Spectra, Energy Levels and Energy Transfer in High Symmetry Lanthanide Compounds

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Abstract The Ln^{3+} ion is situated at a site of octahedral symmetry in crystals of the lanthanide elpasolites, M_2ALnX_6 . The syntheses and crystal structures of M_2ALnX_6 are described, with particular reference to phase transitions. The centrosymmetric environment of Ln^{3+} confers different spectral properties than are observed for most solid-state lanthanide ion systems, and the selection rules are deduced. The vibrational, electronic Raman and electronic spectra of the lanthanide elpasolite systems are presented and discussed. The electronic spectra are described in terms of the $4f^{N}$ - $4f^{N}$ zero phonon line and the vibronic sideband structure and the success of intensity calculations is evaluated. The synergy of one- and two-photon studies is emphasized. The differences with the $4f^{N-}$ $4f^{N-1}5d$ spectra of M_2ALnX_6 are illustrated. The parametrization of the energy level datasets is assessed and the success of recent refinements is analysed. Following a brief review of the theory of energy transfer in crystals, experimental studies of quenching, cross-relaxation, upconversion and photon avalanche in neat and doped elpasolite systems are reviewed. Physical mechanisms are given for spectral features and for energy transfer pathways.

Keywords Cubic crystal \cdot Vibrational Spectra \cdot Luminescence \cdot Absorption \cdot Crystal Field \cdot Vibronic

List of Abbreviati	ons
CF	Crystal field
ED	Electric dipole
EDV	Electric dipole vibronic
EQ	Electric quadrupole
ESA	Excited state absorption
ET	Energy transfer
IR	Infrared
irrep	Irreducible representation
MCD	Magnetic circular dichroism
MCPE	Magnetic circularly polarized emission
TP	Two-photon
ZPL	Zero phonon line

1 Introduction

This review covers the series La^{3+} (4f⁰) to Lu^{3+} (4f¹⁴), including also Y³⁺, which are collectively denoted by Ln^{3+} . It focuses upon neat and doped hexahalide compounds with Ln^{3+} situated at equilibrium sites of octahedral symmetry with the elpasolite structure, M_2ALnX_6 (M⁺, A⁺ are univalent cat-

ions and X⁻ is a halide anion). Ln^{2+} and Ln^{4+} systems; other high symmetry systems such as hexanitritolanthanates(III) [1]; lanthanide ions (Ln^{3+}) at cubic sites in MF₂ (M=Ca, Sr) [2–6] or MCaF₃ [7] crystals where charge compensation is required; as well as lower symmetry elpasolite systems, are mostly not included. This review covers the synthesis, structures, spectra and ET phenomena of lanthanide elpasolites. It is written for chemists so mathematical treatments and details of instrumentation have been omitted but can be consulted from the references.

The aims of the study of the electronic spectra of M₂ALnX₆ systems are to obtain information about the interaction of the vibrational part of the CF with the paramagnetic ion, and to determine the energies and symmetry properties of the vibrational modes. One of the outcomes of the spectral analysis is a CF energy level diagram, which can test theoretical models of lanthanide ion systems. The detailed knowledge of the energy level schemes and of the vibrational properties is then essential for an understanding of the ET phenomena between lanthanide ions. A distant hope remains for the ability to tailor-make materials, aided by CF calculations, which are efficient phosphors, upconverters and solid-state laser materials. The rationale for studying lanthanide elpasolites is that they comprise the most symmetric crystal system available for Ln³⁺, and serve as model systems for our understanding of static and dynamic processes in the solid-state. Although the structural simplicity is manifested by highly degenerate electronic energy levels of Ln³⁺, it is not evident in the electronic spectra and ET phenomena of these systems, which as yet, require more detailed understanding.

