to rationalize the rich vibronic structure of lanthanide type crystals, such as Cs₂NaDyCl₆ and Cs₂NaHoCl₆, in the space group Fm3m (O5h). These systems are known to be highly relativistic and as a consequence, major corrections to previous model calculations should be taken into account so as to explain from a semi-quantitative viewpoint, the observed spectral intensities. We have decided to tackle this study taking special care, of both the physics and the chemistry involved with special emphasis on the theoretical model to be employed as well as, in the strategy to be followed to rationalize the available experimental data. This paper aims to advance our understanding of the intensity mechanisms, associated with observed radiative transitions, say for complex highly relativistic systems, in the solid state physics. The spectral intensities associated with superpositions (juxtapositions) of peaks and/or bands in the absorption and emission spectra are considered in detail and a preliminary working methodology is put forward with reference to the Cs₂NaDyCl₆ and Cs₂NaHoCl₆ crystals.

Keywords: Spectral intensities; Cs₂NaDyCl₆ and Cs₂NaHoCl₆ systems

1. Introduction

It is well recognized that the elpasolite type crystals are relevant for a series of studies in broad areas of linear and non-linear optics. The efforts of many research works have been focused with both the identification and assignments of new electronic transitions, in both absorption and emission at low temperature. This is to avoid to the maximum extend phase transitions, the presence of some unwanted impurities and to enhance some optical properties and their associated resolution. In this broad area of research, much attention has 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 literatures [1–4]. We do realize that in spite of all of these attempts, there is a need for more comprehensive and detailed studies of the fundamental principles governing these processes. Along these lines, we have carried out a detailed literature search and have decided to advance our understanding of both new and generalized theoretical models, which results should indeed be tested against the experimental data available. The theoretical models to be employed should, then include, a minimum set of parameters to be fitted from experimental data (since this data is either scarce or incomplete for the many systems reported). Our understanding is that a supra parameterization of the calculation model may obscure both the physics and the chemistry of the problem we want to study and therefore decided to keep our model as simple and flexible as possible. The results of the experimental data indicate that there is an inherent complexity with reference to these systems so we have arrived to the conclusion that a more aggressive strategy should be considered so as to explain the observed rich vibronic structures associated with the spectra for these crystals.
In this work, we deal with some complicated excitations for the Cs₂NaDyCl₆ and Cs₂NaHoCl₆ systems, knowing that almost none of these excitations are expected to be pure and in most cases these are more likely to be explained as the result of the superposition of several transitions which occur roughly at the same energy.

In the current research work [1,2], we have chosen crystals of the lanthanide type for several reasons: (a) single site symmetry for the lanthanide ions, (b) pure octahedral coordination at room temperature, (c) isostructural 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 a/\sqrt{2}, through space (or a through bonds) which reduces lanthanide–lanthanide interactions relative to simpler systems, e.g. LaBr₃. Low temperature phase transitions from cubic to tetragonal symmetries have been observed in the Cs₂NaLnX₆ crystals and this symmetry descent has been studied carefully in both the chloride and bromide systems. A practical and useful approximation to the family of the stoichiometric lanthanide type crystals. This approximation is hardly applicable to systems such as A₂BLnF₆, due to the significant dispersion between the LO–TO, \( \tau_{1u} \)-symmetry modes. In spite of this fact, we may also add that for the Chloride elpasolite-type crystals, this assumption is not too unrealistic and it is seen from both the emission and the absorption spectra that the most prominent spectral features are associated with the odd parity normal modes of the cluster. When this physical model is adopted to describe the most intense features in the spectra of these crystals, we should bear in mind that the observed vibrational frequencies are both temperature- and host-dependent.

It is customary, in the literatures [2–4], to employ the following convention for the odd parity frequencies, relating the 7 to the 7-atom systems: \( \nu_6(10) \leftrightarrow \nu_3(7,\text{stretching–}t_{1u}), \nu_7(10) \leftrightarrow \nu_4(7,\text{bending}) \) and also: \( \nu_{10}(10) \leftrightarrow \nu_6(7,\text{bending–}t_{2g}) \). Furthermore, for the Cs₂NaLnCl₆ crystals; Ln = Pr, Eu, Tb, Dy, Ho, Er, Tm, in several cases, the 10 fundamental vibrational frequencies \( \nu_i(i=1–10) \), corresponding the 10-atoms system model, have been collected and reported by Tanner [2] For illustrative purposes and simplicity of the vibronic model, we will assume that the hyper-surfaces corresponding to the terminal states of the excitation have roughly the same shape and are only vertically displaced to one another (along the totally symmetric normal modes of vibration; i.e. the breathing mode). Also that the energy gap between these states is large enough so as to allow the use of the crude Born–Oppenheimer approximation.

