

# Spectral Intensities for the Emission $|^4S_{3/2}\Gamma_8\rangle \rightarrow |^4I_{15/2}\Gamma\rangle$ in the $\text{Cs}_2\text{NaErCl}_6$

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*(Received November 5, 2003; in final form January 12, 2004)*

We report explicit vibronic intensity calculations for the  $|^4S_{3/2}\Gamma_8\rangle \rightarrow |^4I_{15/2}\Gamma\rangle$  excitations in the  $\text{Cs}_2\text{NaErCl}_6$  elpasolite-type systems, based upon new and updated experimental data, obtained from optical absorption measurements made at 10 K, in the energy range from 6,000 up to 26,000  $\text{cm}^{-1}$ . Our calculation model is a generalization of the vibronic crystal field-ligand polarization method and the calculation is performed using a minimum set of adjustable parameters — all and each of them have a clear physical meaning. Our strategy was chosen so as to make a significant distinction with previous calculations, performed by other authors, who have worked out a model originated from a supra-parameterized scheme, within the framework of the superposition model of Newman. Throughout the course of the current work, it is shown that our model is suitable to handle this kind of calculations and also that the numerical results obtained are in fairly good agreement with experiment.

PACS numbers: 32.70.Cs

## 1. Introduction

Vibronic side bands are usually associated with electric dipole transition moments in centrosymmetric rare-earth systems. Several pioneer calculations cor-

responding to vibronic line strengths for these systems have been developed in a collection of papers by Judd [1], Richardson and co-workers [2–5] and Satten et al. [6]. In these research works, both the static and the dynamic contributions to the total transition dipole moments were included, and a calculation scheme was developed to parameterize the energy matrix as well as to modulate the observed spectral intensities. In all of these calculations, we have employed a seven atom model system (7-atoms), such as  $\text{LnX}_6^{3-}$ , where the  $\text{Ln}^{3+}$  ions are associated with octahedral sites of symmetry and are directly bonded to a total of six halide ions. However, less attention has been focused on non-centrosymmetric complex ions, though the models developed by Richardson et al. [2–5] are, in principle, suitable to accommodate any group–subgroup symmetry chain. It must be said that the vibronic side bands in non-centrosymmetric crystals are substantially weaker than the pure zero phonon line ( $0 \rightarrow 0'$ ), though some stronger vibronic features are also to be expected. In passing, let us say that the weakness of vibronic lines in systems such as  $\text{Eu}^{3+}$  in  $\text{LaNbO}_4$  were observed [7], nevertheless some stronger vibronic lines were also reported for other lanthanide(3+) type compounds [8], to a certain extent somehow unexpected. Also some stronger vibronic lines have been attributed to the  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  emission for the  $\text{Gd}^{3+}$  ion, as reported by Blasse and Brixner [9]. A general conclusions may be stated as follows: the intensities of vibronic transitions may differ by, say an order of magnitude or so, depending upon the host lattice.

There is also available some solid evidence, which indicates that the vibronic spectra of systems such as  $\text{Eu}(\text{AP})_6\text{I}_3$  and  $\text{Eu}(\text{AP})_6(\text{ClO}_4)_3$ , in centrosymmetric environments, show up the appearance of strong vibronic lines, most probably associated with high-energy internal ligand vibrations, their intensities being comparable with the transition combined with the metal chromophore [10]. In a latter work by Stręk et al. [11], these authors took a general view of the general problem of vibronic transitions in lanthanide(3+) type compounds with reference to systems, in which internal ligand vibrations may be observed. The strategy followed by these authors was based upon the independent system model for which both the static and the dynamic contributions to the dipole strengths are taken into account. The main goal of their research was to work out identities to estimate amplitude of vibronic transitions associated with the internal ligand vibrations. They showed that the second-order theory is not adequate to rationalize the presence of high-energy phonon side bands in connection with these vibrations. It is also to be noticed that the lowest order non-vanishing terms, which are most likely to accommodate the ligand vibrations, are derived from a third-order perturbation calculations and, as a result, it is straightforward to conclude that the intensities associated with these vibronic lines should be weaker. Further studies were performed by Flint and Greenough [12] for  $\text{Cr}(3+)$  complex ions, in octahedral symmetry and also by Berry and co-workers [10] with reference to systems such as  $\text{Eu}(\text{AP})_6\text{X}_3$ . In a subsequent work, Acevedo et al. [13, 14] showed that as for

the  $\text{Cr}(\text{NH}_3)_6^{3+}$  ion, in the octahedral point molecular group, the observed vibronic intensities associated with vibrational modes of the same type and symmetries, corresponding to the odd-parity symmetry blocks (a)  $\tau_{1u}[\delta(\text{N}-\text{Cr}-\text{N}), \rho(\text{Cr}-\text{N}-\text{H})]$  and (b)  $\tau_{2u}[\delta(\text{N}-\text{Cr}-\text{N}), \rho(\text{Cr}-\text{N}-\text{H})]$  show intensities which are comparable in magnitude.

The most likely explanation lies on the generally accepted assumption, which suggests that the unexpected high observed intensity may be rationalized on the assumption that it is the  $\text{NH}_3$ - lone pair motion out of the inter-nuclear axis  $\text{Cr}-\text{N}-\text{H}$  responsible for these spectral intensities. As for monoatomic ligand subsystems, the electronic spectra of lanthanide ions imbedded in cubic elpasolite crystals [15] show up magnetic dipole and/or electric quadrupole allowed electronic transitions together with extensive vibronic side bands.

It is known from experiment that the three  $\Gamma_1 \rightarrow \Gamma_2 + \nu_k$ ,  $k = 3, 4, 6$  transitions are the most intense features in the spectrum. In all previous calculations, using the 7-atom model, the basic assumptions have been as follows: (a) The coupling between the internal and the external modes of vibrations is either too small and/or negligible. (b) The potential energy surfaces of the terminal electronic states involved in the transition have the same shape and are only vertically displaced to one another, along the breathing mode coordinate ( $\alpha_{1g}$ ) and (c) The energy gap between the terminal electronic states is large enough so that the vibronic states may be represented, employing the crude Born–Oppenheimer approximation.

Richardson and co-workers [3, 5, 15–19] have applied vibronic coupling models to the parameterization of the vibronic intensities in the elpasolite-type crystals, within the framework of the approximations (a), (b), and (c), stated above in the text. In all of these calculations the strategy followed by these authors has been to rely upon rather full parameterization models, either when a combined crystal field-closure-ligand polarization or a generalization of the superposition models are employed [5, 17–25]. In spite of these authors efforts, it is known that the database available is either scarce or incomplete or both, then it does seem appropriate not to work with supra-parameterized models and instead, to develop vibronic schemes characterized as having a fewer parameters to be fitted from the available experimental data.

It is interesting to examine the physical basis of the superposition model of Newman [20–23]. A subsequent calculation performed by Richardson et al. [5] utilized an extension of this approach so as to fit the spectral intensities associated with transitions of the type  $\Gamma_1 \rightarrow \Gamma_2 + \nu_6$ , for the  $\text{U}(\text{Br}_6)^{2-}$  complex ion. In this paper, we found that the number of parameters to be fitted from experiment exceeds largely the available data.