2 Synthesis

Meyer [8] reviewed the synthesis and structure of elpasolites in 1982. The preparation of the precursors, the anhydrous lanthanide halides has been reviewed by Taylor [9], Taylor and Carter [10] and Corbett [11, 12]. A versatile solid-state method to the synthesis of LnX₃ (X=Cl, Br, I) is the ammonium chloride route [13, 14]. The phase diagram of the ternary system CsCl-NaCl-LaCl₃ has been investigated by differential thermal analysis and X-ray diffraction and only one congruently melting compound Cs₂NaLaCl₆ was found [15]. The chloroelpasolites Cs₂NaLnCl₆ are conveniently prepared by the dissolution of the appropriate lanthanide oxide in hot, concentrated HCl, followed by the addition of solid CsCl and NaCl, and then evaporation to dryness [16]. The powdered product is hygroscopic and may be converted to the anhydrous form by pumping under vacuum, or with the passage of dry HCl gas, at about 450 °C. The powder is then sealed inside a quartz tube and passed through a Bridgman furnace at the appropriate temperature. The melting points of Cs₂NaLnCl₆ are generally >800 °C. As an alternative prepa-

ration, the stoichiometric quantities of dry LnCl₃, CsCl and NaCl are sealed into a quartz tube, which is passed through the Bridgman furnace [8]. The resulting crystals are deliquescent and should be handled in a dry box, where they can be cut, polished and sealed in resin. Coating the crystal with liquid paraffin oil or vacuum grease affords temporary prevention from moisture attack. Baud et al. [17] have utilized the solid-state reaction of a mixture of constituent chlorides to prepare the series Cs₂KLnCl₆. The series Cs₂LiLnCl₆ have been prepared from the dissolution of CsCl, LiCl (or Li₂CO₃) and the lanthanide oxide in concentrated HCl, and then by the passage of HCl gas for two days at 500 °C over the resulting powder after evaporation [18]. The series Rb₂NaLnCl₆ [19] and Cs₂AgLnCl₆ [20] were prepared similarly. Alternatively, the reaction of CsLu₂Cl₇ with Li in a Ta tube for 19 days at 500 °C gives Cs₂LiLuCl₆ [21]. The solid-state halide method is equally applicable for the synthesis of complex bromides [22] and fluorides [23, 24], provided that the appropriate container and temperature are selected [8]. Bromides are hygroscopic but the fluorides are harder crystals and more stable in air. A lower temperature route to hexafluoroelpasolites is available by the hydrothermal method [25], in which aqueous solutions of the fluorides MF and AF, together with the lanthanide oxide, are heated at about 480 °C and pressures of 100-150 MPa. The fluorides Cs₂ALnF₆ have also been prepared by direct fluorination [26, 27] or hydrofluorination [28] of the corresponding chlorides or oxides. The flux [29, 30] and bifluoride [31] methods which have been employed for d- and p-block hexafluoroelpasolites have not been utilized for the corresponding lanthanide ion complexes. The series Cs₂ALnI₆ (A=Na, Li) was prepared by the solid-state reaction of CsI, AI, Ln metal and I_2 at 300 °C [32].

3 Structure

The structure of the mineral elpasolite, K_2NaAlF_6 (M_2ALnX_6 type, [33]) occupies an intermediate position between perovskite ($MLnX_3$, where Ln=A) and antifluorite (M_2LnX_6 , where there are no A^+ ions) types. The elpasolite system M_2ALnX_6 , where $r(M^+)>r(A^+)$, crystallizes in the face-centred cubic space group *Fm3m* (No. 225). The $4Ln^{3+}$ are located at (a) (0,0,0) at an octahedral (O_h) site in 6-coordination with Cl^- , with the $4A^+$ at (b) ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$), also at an O_h site. The 8M⁺ are situated at (c) ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$) in a simple cubic lattice; and $24X^-$ are at (e) (x00), being shared by Ln^{3+} and A^+ so that the LnX_6 and AX_6 octahedra are interconnected (Fig. 1a–c). The free parameter x depends mostly upon the relation between the A^+ and Ln^{3+} radii and is in the range from 0.225 to 0.275 [28]. The lattice spacing is large (about 1 nm) so that the closest Ln-Ln distance is about 0.7 nm, being much larger than in dimeric systems (e.g. 0.38 nm in $Cs_3Yb_2Br_9$ [34]) where Ln-Ln interactions