Next and within the independent system model (ISM) [4], the total transition dipole moment may be partitioned into a sum of two contributions, from both the crystal field and the

2. Vibronic model, discussion and results

The Cs₂NaDyCl₆ and Cs₂NaHoCl₆ systems: Our strategy and model calculation to be employed in the current work is as follows [2,3]: (a) a 10-atom system model is considered as representative of a sub-cell for the crystal, (b) as a result; 24 vibrational degrees of freedom should be included as well as a one \( t_{1g} \)-rotatory mode (inactive both in Raman and in IR). Thus, the vibrational representation of the normal modes for the crystal may be partitioned as follows: \( \Gamma_{\text{ vib}} = \alpha t_{1g}(S_1) + e_g(S_2) + t_{1g}(S_3) + 2t_{2g}(S_4, S_5) + 4t_{1u}(S_6, S_7, S_8, S_9) + 2t_{2u}(S_{10}) \).

It is well recognized, that in order to make some progress in the understanding of the electronic spectra for this type of systems, it is crucial to model a sensible and reasonable vibrational interacting force field. It is then a challenge to work out a proper description for the normal modes of vibrations, in order to produce a sensible set of amplitudes of vibrations (i.e., the L-matrix, relating both the symmetry to the normal coordinates for the crystal). We have undertaken, this study with reference to the family of the stoichiometric lanthanide type crystals. This has been done using a total of 72 internal coordinates and 98 internal Hooke-type force constants [3].

In passing, let us emphasize that for these crystals, the experimental data available is both scarce and limited; and this is indeed an awkward point to deal with and as a consequence some criteria should be introduce so as to choose a sensible set of approximations, when dealing with spectral intensity calculations. Also, when this view is adopted, the results will be approximate and should, therefore be regarded as good as could be expected from simple model calculations. At this point, it is appropriate to argue that our strategy is mainly focused to put forward both simple and flexible models, which may prove to be appropriate and useful to accommodate a number of terms in the Hamiltonian for the system. When these simple ideas are put into practice, then an obvious starting point may be formulated and this suggests as a starting point the neglect of the coupling between the internal and the external vibrations for the whole crystal (Fig. 1). We observe from this figure, that in this approximate model (7-atoms system model) the coupling between the internal vibrations of the [LnCl₆³⁻] cluster, to the vibrations associated with the Cs⁺ and the Na⁺ counter ions is considered to be either too small or negligible. This approximation is hardly applicable to systems such as A₂BLnF₆, due to the significant dispersion between the LO–TO, \( \tau_{1u} \)-symmetry modes. In spite of this fact, we may also add that for the Chloride elpasolite-type crystals, this assumption is not too unrealistic and it is seen from both the emission and the absorption spectra that the most prominent spectral features are associated with the odd parity normal modes of the cluster. When this physical model is adopted to describe the most intense features in the spectra of these crystals, we should bear in mind that the observed vibrational frequencies are both temperature- and host-dependent.

Next and within the independent system model (ISM) [4], the total transition dipole moment may be partitioned into a sum of two contributions, from both the crystal field and the
ligand polarization models. It is therefore straightforward to show that the dipole strength should be written as
\[ D_{1\rightarrow 2} = D_{1\rightarrow 2}^{\text{FF}} + D_{1\rightarrow 2}^{\text{LP}} + D_{1\rightarrow 2}^{\text{C(LP)}} \]

Furthermore, it is well known, that the interference terms \( D_{1\rightarrow 2}^{\text{C(LP)}} \) is a signed quantity, though special care should be placed upon the choice of the phases for both eigenfunctions and operators [3,4].

2.1. Vibronic intensities for the Cs2NaDyCl6 system

A vast amount of spectroscopic experimental data is available from Tanner et al. [5,6], and references there in, from emission and absorption, for systems such as: (a) dilute and doped Cs2NaGdCl6:DyCl63− and (b) pure stoichiometric Cs2NaDyCl6, in the temperature range: 5–300 K. With reference to the emissions, the following excitations have been considered: \(^{2}\text{F}_{9/2} \rightarrow ^{4}\text{H}_{15/2}(\lambda = 15/2,13/2,11/2,9/2)\). Do observe that for the sake of simplicity, we have chosen to use the notation for the free ion spectroscopic terms (\(^{2S+1}L_{J}\)). We have diagonalized the energy matrix and obtained a set of representative symmetry adapted wave functions in the group–subgroup chain: SO3 \( \supseteq \) O6, so as to estimate both the total and the relative vibronic intensity distributions for the excitations quoted above. The details of the calculations are not given here, for the sake of brevity, though could be obtained upon request from RA. A nine emission spectrum at 20 K has been reported for the doped Cs2NaGdCl6:DyCl63− system, where the assignments are given and the various peaks labelled from 1–41 [6].