In an additional effort, Acevedo et al. [26] focused the attention upon those factors: electronic and vibrational in character, which are most likely to play a major role in determining the spectral intensities for these systems. This re-

search work was carried out with reference to the two absorptions, namely the  $\Gamma_6(^2F_{7/2}) \rightarrow (\Gamma_7, \Gamma_8)(^2F_{5/2}) + \nu_k$ , involving the three odd parity normal modes of vibrations for the  $\text{YbCl}_6^{3-}$  clusters. In a recent paper, Acevedo and co-workers [27] reported vibronic calculations for the  $|(^4I_{15/2})\Gamma_k\rangle \leftarrow |(^4I_{13/2})\Gamma_l\rangle$  emissions of the  $\text{Er}^{3+}$  ion, in the  $\text{Cs}_2\text{NaErCl}_6$  elpasolite-type system.

Previous experimental and theoretical studies, performed by Richardson et al. [19, 28] and references therein, using a full parameterization approach, obtained an accurately determined set of energy levels for the  $\text{Cs}_2\text{NaErCl}_6$  system, up to about  $26,500 \text{ cm}^{-1}$ . Also these authors based upon these results (eigenvalues and eigenfunctions) decided to work out transition dipole magnetic moments, which are shown to be in close agreement with the experimental data. Our approach [27] was based upon simple model calculations for some selected excitations of  $\text{Er}^{3+}$  ion, in the above mentioned host.

We concluded in principle that there are several sources for disagreement between the reported experimental data and our theoretical predictions. In order to explain some discrepancies, we may also argue that the reported assignments for a variety of peaks in the spectra is very likely to correspond to a juxtaposition of vibronic transitions, rather than unambiguously determined excitations. There are though some complexities which should be worked and analyzed further and many of the approximations were studied so as to accommodate a number of factors which are known to play a substantial role in the general theory of vibronic transitions and their intensity mechanisms. We appreciate the need for further and deeper theoretical works along these lines, and we have decided to study the  $|(^4S_{3/2})\Gamma_8\rangle \rightarrow |(^4I_{15/2})\Gamma\rangle$  transitions in the  $\text{Cs}_2\text{NaErCl}_6$  type elpasolite.

The choice of these excitations was influenced mainly by the rather unexpected intensity for these excitations, for which the static selection rule  $\Delta J = 6$  is operative. New and updated experimental data for this system has been reported by Crooks et al. [29]. These authors reported the optical absorption measurements at 10 K for the  $\text{Cs}_2\text{NaErCl}_6$  elpasolite in the energy range from 6,000 to  $26,000 \text{ cm}^{-1}$ . Their calculation was based upon what these authors regard as absolute line intensities for a number of transitions, and employing a vibronic version of the method of Newman [22] they worked out a set of optimized intrinsic intensity parameters for the  $\text{ErCl}_6^{3-}$  complex ion. The model was tested and their results, at first glance, showed that the numerical overall agreement between experiment and the theoretical predictions seems to be reasonable. In spite of this apparent success, these authors claim that the signs of the  $A_t^{-\lambda}$  parameters agree for all odd parity modes, with the exception of the sign for  $A_5^{-6}$  parameter, associated with the  $\tau_{2u}$ -bending mode ( $\nu_6$ ). In their paper, the authors claimed that the overall signs for the intrinsic parameters  $A_t^{-\lambda}$  are consistent with the signs found in other materials and for the zero-phonon case. In view of these and related calculations, performed somewhere else, we decided to tackle the vibronic intensity calculations for a number of transitions for which the static selection rule  $\Delta J = 6$  becomes

operative. Our model and strategy employed differs notably from that of Crooks et al. [29].

We will attempt to explain the observed intensities for this system, assuming a two steps photon radiative cascade (“a two-jump excitation path”), which certainly involves intermediate electronic states.

This paper is mainly devoted to the mechanistic aspects of radiative transitions and the need for developing more suitable and meaningful models to explain spectral intensities in relativistic systems. The calculation will be performed, using a seven atom system model.

The above is a consequence of the well known experimental evidences, which both suggests and indicates that for the radiative transitions the promoting modes are mainly localized on the  $\text{ErCl}_6^{3-}$  moiety [29]. The experiment validates the use of our seven atom system model to be employed throughout the course of the current work.

## 2. Synthesis and structural characterization

The sample was obtained by means of a solid state reaction, in  $\text{N}_2$  atmosphere, utilizing stoichiometric quantities of  $\text{CsCl}$ ,  $\text{NaCl}$ , and  $\text{ErCl}_6$ . Before the thermal treatment the product was dried out at  $105^\circ\text{C}$  so as to eliminate any residual of  $n\text{-C}_6\text{H}_6$ .

The thermal analysis technique (DTA/TGA) allowed us to find the most suitable temperatures to perform the thermal analysis and in this way, to facilitate the crystallization procedure for the system. As for the  $\text{Cs}_2\text{NaErCl}_6$  elpasolite system, the critical crystallization temperature is reached at  $837.9^\circ\text{C}$ . Also the structural determination and the analysis of the impurities were performed, using X-ray fluorescence and the measured density was  $3.62 \pm 0.01$  (pycnometer, LANGER 450, under vacuum). The structural characterization of this elpasolite system was obtained by means of X-ray diffraction measurements (DRX-powder studies) and the profiles were refined employing the method put forward by Rietveld [30]. The operational conditions of the X-ray generator were of 20 mA and 40 kV, with a Cu anode and a Ni filter, corresponding to a wavelength of about  $1.5444 \text{ \AA}$ . The range scanned was from  $12^\circ$  up to  $79^\circ$  ( $2\theta$ ) at room temperature. Finally, the average atomic positions were found as follows:  $4\text{Er}^{3+}(0, 0, 0)$ ,  $4\text{Na}^+(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ,  $8\text{Cs}^+(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ ,  $24\text{Cl}^{-1}(\frac{1}{4}, 0, 0)$ , and the lattice parameter as follows:  $a_0 = 10.7089 \text{ \AA}$ .

## 3. Theoretical models and vibronic calculations

The formal theory of the vibronic coupling (vibronic crystal field-ligand polarization, VCF-LP) has been developed for both centrosymmetric and non-centrosymmetric complex ions, hosted in crystals in different space groups. Richardson et al. [3, 16, 24] (and references therein) have carried out a number of

calculations of vibronic intensities in the rare earths ( $\text{ReZ}_6^{2-}$ ) and the lanthanide ( $\text{LnZ}_6^{3-}$ ) halide complex ions. Similarly, and over the last two decades, our group has been engaged in spectral intensity calculations for the elpasolite-type systems, using a generalized version of the vibronic crystal field-with and without invoking closure approximation-ligand polarization model [26, 31–33].

As we explained in Sec. 1, we have decided to develop both a vibronic model and a calculation method to account for the observed intensities of the  $|(^4S_{3/2})\Gamma_8\rangle \rightarrow |(^4I_{15/2})\Gamma\rangle$  ( $\Gamma = \Gamma_6, \Gamma_7, \Gamma_8^a, \Gamma_8^b, \Gamma_8^c$ ) emissions in the  $\text{Er}(3+)$  elpasolite-type system. It is interesting to realize that on the basis of new and updated experimental data [29] we observed that these excitations exhibit overall oscillator strengths of about  $10^{-9}$ , and based upon theoretical considerations, we realize that for these transitions a one-step mechanism path, connecting the terminal electronic states, is most likely to induce intensities in the range of  $10^{-10}$  to  $10^{-12}$ , and therefore further theoretical work is needed.