Fig. 1a–d Crystal structure of M_2ALnX_6 and coordination environment of Ln^{3+} : **a** packing of ions in the crystal lattice, showing the octahedral coordination of Ln^{3+} and A^+ ; **b** packing along the **c** axis in the **ab** plane; **c** packing in the **ab** plane along the [110] direction at **c**=1/4; **d** rotation of the LnX_6^{3-} octahedra in the distorted phase

have ramifications in the electronic spectra. The local environment of Ln^{3+} in $Cs_2NaLnCl_6$ has been compared with that in $Cs_3Ln_2Cl_9$ [35], since both systems have six Cl^- nearest neighbours at about 0.25 nm distant. However, a further Ln^{3+} ion is the second nearest neighbour in the latter system, but only the fourth nearest in $Cs_2NaLnCl_6$. Figure 2a shows the variation of the lattice parameter, |a|, of the unit cell of Cs_2NaLnX_6 with the 6-coordinate ionic radius (r) of Ln^{3+} . In each case the r=0 intercept differs by no more than 5% from $2r(Na^+)+4r(X^-)$.

The major structural interest concerning elpasolites concerns the wide variety of phase transitions which these systems undergo. Usually the structural distortions are associated either with rotations of the octahedra LnX_6^{3-} to give a tetragonal phase (space group $I4/m-C_{4h}^{5}$), or with a combination of octahedron rotations and M⁺ ion displacements from their equilibrium positions in the tetragonal phase to give a monoclinic phase ($P12_1/n1$) [36]. For the series Cs₂NaLnCl₆, investigations of the cubic to tetragonal phase transition have been carried out by heat capacity measurements [37–39], inelastic neutron scattering [40, 41], electron spin resonance [42, 43], nuclear magnetic resonance [44] and X-ray diffraction [45]. The results show that the early members of the series Cs₂NaLnCl₆ undergo this phase transition at



Fig. 2 a Plot of lattice parameter of Cs_2NaLnX_6 (X=Cl, Br, F) against 6-coordinate ionic radius of Ln^{3+} (data from [8]). **b** Plot of cubic to tetragonal phase transition temperature, T_C , against lattice parameter extrapolated to T_C (data from [8, 37, 41, 43, 50, 60]). The linear regressions in **b** are shown as a guide to the eye

higher temperatures (for example, 207 K for La [43]), but later members are more resistant to it. The Goldschmidt tolerance factor, t, derived from the consideration of hard-packing of spherical ions [8], is successful in identifying the stable range (when t is in the range 0.8 to 1.0) for the cubic structure of MAX₃ compounds from the ionic ratios of the constituent ions. The modified tolerance factor is deduced by the hard sphere packing in the unit cell of M₂ALnX₆, from Fig. 1b,c [24]:

$$t' = \frac{[r(M_{12}^+) + r(X^-)]}{\sqrt{2} \left\{ 0.5 \left[r(A_6^+) + r\left(Ln_6^{3+}\right) \right] + r(X^-) \right\}}$$
(1)

where the subscript denotes the coordination number. Although t' is capable of predicting the stability ranges of M_2ALnF_6 , it fails for the series M_2ALnCl_6 [8]. This is because the polarizability of X⁻ increases by a factor of 4 from F⁻ to Cl⁻ [8], so that the hard sphere model is not applicable. Meyer has provided an alternative classification of the stability ranges of M_2ALnCl_6 in terms of structure field maps, employing differences in molar volumes with respect to a particular compound [8]. A large number of studies using solidstate nuclear magnetic resonance [46] X-ray diffraction [47–50], heat capacity [51] on lanthanide ion systems, as well as electron spin resonance [52, 53], Raman [54, 55], hydrostatic pressure [56] and calorimetric studies [57] on other systems, have concerned the phase transitions of M_2ALnF_6 . Cubic to tetragonal phase transitions for the series Cs₂NaLnBr₆ occur in the range 316 K (Ln=La) to 173 K (Ln=Gd) [58].