Also the vibronic origins for the \( \Gamma_6 \rightarrow a\Gamma_7, b\Gamma_7, \Gamma_6 \) excitations were located at 17,376, 17,295 and 17,213 (in wave numbers). Our model is based upon a hamiltonian which includes terms such as: monoelectronic effective, bi-electronic (electron–electron repulsion terms), the spin–orbit (this is by far the most important relativistic term in the Hamiltonian) and the non-relativistic crystal field operators.

Next, and after some extensive and hard algebra, we proceed to list the estimated values for the oscillator strengths and relative vibronic intensities for a number of vibronic transitions, (7-atom model and a truncated expansion for the Hamiltonian), 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) \( a\Gamma_8 \rightarrow c\Gamma_8 \).


<table>
<thead>
<tr>
<th>Excitation</th>
<th>( f(v_3)/f(v_2)/f(v_6) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_6 \rightarrow \Gamma_6 )</td>
<td>1.00:21.00:2.40 (n.o)</td>
</tr>
<tr>
<td>( \Gamma_6 \rightarrow \Gamma_7 )</td>
<td>1.00:1.13:1.60 [1.00:0.00:2.00]</td>
</tr>
<tr>
<td>( \Gamma_6 \rightarrow a\Gamma_8 )</td>
<td>1.00:0.00:0.80</td>
</tr>
<tr>
<td>( \Gamma_6 \rightarrow b\Gamma_8 )</td>
<td>1.00:20.00:20.00</td>
</tr>
<tr>
<td>( \Gamma_6 \rightarrow c\Gamma_8 )</td>
<td>1.00:2.00:1.20</td>
</tr>
<tr>
<td>( a\Gamma_8 \rightarrow \Gamma_6 )</td>
<td>1.00:60.1:1.30 [1.00:1.00:2.00]</td>
</tr>
<tr>
<td>( a\Gamma_8 \rightarrow \Gamma_7 )</td>
<td>1.00:2.01:0.70</td>
</tr>
<tr>
<td>( a\Gamma_8 \rightarrow a\Gamma_8 )</td>
<td>1.00:74.00:0.50 [1.00:1.00:1.00]</td>
</tr>
<tr>
<td>( a\Gamma_8 \rightarrow b\Gamma_8 )</td>
<td>1.00:50.50:40 [1.00:0.70:0.30]</td>
</tr>
<tr>
<td>( a\Gamma_8 \rightarrow c\Gamma_8 )</td>
<td>1.00:2.01:1.80 [1.00:1.20:1.20]</td>
</tr>
</tbody>
</table>

The vibronic transition \( \Gamma_6 \rightarrow a\Gamma_8 + v_6 \) 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 \( \Gamma_6 \rightarrow a\Gamma_8 + v_6 \) excitation is likely to be obscured in that energy region, (5) this corresponds to a situation in which only the \( \Gamma_6 \rightarrow a\Gamma_8 + v_6 \) can be observed, (6) here, the transition \( a\Gamma_8 \rightarrow \Gamma_6 + v_3 \) 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 \( a\Gamma_8 \rightarrow a\Gamma_8 + v_6 \) for \( k = 4, 6 \) are, 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.

It is observed that the overall agreement between the estimated and the observed spectral intensities is fair, though the intrinsic limitations of this simple model calculation. Further refinements, should be introduced and a generalized vibronic model using the 10-atoms system model employed. Our belief is that the \( L \)-matrix relating the sets of symmetry to the normal coordinates for the crystal plays a major role so it is crucial to reformulate the whole model and to work out some kind of vibronic lattice dynamic approach. A substantial amount of work along these lines is in progress in our laboratory and we have managed to work out a sensible description for the dynamic matrix, by including the short, the medium and the long-range interactions for the elpasolite type crystals.

2.2. Vibronic intensities for the Cs2NaHoCl6 system

For this system, there is a number of experimental studies [7–12] and a set of interesting vibronic transitions which deserve to be studied, nevertheless based upon our previous experience, we have chosen the excitation at about 488 nm corresponding to the \(^{5}\text{F}_{3} \rightarrow ^{3}\text{I}_{2}\) emission. This is due to the fact that the terminal electronic states have the same spin multiplicity and one might reasonably expect a rather clean and well-resolved spectrum. We have found that the corresponding vibronic transitions may be, to a good degree of approximation be located as given in Table 2. We have therefore decided to study and to eventu-
The $\text{Cs}_2\text{NaHoCl}_6$ crystal