As we showed in Sec. 2, the  $\text{Cs}_2\text{NaErCl}_6$  elpasolite system belongs to the space group  $Fm\bar{3}m(O_h^5)$ , and the  $\text{Er}^{3+}$  ions occupy octahedral sites of symmetry. The vibrational symmetry species for these crystals are as follows [34, 35]:  $\text{Na}^+(\tau_{1u})$ ,  $\text{Cs}^+(\tau_{1u} + \tau_{2g})$  and for the  $\text{ErCl}_6^{3-}$  clusters, we obtain the vibrational representation:  $\Gamma_{\text{vib}} = \alpha_{1g}(\nu_1) + \varepsilon_g(\nu_2) + \tau_{1u}(\nu_3) + \tau_{1u}(\nu_4) + \tau_{2g}(\nu_5) + \tau_{2u}(\nu_6)$ . It can be noticed that, in addition to the fifteen degrees of freedom for the clusters, there are four lattice modes according to the following symmetry species:  $2\tau_{1u}$  (IR active),  $\tau_{2g}$  (Raman active) and  $\tau_{1g}$  (inactive). In a classic paper, Lentz [34] and latter Ning et al. [35] discussed the vibrations for both the  $\text{A}_3\text{B}'\text{X}_6$  and the  $\text{A}_2\text{BB}'\text{X}_6$  crystals. When a modified version of a valence type force field is employed, a total of ten unknown internal force constants are needed to estimate the fundamental vibrations in the  $\mathbf{k} = \mathbf{0}$  point. In these two papers [34, 35] the notation introduced by Lentz for the symmetry coordinates is preserved:  $S_i$ ,  $i = 1-10$  so as to describe the symmetry coordinates (along the polarization direction of the crystal). When this notation is adopted, the symmetry blocks become:  $\alpha_{1g}$  ( $1 \times 1$ ),  $\varepsilon_g$  ( $1 \times 1$ ),  $\tau_{1g}$  ( $1 \times 1$ ),  $\tau_{1u}$  ( $4 \times 4$ ),  $\tau_{2g}$  ( $2 \times 2$ ), and  $\tau_{2u}$  ( $1 \times 1$ ).

The next step is to find a suitable potential energy function and by means of a semi-empirical method to solve the vibrational equations of motion, which will eventually lead us to solve the secular determinant  $|GF - \lambda E| = 0$  [36, 37]. As for the intensity calculations, we are interested in obtaining the odd parity normal modes of vibrations for the system. A proper strategy involves solving the dynamic matrix, including both the short- and the long-range interaction terms. This is indeed a major task and a fairly complete set of new and updated experimental data for the crystal is required promptly.

A zero-order calculation, including only the short-range interaction contributions to the dynamic matrix, was performed for a series of selected elpasolite-type systems by Ning et al. [35]. This calculation was carried out for lanthanide elpasolite systems, using data obtained from room temperature to 10 K. Also, the

10 vibrational frequencies of the model, employed to modulate the crystals, were fitted using a modified version of the standard valence force field. An approximate set of internal coordinates was obtained, showing up to a first approximation the extent of the mixing in the internal and the external modes of vibrations (for additional details of this calculation, the reader is referred to the paper of these authors).

In our current work, we are aware that this task can partially be achieved, solving the equation of motion for the system, using as a basis the symmetry coordinates corresponding to the symmetry blocks:  $\tau_{1u}(S_6, S_7, S_8, S_9)$  and  $\tau_{2u}(S_{10})$ . Next, we write the transformation matrix  $S = LQ$ , which relates the set of the symmetry coordinates to the corresponding set of normal coordinates of the system. It is well known that the  $L$  matrix depends upon the details of the interacting vibrational force field, i.e.,  $L = L(F)$ . Also, the extent of the coupling between the internal and the external modes of vibrations for the crystal is small [29], because of the assumption that the more efficient promoting modes belonging to the clusters  $\text{ErCl}_6^{3-}$  seem to be appropriate and well founded. A close examination of Refs. [34, 35] indicates that if this coupling is neglected then we may make the following symmetry assignments:  $S_6 = S$  (stretching;  $\tau_{1u}$ ),  $S_7 = S$  (bending;  $\tau_{1u}$ ). Thus and within the seven atom system approximation, the odd-parity normal modes of vibrations corresponding to the three moiety modes may be written as follows:  $S_{3t} = L_{33}Q_{3t} + L_{34}Q_{4t}$ ,  $S_{4t} = L_{43}Q_{3t} + L_{44}Q_{4t}$ , and  $S_{6t} = L_{66}Q_{6t}$ :  $t = a, b, c$  [38–40]. We recognize that this calculation is rather approximate and the long-range interaction contributions to the dynamic matrix were left out, therefore a re-examination of the methodology employed is most needed, in any future model calculation.

### 3.1. The vibronic crystal field-closure-model (VCF-closure-model)

In this section we give a short review of the relevant master equations used throughout the course of current work to estimate the vibronic crystal field-closure contribution to the total transition dipole moment, for parity forbidden but vibronically allowed  $f \rightarrow f$  electronic transition in cubic environments. For details concerning the derivations of equations and the approximations employed, the reader is referred to Refs. [26, 29, 40]. In a previous paper [27] we showed some basic equations which enabled us to deal with the vibronic intensity calculations for the seventy five vibronically allowed  $|(^4I_{15/2})\Gamma_k\rangle \rightarrow |(^4I_{13/2})\Gamma_i\rangle + \nu_m$ ,  $m = 3, 4, 6$ , absorptions in this elpasolite.

In this work we will introduce a more sophisticated model and a set of master, symmetry adapted equations to deal with these vibronic intensity calculations. It can be shown [33, 38, 39] that when closure is adopted, the explicit nature of these intermediate electronic states becomes totally irrelevant except for the choice of some kind of effective energy gap. The latter corresponds to a virtual  $f \rightarrow d$  and/or  $f \rightarrow g$  excitations.

Thus for the  $|\alpha_1(L_1SJ_1)\Gamma_1\gamma_1l\rangle \rightarrow |\alpha_2(L_2SJ_2)\Gamma_2\gamma_2m\rangle$  electronic transition, the  $\beta$ -th component to the transition dipole moment (VCF-closure-model) becomes

$$\begin{aligned} \mu_{1\rightarrow 2}^{\text{CF},\beta} &= -\frac{2Ze}{\Delta E} \sum_{\nu_i} S_{\nu_i} \sum_{\Gamma,\gamma} \sum_{i,\tau} A_{\nu_i}^{\Gamma\gamma}(i,\tau) \sum_{\bar{\Gamma},\bar{\gamma}} \lambda(\bar{\Gamma})^{1/2} (-1)^{\bar{\Gamma}+\bar{\gamma}^\dagger} \\ &\times V \begin{pmatrix} T_1 & \Gamma & \bar{\Gamma} \\ \beta & \gamma & \bar{\gamma}^\dagger \end{pmatrix} (-1)^{\Gamma_1+\gamma_1^\dagger} \sum_u V_u \begin{pmatrix} \Gamma_1 & \Gamma_2 & \bar{\Gamma} \\ \gamma_1^\dagger & \gamma_2 & \bar{\gamma} \end{pmatrix} \\ &\times \langle \alpha_1(L_1SJ_1)\Gamma_1l \parallel O^{\bar{\Gamma}}(T_1\Gamma|i,\tau) \parallel \alpha_2(L_2SJ_2)\Gamma_2m \rangle_u. \end{aligned} \quad (1)$$