The number of formula units per unit cell is unchanged in the initial displacive phase transition, and the space group is reduced to the $I4/m-C_{4h}^{5}$ tetragonal subgroup. The only phonons affected by a transition involving no change in the number of molecules per unit cell are those of infinite wavelength in the cubic structure. The transition is associated with the instability of only one lattice vibration, with all other vibrations showing no changes, and the determination of the particular vibration is discussed by Ihringer [50]. In fact, the τ_{1g} lattice vibration (see Sect. 5) in the low temperature structure effectively collapses at T_c , and is called a soft mode, i.e. the single zone centre mode *i* for which the frequency vanishes at the phase transition temperature, obeying an equation of the type

$$\omega_i^2 = \text{constant} \times (T - T_c) \tag{2}$$

with temperature *T*. This produces a rotation of the LnX_6^{3-} octahedra, by about 5° at 17 K in the case of Rb_2NaHoF_6 [50], and brings four of the 12 X⁻ ions surrounding each M⁺ into contact with it, thereby reducing the unit cell volume by a few percent. The tetragonal domains are long range and randomly oriented in the crystal along the four-fold cubic axes [59], Fig. 1d. The τ_{1g} (O_h) soft mode is inactive in the Raman spectrum of the cubic phase, but is potentially active [$\alpha_g + \epsilon_g(C_{4h})$] in the Raman spectrum below T_c [55].

The $Fm3m \rightarrow I4/m$ transition is second order since it is characterized by discontinuities in the second derivatives of the free energy, such as heat capacity [37]. Figure 2b shows that for some Ln^{3+} , a linear relation exists between T_c and the lattice constant extrapolated to the phase transition temperature. Actually, the T_c =0 intercept from linear regression in Fig. 2b for the Cs₂NaLnCl₆ series is 1070.4 pm, which suggests that these compounds

with smaller unit cells than this value (i.e. $Ln^{3+}=Er^{3+}$, Tm^{3+} , Yb^{3+} , Lu^{3+}) do not undergo the phase transition. However, apparent exceptions to this behaviour are Cs₂NaGdCl₆ [59] (not shown in Fig. 2b), and Cs₂NaTmCl₆ [44] which are stable down to the mK range. Krupski has calculated the phase transition temperatures, and the slopes in Fig. 2b from a rigid sphere model, in which the M⁺ cation sits inside a rhombic dodecahedral cavity of 12 neighbouring X⁻ anions. In the rigid sphere model, the T_C =0 intercept in Fig. 2b represents the case when M⁺ and X⁻ are in mutual contact, i.e.

$$|\mathbf{a}|(T_C = 0) = 2\sqrt{2}[(R(M^+) + R(X^-))]$$
(3)

where *R* is the Pauling 12-fold coordination radius. In agreement with this, from Fig. 2b, the derived sum of the radii of the Cs⁺ and X⁻ ions from the intercepts of the plots of Cs₂NaLnX₆ (X=Cl, Br) are <0.62% greater than the sum of the corresponding 12-coordinate ionic radii.

In some cases, the above cubic to tetragonal transition is followed by other types, such as the $O_h^5 \rightarrow C_{4h}^5 \rightarrow C_{2h}^3 \rightarrow C_{2h}^5$ phase transitions of Cs₂RbDyF₆ [49, 54]. A first-order phase transition, involving a cooperative Jahn-Teller distortion has been reported for Cs₂NaHoCl₆ at low temperature, 150 mK [61].