Table 3

The $\text{Cs}_2\text{NaHoCl}_6$ crystal

<table>
<thead>
<tr>
<th>Excitation false origins</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\Gamma_4 \rightarrow \Gamma_2$</td>
<td>9890(18)</td>
<td>10,036(11)</td>
<td>10,059(9)</td>
</tr>
<tr>
<td>(2) $\Gamma_4 \rightarrow \Gamma_3$</td>
<td>9857(20)</td>
<td>10,003(13)</td>
<td>10,026(12)$^2$</td>
</tr>
<tr>
<td>(3) $\Gamma_4 \rightarrow \alpha \Gamma_4$</td>
<td>9981(14)$^3$</td>
<td>10,127(5)</td>
<td>10,150(4)$^4$</td>
</tr>
<tr>
<td>(4) $\Gamma_4 \rightarrow \alpha \Gamma_5$</td>
<td>9981(14)$^3$</td>
<td>10,127(5)</td>
<td>10,150(4)$^4$</td>
</tr>
<tr>
<td>(5) $\alpha \Gamma_4 \rightarrow \beta \Gamma_4$</td>
<td>9829(21)</td>
<td>9,975(14)$^3$</td>
<td>9,981(13)$^4$</td>
</tr>
<tr>
<td>(6) $\alpha \Gamma_4 \rightarrow \beta \Gamma_5$</td>
<td>9877(19)</td>
<td>10,023(2)$^3$</td>
<td>10,046(10)</td>
</tr>
</tbody>
</table>

The $|\ell F_3\text{iso}\Gamma_k\rangle \rightarrow |\ell F_1\beta\Gamma_l\rangle + v_m$ transitions energy levels and assignments (lines labelled as 12, 13 and 14 do match with vibronic transitions of the $\Gamma_k \rightarrow \Gamma_l + v_m$, and this point should not be overlooked when dealing with the vibronic intensity distributions and overall oscillator strengths. The energy values are given in cm$^{-1}$).

ally put forward a strategy to deal with the overall intensities of excitations due to the superposition of additional feature in the spectra. As it is seen, the lines labelled as 12, 13 and 14 match perfectly well with excitations of $\Gamma_1 \rightarrow \Gamma_2 + v_3$ 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 in study and therefore, a kind of summation of these surfaces should be carried out, when dealing with theoretical and experimental studies (non-pure vibronic transitions). For the sake of completeness and brevity, we list an estimate of the vibronic intensity distributions; associated with these excitations, see Table 3. The notations is as follows: (1) $\alpha \Gamma_4 \rightarrow \Gamma_2$, (2) $\alpha \Gamma_4 \rightarrow \Gamma_3$, (3) $\alpha \Gamma_4 \rightarrow \alpha \Gamma_4, \alpha \Gamma_2$, (4) $\alpha \Gamma_4 \rightarrow \beta \Gamma_4$ and (5) $\alpha \Gamma_4 \rightarrow \beta \Gamma_5$.

The experimental values are shown in square brackets and the summation corresponding to each of the vibronic transitions should be handled with most care.

This procedure must be carried out considering at the very least the orbital degeneracy for the electronic states involved in the overall transition. A complete review for this system will be discussed somewhere else, with reference to similar systems. The lack of space precludes us of considering in detail the methodology employed, however we have pointed out the need for considering in an explicit way the superposition of peaks in a given spectrum for this kind of complex stoichiometric lanthanide systems.

In this short paper, we aim to suggest a possible way to deal the superposition of vibronic transitions. We could improve this calculation by taking into account a more expanded basis set and some other small refinements in the model. Although

3. Conclusions

The calculations carried out in this research work show that for some lanthanide type crystals, the 7 atoms approximation may be employed with a fair degree of success. In all of these situations, we have assumed that the coupling between the internal and the external vibrations is either small or negligible. Though, we recognize that this is not true for systems such as: $\text{A}_2\text{BL}_n\text{F}_6$ crystals in the $\text{Fm}^3\text{m}$ space group, since the observed dispersion between the LO–TO modes is large enough to make this model unrealistic. For these latter systems, the calculation model must be generalized to include all contributions (short up to long-range) interaction terms in the dynamic matrix. This is a magnificent piece of work, currently in progress in our laboratory.

Our experience indicates that it is necessary to improve our knowledge about the description of the normal modes of vibrations so as to have a better description of the vibrational factors which play an important role as far as the vibronic intensities are concerned. Finally but not at last, the two $\text{Cs}_2\text{NaDyCl}_6$ and $\text{Cs}_2\text{NaHoCl}_6$ lanthanide type systems studied in this work, have been reasonable modeled and the estimated relative vibronic intensity distributions reproduced with a fair degree of success. A step in this direction has been achieved and we have managed to work out a strategy and model to deal with the vibrations of the 10-atom model as described somewhere else [3].

Deviation from experimental data may always be explained based on an incomplete set of experimental data and the simplicity of the model. Any supra parameterization scheme has been avoided throughout the course of the current work.

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