Next, when the symmetry adapted vibronic crystal field coefficients  $W_{(k,u)}^{[(T_1\Gamma)\bar{\Gamma};i,\tau]}[\Gamma_1J_1|\Gamma_2J_2]$  are introduced, we may write the identity

$$\begin{aligned} &\langle \alpha_1(L_1SJ_1)\Gamma_1l \parallel O^{\bar{\Gamma}}(T_1\Gamma|i,\tau) \parallel \alpha_2(L_2SJ_2)\Gamma_2m \rangle_u \\ &= \sum_k W_{(k,u)}^{[(T_1\Gamma)\bar{\Gamma};i,\tau]}[\Gamma_1J_1|\Gamma_2J_2] \langle \alpha_1(L_1S)J_1 \parallel C^k \parallel \alpha_2(L_2S)J_2 \rangle, \end{aligned} \quad (2)$$

where

$$\begin{aligned} W_{(k,u)}^{[(T_1\Gamma)\bar{\Gamma};i,\tau]}[\Gamma_1J_1|\Gamma_2J_2] &= \sum_{\gamma_1,\gamma_2,\bar{\gamma}} (-1)^{\Gamma_1+\gamma_1^\dagger} \\ &\times V_u \begin{pmatrix} \Gamma_1 & \Gamma_2 & \bar{\Gamma} \\ \gamma_1^\dagger & \gamma_2 & \bar{\gamma} \end{pmatrix} \sum_{M_1,M_2,q} C^*(\alpha_1J_1M_1|\Gamma_1\gamma_1l) \\ &\times C(\alpha_2J_2M_2|\Gamma_2\gamma_2m) P_{k,q}^{\bar{\Gamma}\bar{\gamma}}(T_1\Gamma|i,\tau) (-1)^{\Gamma_1+\gamma_1^\dagger} \begin{pmatrix} J_1 & k & J_2 \\ -M_1 & q & M_2 \end{pmatrix}. \end{aligned} \quad (3)$$

Full tabulations for the vibronic crystal field coupling constants  $A_{\nu_i}^{\Gamma\gamma}(i,\tau)$ , the symmetry adapted  $V$ -coefficients, the coupled vibronic operators  $O^{\bar{\Gamma}}(T_1\Gamma|i,\tau)$ , the  $3j$ -symbols, and the symmetry coordinates may be found in [33, 38–40] and references therein. Also, further details and tabulations may be obtained upon request from R.A.

### 3.2. The vibronic ligand polarization model (VLP-model)

For isotropic ligands, the dynamic contribution to the total transition dipole moment adopts a rather simple form. Thus, the  $\varepsilon$ -th vector component may be written as given below

$$\begin{aligned} \mu_{1\rightarrow 2}^{\text{LP},\varepsilon} &= (-1)^{\Gamma_1+\lambda_1^\dagger} \sum_{k,t} S_{kt} \sum_{\Gamma,\gamma} \sum_{i,\tau} B_{k,t}^{\Gamma\gamma,\varepsilon}(i,\tau) \sum_r V_r \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1^\dagger & \gamma_2 & \gamma \end{pmatrix} \\ &\times \langle \alpha_1(L_1SJ_1)\Gamma_1l \parallel M^{\Gamma}(i,\tau) \parallel \alpha_2(L_2SJ_2)\Gamma_2m \rangle_r. \end{aligned} \quad (4)$$



The reduced matrix elements, on the right hand side of the above identity may be further simplified, by taking advantage of the irreducible tensor algebra [41–46]. To achieve this simplification, we define the symmetry adapted coefficients as given below

$$\begin{aligned} Z_{(i,\tau)r}^F[l\Gamma_1 J_1 | m\Gamma_2 J_2] &= \sum_{\gamma_1, \gamma_2, \gamma} (-1)^{F_1 + \gamma_1^+} V_r \begin{pmatrix} \Gamma_1 & \Gamma_2 & \bar{\Gamma} \\ \gamma_1^+ & \gamma_2 & \gamma \end{pmatrix} \\ &\times \sum_{M_1, M_2} \sum_q R_{i,q}^{\Gamma\gamma}(\tau) C^*(\alpha_1 J_1 M_1 | \Gamma_1 \gamma_1 l) \\ &\times C(\alpha_2 J_2 M_2 | \Gamma_2 \gamma_2 m) (-1)^{J_1 - M_1} \begin{pmatrix} J_1 & i & J_2 \\ -M_1 & q & M_2 \end{pmatrix} \end{aligned} \quad (5)$$

for  $r = 1, 2$ . Thus, in terms of these coefficients, we may write the general identity

$$\begin{aligned} \langle \alpha_1(L_1 S J_1) \Gamma_1 l || M^F(i, \tau) || \alpha_2(L_2 S J_2) \Gamma_2 m \rangle_r \\ = Z_{(i,\tau)r}^F[l\Gamma_1 J_1 | m\Gamma_2 J_2] \langle \alpha_1(L_1 S) J_1 || D^i || \alpha_2(L_2 S) J_2 \rangle, \end{aligned} \quad (6)$$

where

$$D_m^l = -(er^l) \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\theta, \phi).$$

The actual evaluation of these coefficients may be accomplished utilizing the tabulations given by Griffith [44], Dobosh [45], and Rotemberg et al. [46].

### 3.3. Application: the $|(^4S_{3/2})F_8\rangle \rightarrow |(^4I_{15/2})F\rangle$ emissions for the $ErC_6^{3-}$ ions in $Cs_2NaErCl_6$ crystal

Richardson et al. [19, 47] (and references therein) studied the optical excitation and emission spectra for this material. Detailed assignments were suggested for both the  $^4S_{3/2} \rightarrow ^4I_{15/2}$  and the  $^4F_{9/2} \rightarrow ^4I_{15/2}$  emissions. These experimental results together with previous experimental studies allowed these authors to locate about 35 crystal field energy levels spanning 11 multiplets of the  $Er^{3+}$  ion in the  $Cs_2NaErCl_6$  crystal. The energy levels obtained by an optimization procedure provided good agreement with experiment.

Excitation spectra for the  $^4S_{3/2} \rightarrow ^4I_{15/2}$  emission were reported at several temperatures over the 340–540 nm spectral region. It was found that the intensity of the bands observed in this region decrease as the temperature of the sample is increased. The exception is the  $^4G_{11/2} \rightarrow ^4I_{13/2}$  emission, for which it is observed that its intensity increases as the temperature increases. A very detailed discussion may be found in [19], regarding the line assignments for this transition at 15 K (the reader is referred to Fig. 1 and Table IV in Ref. [19]).

In a latter paper, Tanner et al. [48] undertook a thorough analysis of the spectral data and made comparative energy level parameterizations for the trivalent lanthanide ions in cubic elpasolite systems. The reader is referred to Table 15

(energy levels for the  $\text{Cs}_2\text{NaErCl}_6$  and  $\text{Cs}_2\text{LiErCl}_6$  elpasolites) and to Fig. 4 (luminescence spectra of the  $\text{Cs}_2\text{NaErCl}_6$  and  $\text{Cs}_2\text{LiErCl}_6$  elpasolites at 20 K), in Ref. [48], for details of the assignments and spectral intensities between 18.200 and 17.660  $\text{cm}^{-1}$ . It is clear from these experimental works that all and each of the assignments have been done on the basis of a simple and direct one-photon transitions, assisted by the odd parity normal modes of the  $\text{ErCl}_6^{3-}$  clusters in these elpasolites. It may also be observed from the spectra reported by Richardson et al. [19] and Tanner et al. [48] that the understanding of the intensity mechanisms associated with the  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  and the  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$  emissions is by no means a trivial task, by employing a simple and direct one-photon mechanism.