4 Spectral Selection Rules

The various optical spectra caused by the interaction of electromagnetic radiation with wavevector $|\mathbf{k}_i|=2\pi/\lambda$ with a crystal are governed by corresponding spectral selection rules. The scalar quantity \mathbf{k}_i ranges from 10 to 50,000 cm⁻¹ for infrared to ultraviolet radiation. On the other hand the range of values of $|\mathbf{k}|$ of the crystal lattice (vibration) wave in the first Brillouin zone, i.e. the unit cell of the reciprocal lattice is $[1/|\mathbf{a}|\sim 1/(10^{-7} \text{ cm})]$. The changes in wavevector (or momentum) of the lattice wave which accompany Raman scattering or infrared absorption are thus very small compared to the size of the Brillouin zone. To a first approximation we then have the selection rules \mathbf{k} =0, i.e. only the phonons at the zone centre, or the in-phase motions in all primitive unit cells of the crystal can be involved. The situation corresponds to a lattice wave phonon having infinite wavelength.

The intensity of a spectral transition is calculated from matrix elements involving the initial and final state wavefunctions and the transition operator. This leads to selection rules, as for multielectron atoms, in terms of restrictions upon the values of *S*, *L* and *J* in the transition (Table 1). Considering the selection rules for vibrational spectra, the k=0 phonons of the initial and terminal states transform as Γ_i and Γ_b respectively, of the point group

Table 1 Transformation	properties under	point group O_h of o	perators to	r interaction of radiation with single cryst	als, and related a	selection rules
Type of spectrum	Operator	Irrep(s) in O_h	Ref.	SLJ selection rules ^a	Allowed terminal	states ^b from
					$\Gamma_{ m lg}$ initial state	$\Gamma_{ m 8g}$ initial state
Vibrational infrared	ED	Γ_{4u}	[62]	-	$\Gamma_{4u} \equiv \tau_{1u} (v)$	$\Gamma_{4\mathrm{u}} \equiv \tau_{1\mathrm{u}} (\mathrm{v})$
Vibrational Raman Flectronic Raman	Polarizability Polarizability	$\Gamma_{1g}, \Gamma_{3g}, \Gamma_{5g}$ [$\Gamma, \Gamma, \Gamma_{2}, \Gamma_{2}$]	[62] [63]	- AS=0: AT <2: AI<2:	$\Gamma_{1g} \equiv \alpha_{1g}, \Gamma_{3g} \equiv \epsilon_g,$ $\Gamma, \Gamma, \Gamma,$	$\Gamma_{5g} \equiv au_{2g} (v)$ $\Gamma_{c} \Gamma_{c} \Gamma_{c} (ho)$
	humanana i	$[1 + 1g^2 + 3g^3 + 3g^3]$	[60]		Γ_{4g} (e) Γ_{4g} (e)	• 0g) • /g) • 8g • V
One photon electronic	ED	Γ_{4u}	[64]	$\Delta S=0; \Delta L \leq 1; \Delta f \leq 1; J=0 \leftrightarrow J=0 \text{ and } I=0 \leftrightarrow J=0$	$\Gamma_{4u}^{\delta}(e)$	$\Gamma_{6u}, \Gamma_{7u}, \Gamma_{8u}$ (e)
n ansinon	Induced ED	Mot annlicable	[לא לב]	$r = 0 \rightarrow r = 0$ are rototractic v $c = 0 \rightarrow r = 1 \rightarrow 0 \rightarrow r = 1 \rightarrow 0$	Mot amiliable	Mot amilicable
		in 0. symmetry	[00,40]	△→→∪; △⊥ ∑⊍; △/ ∑⊍; II)=∪ ∪I) =∪, ∧1 -⊃ 1 6. I-∩→I-∩ and I-∩→I-∩	in 0. symmetry	in 0. symmetry
				are forbidden		
	MD	$\Gamma_{4 m g}$	[65]	$\Delta S=0; \Delta L=0; \Delta J \leq 1; J=0 \leftrightarrow J=0 \text{ and }$	Γ_{4g} (e)	$\Gamma_{6g}, \Gamma_{7g}, \Gamma_{8g}$ (e)
		2		$L=0 \leftrightarrow L=0$ are forbidden)	2 2
	EQ	Γ_{3g}, Γ_{5g}	[99]	$\Delta S=0; \Delta L \leq 2; \Delta J \leq 2; J=0 \leftrightarrow J=0 \text{ and}$	$\Gamma_{3g}, \Gamma_{5g}(e)$	$\Gamma_{6g}, \Gamma_{7g}, \Gamma_{8g}$ (e)
				$L=0 \leftrightarrow L=0$ are rordidgen		
	ED Vibronic	$\Gamma_{4\mathrm{u}}$ (see Sect. 7.4)	[67, 68]	$\begin{array}{l} \Delta S=0; \ \Delta J \leq 6; \ \Delta L \leq 6; \ \text{if } J=0 \text{ or } J=0, \ \Delta J =2, \\ 4, \ 6; \ J=0 \leftrightarrow J=0 \text{ and } L=0 \leftrightarrow L=0 \end{array}$	See Table 4	See Table 4
				are forbidden		
One colour TP electronic transition	TP	$[\Gamma_{1g}, \Gamma_{3g}, \Gamma_{5g}]^{s}$	[69–71]	Depends upon approximation order, e.g. $\Delta S=0$; $ \Delta J \leq 2$; $ \Delta L \leq 2$; for	$\Gamma_{1g}, \Gamma_{3g}, \Gamma_{5g}$ (e)	$\Gamma_{6g}, \Gamma_{7g}, \Gamma_{8g}$ (e)
				second-order Axe process (see Sect. 10)		
^a Additional one-electr	on quantum num	ther selection rules	are not inc	luded here, see for example [65]		