As we shall see, the observed spectral intensity for the assigned excitation is about  $10^{-9}$  (somehow an unexpected high value for the oscillator strengths. A static  $\Delta J = 6$  selection rule is in this case operative and therefore, a conventional and straightforward calculation would be both inadequate and unrealistic). In this research paper, we have decided to focus our attention upon the  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  emissions in the  $\text{Cs}_2\text{NaErCl}_6$  crystal, for which a conventional calculation would produce a calculated oscillator strengths in the range of  $10^{-10}$ – $10^{-12}$ .

New and updated experimental data [29] indicates that the observed overall spectral intensities are at least one order of magnitude stronger ( $10^{-9}$ ) and we also notice from the spectra that the associated vibronic structure is rich. As it was told previously, the assignments have been made on the basis of a vibronic, one-photon electric dipole mechanism involving transitions of the type:  $|({}^4\text{S}_{3/2})\Gamma_8\rangle \rightarrow |({}^4\text{I}_{15/2})\Gamma\rangle + \nu_m$ ,  $m = 3, 4, 6$ .

The main goal of this research work is to focus our attention upon those mechanistic factors, which are most likely to both influence and determine the observed oscillator strengths for this type of systems. Our mechanistic assumption to account for the observed spectral intensity should be regarded as a first attempt to remove many of the approximations employed in previous vibronic intensity calculations for a variety of systems.

Due to the fact that for these excitations the selection rule  $\Delta J = 6$  is operative and also that the reported spectral intensity is about  $10^{-9}$  [29], we will assume a “two-step quantum jump” as the intensity mechanism, whereby the  $|({}^4\text{S}_{3/2})\Gamma_8\rangle \rightarrow |({}^4\text{I}_{15/2})\Gamma\rangle$  emissions acquire their intensities from a radiative path, given by the chain:  $|({}^4\text{S}_{3/2})\Gamma_8\rangle \rightarrow |({}^4\text{I}_{11/2})\Gamma'\rangle \rightarrow |({}^4\text{I}_{15/2})\Gamma\rangle$ , with full participation of tensor operators of ranks 4 and 2, respectively.

When the above intensity mechanism is adopted, the overall  $|({}^4\text{S}_{3/2})\Gamma_8\rangle \rightarrow |({}^4\text{I}_{15/2})\Gamma\rangle$  emissions borrow their intensities from two sources, namely the  $|({}^4\text{S}_{3/2})\Gamma_8\rangle \rightarrow |({}^4\text{I}_{11/2})\Gamma'\rangle$  and the  $|({}^4\text{I}_{11/2})\Gamma'\rangle \rightarrow |({}^4\text{I}_{15/2})\Gamma\rangle$  excitations. Next and for the sake of simplicity in the notation, we will label the terminal electronic states as follows:  $|1\rangle = |({}^4\text{S}_{3/2})\Gamma_8\rangle$ ,  $|2'\rangle = |({}^4\text{I}_{11/2})\Gamma'\rangle$  and  $|3\rangle = |({}^4\text{I}_{15/2})\Gamma\rangle$ .

Within the framework of this proposed intensity mechanism, the transition dipole moment may be (within the constraints of our assumption) partitioned into

two contributions to give

$$\mu_{1\rightarrow 2} = \mu_{1\rightarrow 2'}(k=4) + \mu_{2'\rightarrow 2}(k=2), \quad (7)$$

where the rank of the tensors connecting the terminal vibronic states are given in brackets.

A close look at Eqs. (1), (2) and (3) indicates that within the framework of a VCF-closure-LP model, the relevant matrix elements to be evaluated are as follows: (a) for the VCF-model:  $\langle \alpha_1(L_1S_1J_1)F_1l || O^F(T_1F|i, \tau) || \alpha_2(L_2S_2J_2)F_2m \rangle_r$  and (b) for the VLP-model:  $\langle \alpha_1(L_1S_1J_1)F_1l || M^F(i, \tau) || \alpha_2(L_2S_2J_2)F_2m \rangle_r$ , where  $r = 1, 2$  when applicable.

Next we list in Table I the symmetry constraints for operators and vibronic states involved in our mechanism proposal.

TABLE I  
The  $|(^4S_{3/2})F_8\rangle \rightarrow |(^4I_{15/2})F\rangle + \nu_m$  ( $m = 3, 4, 6$ ) emissions in  $\text{Cs}_2\text{NaErCl}_6$ .

Terminal states $ 1\rangle \rightarrow  2\rangle$	Intermediate states $ 2'\rangle$	Symmetry of the operators	
		$ 1\rangle \rightarrow  2'\rangle$	$ 2'\rangle \rightarrow  2\rangle$
$\Gamma_8 \rightarrow \Gamma_6$	$\Gamma_6$	$\Gamma_3, \Gamma_4, \Gamma_5$	–
$\Gamma_8 \rightarrow \Gamma_6$	$\Gamma_7$	$\Gamma_3, \Gamma_4, \Gamma_5$	$\Gamma_5$
$\Gamma_8 \rightarrow \Gamma_6$	${}^{a,b}\Gamma_8$	$\Gamma_1, \Gamma_3, {}^{a,b}\Gamma_4, {}^{a,b}\Gamma_5$	$\Gamma_3, \Gamma_5$
$\Gamma_8 \rightarrow \Gamma_7$	$\Gamma_6$	$\Gamma_3, \Gamma_4, \Gamma_5$	$\Gamma_5$
$\Gamma_8 \rightarrow \Gamma_7$	$\Gamma_7$	$\Gamma_3, \Gamma_4, \Gamma_5$	–
$\Gamma_8 \rightarrow \Gamma_7$	${}^{a,b}\Gamma_8$	$\Gamma_1, \Gamma_3, {}^{a,b}\Gamma_4, {}^{a,b}\Gamma_5$	$\Gamma_3, \Gamma_5$
$\Gamma_8 \rightarrow {}^{a,b,c}\Gamma_8$	$\Gamma_6$	$\Gamma_3, \Gamma_4, \Gamma_5$	$\Gamma_3, \Gamma_5$
	$\Gamma_7$	$\Gamma_3, \Gamma_4, \Gamma_5$	$\Gamma_3, \Gamma_5$
	${}^{a,b}\Gamma_8$	$\Gamma_1, \Gamma_3, {}^{a,b}\Gamma_4, {}^{a,b}\Gamma_5$	$\Gamma_3, {}^{a,b}\Gamma_5$

Next we rewrite Eqs. (1) and (4) as given below

$$\mu_{1\rightarrow 2}^{\text{CF},\alpha} = \sum_{k,t} U_k^{\text{CF},\alpha} S_{kt} \quad (9)$$

and, for the ligand polarization contribution, the identity becomes

$$\mu_{1\rightarrow 2}^{\text{LP},\alpha} = \sum_{k,t} U_k^{\text{LP},\alpha} S_{kt}. \quad (10)$$

The symmetry coordinates  $\mathbf{S}$  are related to the normal coordinates by means of the transformation matrix  $\mathbf{S} = \mathbf{LQ}$ , where  $\mathbf{L} = \mathbf{L}(\mathbf{F})$ , that is the  $\mathbf{L}$  matrix depends upon the details of the interacting vibrational force field. Furthermore, when the coupling between the internal and the external modes of vibrations of the same symmetry is neglected, the  $\mathbf{L}$  matrix becomes

$$\mathbf{L} = \begin{pmatrix} L_{33} & L_{34} & 0 \\ L_{43} & L_{44} & 0 \\ 0 & 0 & L_{66} \end{pmatrix}. \quad (11)$$

Further and for the sake of completeness and simplicity, we will introduce the  $\beta_k^{M,\alpha}$  quantities for  $k = 3, 5, 6$  and  $M = \text{CF}$  or  $\text{LP}$ , and we write the transformations

$$\begin{pmatrix} \beta_3^{M,\alpha} \\ \beta_4^{M,\alpha} \\ \beta_6^{M,\alpha} \end{pmatrix} = \begin{pmatrix} L_{33} & L_{43} & 0 \\ L_{34} & L_{44} & 0 \\ 0 & 0 & L_{66} \end{pmatrix} \begin{pmatrix} U_3^{M,\alpha} \\ U_4^{M,\alpha} \\ U_6^{M,\alpha} \end{pmatrix}, \quad \text{where } \alpha = 0, \pm 1. \quad (12)$$

It is important to realize that the mixing in of the two  $\tau_{1u}$  moiety symmetry coordinates is essential to describe the normal modes of vibrations for the  $\text{ErCl}_6^{3-}$  cluster in the  $\text{Cs}_2\text{NaErCl}_6$ .

The extent of the mixing depends critically upon the details of the vibrational force field ( $\mathbf{F}$ ). In this work we follow the convention put forward by Griffith, for point molecular groups [41, 44], and the component of the electric dipole operator in the natural basis is related to the Cartesian basis as follows:

$$\begin{pmatrix} \mu_{+1} \\ \mu_0 \\ \mu_{-1} \end{pmatrix} = \begin{pmatrix} -\frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 \\ +\frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mu^X \\ \mu^Y \\ \mu^Z \end{pmatrix}. \quad (13)$$

In Table II we collect together both the crystal field  $U_k^{\text{CF},0}$  and the ligand polarization  $U_k^{\text{LP},0}$  electronic factors, see Eqs. (9) and (10).

Next a close look at Eqs. (9)–(12) suggests that the total oscillator strength for each of the vibronic origins may be written as follows:

$$D_{1 \rightarrow 2}(\nu_k) = \sum_{\alpha=0,\pm 1} \left\{ \left[ \beta_k^{\text{CF},\alpha} \right]^2 + \left[ \beta_k^{\text{LP},\alpha} \right]^2 + 2 \left[ \left( \beta_k^{\text{CF},\alpha} \right) \left( \beta_k^{\text{LP},\alpha} \right) \right] \right\} \\ \times | \langle 0 | Q_k | 1 \rangle |^2 = D_{1 \rightarrow 2}^{\text{CF}} + D_{1 \rightarrow 2}^{\text{LP}} + D_{1 \rightarrow 2}^{\text{CF,LP}}. \quad (14)$$

The above identity indicates that the total oscillator strength for each vibronic origin ( $\nu_k$ ,  $k = 3, 4, 6$ ) is made up of three terms: the crystal field (VCF), the ligand polarization (VLP), and the interference (CF, LP). The latter coupled interaction term results from the coupling among the crystal field and the ligand polarization transition dipole moments.

It is interesting to bear in mind that this so-called interference term is a signed quantity, and therefore it may either sum or subtract intensity from the diagonal terms VCF and VLP, respectively.

The above discussion is relevant and therefore we should choose the phases of both the wave functions and the tensor operators correctly to obtain the right sign for this cross term (CF, LP). Furthermore, a close look at Table II indicates that in units of the electron charge the electronic factors  $V_k^{M,\alpha}$  for  $M = \text{CF}$  or  $\text{LP}$ ,  $k = 3, 4, 6$  and  $\alpha = 0, \pm 1$  have been expressed in terms of quantities such as:

TABLE II

Crystal field contributions. The  $V_k^{\text{CF},0} = (U_k^{\text{CF},0}/C_{4,2})$ ,  $k = 3, 4, 6$  electronic factors (the corresponding values for the ligand polarization model are given in brackets, though in units of  $a_{4,2}$ ).

$( 1\rangle \rightarrow  2'\rangle)$	$V_3^{\text{CF},0}$	$V_4^{\text{CF},0}$	$V_6^{\text{CF},0}$
$\Gamma_8 \rightarrow \Gamma_6$	-0.07620 [-0.44513]	+0.02856 [+0.29143]	-0.01122 [+0.08874]
$\Gamma_8 \rightarrow \Gamma_7$	-0.18450 [-0.18752]	+0.06918 [+0.27636]	+0.19376 [-0.23724]
$\Gamma_8 \rightarrow {}^a\Gamma_8$	+0.02730 [-1.08530]	-0.01020 [-0.40020]	-0.14936 [+0.46748]
$\Gamma_8 \rightarrow {}^b\Gamma_8$	+0.15416 [+3.04050]	-0.05780 [+1.23930]	-0.03464 [+0.40546]
$( 2'\rangle \rightarrow  2\rangle)$	$V_3^{\text{CF},0}$	$V_4^{\text{CF},0}$	$V_6^{\text{CF},0}$
$\Gamma_6 \rightarrow \Gamma_7$	+ 0.01068 [+0.09062]	+0.00534 [-0.03398]	0 [-0.056640]
$\Gamma_6 \rightarrow {}^a\Gamma_8$	-0.011340 [-0.00100]	-0.005670 [+0.00040]	0 [+0.015020]
$\Gamma_6 \rightarrow {}^b\Gamma_8$	-0.004260 [-0.338780]	-0.002130 [+0.12704]	0 [+0.136460]
$\Gamma_6 \rightarrow {}^c\Gamma_8$	-0.146860 [-0.30196]	-0.073430 [+0.11324]	0 [-0.23422]
$\Gamma_7 \rightarrow \Gamma_6$	+0.004410 [+0.03744]	+0.00220 [-0.01404]	0 [-0.02340]
$( 2'\rangle \rightarrow  2\rangle)$	$V_3^{\text{CF},0}$	$V_4^{\text{CF},0}$	$V_6^{\text{CF},0}$
$\Gamma_7 \rightarrow {}^a\Gamma_8$	+0.06530 [+0.15840]	+0.03266 [-0.05940]	0 [-0.03756]
$\Gamma_7 \rightarrow {}^b\Gamma_8$	-0.019180 [+0.14788]	+0.009590 [-0.05546]	0 [-0.07486]
$\Gamma_7 \rightarrow {}^c\Gamma_8$	+0.013700 [+0.16452]	+0.00685 [-0.06168]	0 [-0.02580]
${}^a\Gamma_8 \rightarrow \Gamma_6$	0 [0]	0 [0]	0 [0]
${}^a\Gamma_8 \rightarrow \Gamma_7$	-0.056240 [+0.46054]	-0.028120 [-0.17270]	0 [-0.18308]
${}^a\Gamma_8 \rightarrow {}^a\Gamma_8$	+0.001880 [-0.17674]	+0.000940 [+0.06628]	0 [+0.11046]
$( 2'\rangle \rightarrow  2\rangle)$	$V_3^{\text{CF},0}$	$V_4^{\text{CF},0}$	$V_6^{\text{CF},0}$
${}^a\Gamma_8 \rightarrow {}^b\Gamma_8$	+0.094620 [+0.20862]	+0.047310 [-0.07822]	0 [+0.22938]
${}^a\Gamma_8 \rightarrow {}^c\Gamma_8$	+0.096140 [-0.05464]	+0.048070 [+0.02048]	0 [+0.03414]
${}^b\Gamma_8 \rightarrow \Gamma_6$	0 [0]	0 [0]	0 [0]
${}^b\Gamma_8 \rightarrow \Gamma_7$	-0.070640 [+0.18416]	-0.035320 [-0.06904]	0 [-0.08766]
${}^b\Gamma_8 \rightarrow {}^a\Gamma_8$	+0.09614 [+0.16142]	+0.048070 [-0.06054]	0 [+0.23248]
${}^b\Gamma_8 \rightarrow {}^b\Gamma_8$	-0.011200 [-0.00312]	-0.005600 [+0.00118]	0 [-0.02644]
${}^b\Gamma_8 \rightarrow {}^c\Gamma_8$	-0.004300 [-0.03536]	-0.002150 [+0.01326]	0 [-0.00452]

$C_k = \frac{2e^2\langle r^k \rangle}{[\Delta E]R_0^{k+1}}$  for the crystal field and  $A_k = \frac{\bar{\alpha}_L\langle r^k \rangle}{R_0^{k+3}}$  for the ligand polarization models.