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 $^{\rm b}$ v=vibrational, e=electronic state. s from symmetric; as from antisymmetric direct product of $\Gamma_{4\rm u}\times\Gamma_{4\rm u}$

 O_h for elpasolites.¹ The transition operator also transforms according to a particular irrep, Γ_0 , of O_h (Table 1), so that simple group theoretical selection rules may be formulated to identify whether a particular type of transition is potentially allowed or forbidden. Then the point group selection rule for an allowed vibrational transition is

 $\Gamma_i \times \Gamma_f$ contains Γ_o

(4)

Examples are given in lines 1 and 2 of Table 1 for allowed IR and Raman transitions, respectively.

5 Vibrational Spectra

In order to understand the electronic spectra of the lanthanide hexahaloelpasolites, which are mainly vibronic in character, it is essential to have a firm understanding of the vibrational spectra. The vibrations of elpasolites may be classified in terms of the moiety modes $[v_i (i=1 \text{ to } 6)]$ of the LnX₆³⁻ ion [74], or the vibrations $[S_i (i=1 \text{ to } 10)]$ of the (Bravais) unit cell [75, 76], which are all of the k=0 optical vibrations. The Cartesian displacements of these normal vibrations of M₂ALnX₆ are shown in Fig. 3. From Table 1, it is observed that only τ_{1u} modes are IR active, whilst α_{1g} , ϵ_{g} and τ_{2g} modes are Raman active. Several studies have concerned the room temperature IR spectra of Cs₂NaLnCl₆ [77-81], M₂ALnBr₆ [82] and M₂ALnF₆ [83-85]. Raman spectra at temperatures from 300 to 10 K have been reported for Cs₂NaLnCl₆ [86–94], M₂ALnBr₆ [95–96] and M₂ALnF₆ [25, 83, 97, 98]. The room temperature Raman and IR spectra of Cs₂NaYbCl₆ are shown in Fig. 4a,b. The four Raman bands are assigned to the S₅, S₄, S₂ and S₁ modes, in order of increasing energy, whereas the four IR bands correspond to the S₉, S₇, S₈ and S₆ τ_{1u} modes. The spectra of Cs₂NaLnCl₆ (Ln=Nd, La) in [79] show an additional IR band at 215 cm⁻¹, and since it is not present in the spectrum of ref. [78] it is due to another species. The corresponding spectra of Cs₂KYbF₆ are shown in Fig. 4e,f. The vibrational assignments are collected in Table 2. The energy of S_{10} , and of the low temperature ungerade modes are taken from the vibronic spectra, discussed in Sect. 7.4. Polar vibrations can be longitudinal optic (LO) or transverse optic (TO) (with the energy LO>TO), depending upon the direction of the displacement with respect to the phonon wavevector. The TO-LO splittings are not resolved in the room temperature IR spectra, and there has been some discussion in the literature