The final step is the evaluation of the oscillator strengths and relative vibronic intensity distributions for the three odd parity vibrational modes of motion. All this was carried out within the set of approximation introduced in our current model previously and also in Ref. [27]. We display our result and their comparison, when available with experiment, in Table IIIA, whereas in Table IIIB we collect parameter values employed in the calculation.

TABLE IIIA

Total oscillator strengths and relative vibronic intensities. The  $|({}^4S_{3/2})F_8\rangle \rightarrow |({}^4I_{15/2})F\rangle$  emissions for the  $\text{Cs}_2\text{NaErCl}_6$  crystal.

The ${}^4S_{3/2}U' \rightarrow {}^4I_{15/2}E'$ emission					
Oscillator strengths		$1.085 \times 10^{11} \langle Q(\nu_t) \rangle^2 \Delta\nu_t$		$t = 3$	0.01269
				$t = 4$	0.02873
				$t = 6$	0.03948
Interm.	$f_3$	$f_4$	$f_6$	$f_3 : f_4 : f_6$	Experimental
$E'_{\frac{11}{2}}$	0.0007665	0.0006091	0.0000553	1.00 : 1.77 : 1.03	1.0 : 2.8 : 1.8
$E''_{\frac{11}{2}}$	0.0005926	0.0012842	0.0012199		
$U'_{\frac{11}{2}}{}^a$	0.0006510	0.0000804	0.0004896		
$U'_{\frac{11}{2}}{}^b$	0.0005419	0.0010084	0.0008646		
	0.0025520	0.0029821	0.0026294		
Total oscillator strength: $f = 1.566 \times 10^{-9}$				in units of $A_4^2$	$A_4 = 0.000438e$
The ${}^4S_{3/2}U' \rightarrow {}^4I_{15/2}E''$ emission					
Oscillator strengths		$1.085 \times 10^{11} \langle Q(\nu_t) \rangle^2 \Delta\nu_t$		$t = 3$	0.01286
				$t = 4$	0.02911
				$t = 5$	0.03999
Interm.	$f_3$	$f_4$	$f_6$	$f_3 : f_4 : f_6$	Experimental
$E'_{\frac{11}{2}}$	0.0005414	0.0014992	0.0013997	1.00 : 11.83 : 3.20	1.0 : 0.7 : 2.3
$E''_{\frac{11}{2}}$	0.0016769	0.0014002	0.0022554		
$U'_{\frac{11}{2}}{}^a$	0.0034336	0.0308100	0.0141085		
$U'_{\frac{11}{2}}{}^b$	0.0016834	0.0530646	0.0057426		
	0.0073353	0.0867740	0.0235062		
Total oscillator strength: $f = 2.256 \times 10^{-8}$				in units of $A_4^2$	$A_4 = 0.000438e$
The ${}^4S_{3/2}U' \rightarrow {}^4I_{15/2}U'^a$ emission					
Oscillator strengths		$1.085 \times 10^{11} \langle Q(\nu_t) \rangle^2 \Delta\nu_t$		$t = 3$	0.01288
				$t = 4$	0.02915
				$t = 5$	0.04005
Interm.	$f_3$	$f_4$	$f_6$	$f_3 : f_4 : f_6$	Experimental
$E'_{\frac{11}{2}}$	0.0016242	0.0000466	approx. 0	1.00 : 0.53 : 0.35	1.0 : 2.0 : 0.6
$E''_{\frac{11}{2}}$	0.0062545	0.0113627	0.0007730		
$U'_{\frac{11}{2}}{}^a$	0.0059531	0.0029733	0.0012936		
$U'_{\frac{11}{2}}{}^b$	0.0016110	0.0017752	0.0086588		
	0.0306428	0.0161578	0.0107254		
Total oscillator strength: $f = 1.104 \times 10^{-8}$				in units of $A_4^2$	$A_4 = 0.000438e$

TABLE IIIA (cont.)

The $^4S_{3/2}U' \rightarrow ^4I_{15/2}U^{jb}$ emission						
Oscillator strengths		$1.085 \times 10^{11} \langle Q(\nu_t) \rangle^2 \Delta\nu_t$			$t = 3$	0.01284
					$t = 4$	0.02906
					$t = 5$	0.04005
Interm.	$f_3$	$f_4$	$f_6$	$f_3 : f_4 : f_6$	Experimental	
$E'_{\frac{11}{2}}$	0.0191483	0.0088604	0.0041532	1.00 : 0.83 : 0.20	1.0 : 0.8 : 2.1	
$E''_{\frac{11}{2}}$	0.0002273	0.0007612	0.0017422			
$U^a_{\frac{11}{2}}$	0.0196953	0.0150938	0.0009748			
$U^b_{\frac{11}{2}}$	0.0013187	0.0086250	0.0010944			
	0.0403896	0.0333404	0.0079380			
Total oscillator strength: $f = 1.567 \times 10^{-8}$				in units of $A_4^2$	$A_4 = 0.000438e$	
The $^4S_{3/2}U' \rightarrow ^4I_{15/2}U^{jc}$ emission						
Oscillator strengths		$1.085 \times 10^{11} \langle Q(\nu_t) \rangle^2 \Delta\nu_t$			$t = 3$	0.01267
					$t = 4$	0.02869
					$t = 5$	0.03942
Interm.	$f_3$	$f_4$	$f_6$	$f_3 : f_4 : f_6$	Experimental	
$E'_{\frac{11}{2}}$	0.0766383	0.0200457	0.0169231	1.00 : 0.32 : 0.23	1.0 : 1.0 : 1.6	
$E''_{\frac{11}{2}}$	0.0006234	0.0004935	0.0011314			
$U^a_{\frac{11}{2}}$	0.0024846	0.0003672	0.0000197			
$U^b_{\frac{11}{2}}$	0.0015052	0.0054913	0.0010052			
	0.0812515	0.0262977	0.0190794			
Total oscillator strength: $f = 2.432 \times 10^{-8}$				in units of $A_4^2$	$A_4 = 0.000438e$	

As for the notation: the irreducible representations  $\Gamma_6, \Gamma_7, \Gamma_8$  can also be labeled as  $E', E'', U'$  according to Mullikan. Interm. = Intermediate.

Crooks et al. [29] reports a number of vibronic oscillator strengths for a series of absorption transitions at 20 K from the  $|(^4I_{15/2})a\Gamma_8\rangle$  state to excited electronic energy levels for  $\text{Er}^{3+}$  ion in  $\text{Cs}_2\text{NaErCl}_6$ . The tabulated  $\nu_3$  and  $\nu_4$  vibrational frequencies correspond to the transversal optical (TO) modes, whereas the  $\nu_6$ -vibrational frequency is associated with the zone boundary (ZB) mode. The reader is warned to look throughout the Table III with caution. As for the absorption  $|(^4I_{15/2})a\Gamma_8\rangle \rightarrow |(^4S_{3/2})a\Gamma_8\rangle$  excitation, both the absolute line strengths and relative vibronic intensity calculations are displayed for the sake of comparison and completeness along the discussion.

From Table IV it is seen that as for the overall oscillator strength associated with the excitation:  $|(^4I_{15/2})a\Gamma_8\rangle \rightarrow |(^4S_{3/2})\Gamma_8\rangle$ , we find:  $f = 1.727 \times 10^{-8}$ . We observe that with the exception of the intensity induced by the  $\nu_4(\tau_{1u})$ -bending mode of the cluster, our model is able to rationalize and reproduce

TABLE IIIB

Data set and calculated crystal field energy levels.

Parameter values	Coefficient values	
$\langle r^2 \rangle = 0.2325 \times 10^{-16} \text{ cm}^2$	CF: $C_2/C_4 = \langle r^2 \rangle R_0^2 / \langle r^4 \rangle = 11.1$	
$\langle r^4 \rangle = 0.1527 \times 10^{-32} \text{ cm}^4$	LP: $A_2/A_4 = 11.1$	
$R_0(\text{Er-Cl}) = 2.70 \text{ \AA}$	$C_4/A_4 = (2e^2 R_0^2 / \alpha_L \Delta E) = 6.27$	
$\Delta E$ approximately $90,000 \text{ cm}^{-1}$	$A_4 = 0.000438e$	
Vibrational parameters		
$\nu_3 = 255 \text{ cm}^{-1}$	$\langle Q(\nu_3) \rangle^2 = 6.59 \times 10^{-18}$	$L_{33} = 0.20, L_{34} = 0.01$
$\nu_4 = 114 \text{ cm}^{-1}$	$\langle Q(\nu_4) \rangle^2 = 1.48 \times 10^{-17}$	$L_{43} = -0.13, L_{44} = -0.29$
$\nu_6 = 85 \text{ cm}^{-1}$	$\langle Q(\nu_6) \rangle^2 = 2.03 \times 10^{-17}$	$L_{33} = 0.2375$
Crystal field energy levels		
$E(\frac{3}{2}U')$	18,265 $\text{cm}^{-1}$	
$E(\frac{11}{2}E')$	10,151 $\text{cm}^{-1}$	
$E(\frac{11}{2}aU')$	10,176 $\text{cm}^{-1}$	
$E(\frac{11}{2}bU')$	10,182 $\text{cm}^{-1}$	
$E(\frac{11}{2}E'')$	10,208 $\text{cm}^{-1}$	
$E(\frac{15}{2}aU')$	0 $\text{cm}^{-1}$	
$E(\frac{15}{2}E'')$	25 $\text{cm}^{-1}$	
$E(\frac{15}{2}bU')$	55 $\text{cm}^{-1}$	
$E(\frac{15}{2}E')$	257 $\text{cm}^{-1}$	
$E(\frac{15}{2}cU')$	284 $\text{cm}^{-1}$	

TABLE IV

Total oscillator strength and experimental and calculated vibronic intensity distribution for  $|(^4I_{15/2})a\Gamma_8\rangle \rightarrow |(^4S_{3/2})\Gamma_8\rangle$  excitations.

Excitations	$f/10^{-8}$	$[a]^a$	$[b]^b$	$[c]^c$
$ (^4I_{15/2})a\Gamma_8\rangle + \nu_3 \rightarrow  (^4S_{3/2})\Gamma_8\rangle$	0.519	1.00	1.00	1.00
$ (^4I_{15/2})a\Gamma_8\rangle + \nu_4 \rightarrow  (^4S_{3/2})\Gamma_8\rangle$	0.929	1.79	1.73	0.53
$ (^4I_{15/2})a\Gamma_8\rangle + \nu_6 \rightarrow  (^4S_{3/2})\Gamma_8\rangle$	0.279	0.54	1.65	0.35

<sup>a</sup>exp. [29], <sup>b</sup>cal. [29], <sup>c</sup>this work

in fair agreement both the total and the relative vibronic intensity distribution for this excitation.

We also argue from Table III that our model is able to predict spectral intensities within our expectations for all the excitations involved in the  $|(^4I_{15/2})a\Gamma_8\rangle \rightarrow |(^4S_{3/2})\Gamma_8\rangle$  transitions. For all the excitations, the so-called experimental values have been estimated, assuming a Gaussian shape for the absorption band, and



therefore the oscillator strength becomes:  $f \approx 4.61 \times 10^{-9} \varepsilon_{\max} \bar{\nu}_{1/2}$ . The band width is measured at  $\varepsilon = \frac{1}{2} \varepsilon_{\max}$ .

#### 4. Conclusions

A generalized vibronic intensity calculation was presented for the  $|(^4S_{3/2})I_8\rangle \rightarrow |(^4I_{15/2})I\rangle$  emissions in the  $\text{Cs}_2\text{NaCl}_6$  crystal. A radiative decay cascade was suggested to explain the rather unexpected high observed intensity for these excitations, governed by a static selection rule  $\Delta J = 6$ . The intensity of these excitations may be explained using the mechanistic chain:  $|(^4S_{3/2})I\rangle \rightarrow |(^4I_{11/2})I'\rangle \rightarrow |(^4I_{15/2})I\rangle$ , whereby the intensity is obtained from two sources with the cooperation of the odd parity vibrational modes of the clusters  $\text{ErCl}_6^{3-}$ . Closure procedure was employed to evaluate the vibronic crystal field contribution to the total transition dipole moment, and the transition dipole moment was partitioned into three components, two of the three are diagonal (the crystal field and the ligand polarization) whereas the non-diagonal is referred to as the interference term. A careful analysis of the phases for both wave functions and operators was performed so as to ensure that the sign of the cross term is correct. The calculation was taken throughout, without the inclusion of the coupling between the internal and the external vibrational modes of symmetry. The experimental evidence suggests that this coupling is small and therefore may be neglected in this first-order physical model.

It is worth mentioning that our calculation is not based upon a full parameterization of both, the energy and the intrinsic intensity parameters. We have instead focused our attention upon those factors (electronic and vibrational, in character) which are most likely to influence the rates of decay for the observed absorption and/or emissions for these systems.

We have reasonably succeeded in reproducing to a fair degree of approximation, the overall oscillator strengths for about 60 parity forbidden but vibronically allowed peaks in the emission spectra for this system [27]. We observe that overall agreement among our theoretical predictions and experiment is as good as it could be expected from such a simple model calculation. We are fully aware that lattice dynamic calculations are due to be carried out promptly and we may anticipate that theoretical work in this direction is currently being performed in our laboratories. There is an urgent need for having rather complete data base for these stoichiometric elpasolite-type system, so as to include both the short- and the long-range interaction in the crystals. We also feel that work on phonon dispersion curves along different polarization directions of these crystals is required. Last but not least, it seems that our strategy and model calculation is both useful and flexible to reproduce the observed spectral intensities for a series of lanthanide type crystals. We also recognize the need for more sophisticated theoretical work, covering the mechanistic aspects upon which the observed intensities may be understood and rationalized.

### Acknowledgments

R.A. would like to express his gratitude to the Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, and also to the Universidad Diego Portales (VRA 2049, 2065), for partial financial support to undertake this research and also to the Institute of Low Temperature and Structure Research, Wrocław, Poland, for the hospitality and the pleasant environment provided during the course of the current work.

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