¹ The O_h point group character table and the O (and O^* double group) multiplication table are given in the Appendix. The irreps are labelled Γ_1 , Γ_2 ... herein [72], corresponding to A₁, A₂.... The subscript *g* or *u* is usually not included in the labelling of 4f^N crystal field states since it is even (odd) for even (odd) N, respectively [73].



Fig. 3 Cartesian symmetry coordinate displacements (not to scale) in the normal vibrations of M_2ALnX_6 . The labelling of nuclei is the same as Fig. 1. (After [75])



Fig. 4a–g Infrared, Raman and vibronic spectra of $Cs_2NaYbCl_6$ (**a**–**d**) and Cs_2KYbF_6 (**e–g**): **a** 300 K IR spectrum; **b** 338 K Raman spectrum; **c**, **d** 20 K absorption spectrum of $({}^{2}F_{7/2})\Gamma_{6}\rightarrow\Gamma_{7}$, $\Gamma_{8}({}^{2}F_{5/2})$, respectively; **e** 300 K IR spectrum, **f** 300 K Raman spectrum, **g** 20 K (${}^{2}F_{7/2})\Gamma_{6}\rightarrow\Gamma_{7}({}^{2}F_{5/2})$ absorption spectrum of Cs_2KYbF_6 . (Adapted from [77, 83, 86, 97])

as to which vibronic features correspond to these modes (see Sects. 6 and 7.4). The tabulated values for τ_{1u} vibrations are averaged over the longitudinal and transverse components.

Normal coordinate analyses of the six LnX_6^{3-} moiety vibrations employing several different force fields have been performed using the **GF** matrix method approach [62], which involves the solution of the matrix equation, for a particular symmetry species of vibration:

$$\mathbf{GFL} = \mathbf{L}\Lambda \tag{5}$$

where the **G** and **F** matrices are the inverse kinetic energy matrix and the potential energy matrix, respectively; the L matrix is composed of eigenvectors of the matrix **GF**, which describe the normal vibrations; and the diagonal Λ matrix contains the eigenvalues, λ_i , which are related to the vibrational wavenumbers, $\bar{\nu}_i$, by

Table 2 Vibration	al energy data (cr	n^{-1}) for M_2A	vLnX ₆ (adap	ted from [76	([
Ln	Unit cell g	roup mode ((S _i , i=1-10)	energy (cm ⁻¹	(1					
	$S_1 (v_1) \alpha_{1g}$	$S_2 (v_2) \epsilon_g$	$S_3(-)\tau_{1g}$	$S_4 (v_5) \tau_{2g}$	$S_5(-)\tau_{2g}$	$S_6 (v_3) \tau_{1u}$	$S_7 (\nu_4) \tau_{1u}$	$S_8(-)\tau_{1u}$	$S_9(-)\tau_{1u}$	$S_{10} (v_6) \tau_{2u}$
	Cs ₂ NaLnC	l ₆ at 120-10	K, except ^a a	t 300 K; ^b [99						
La ^a	274	218		111	42					
Ce	279	222	ı	112	46	257	106	ı	I	75
Pr	282	220	16^{b}	114	46	255	105	173	59	77
calc. 1	282	221	,	112		255	105	ı	ı	79
calc. 2	288	226	21	124	48	262	115	165	55	85
Nd	285	228	20	116	46	258	107	177	53^{a}	78
Sm	287	230	ı	118	45	264	107	180	ı	80
Eu	290	228	(21)	118	47	260	105	176	(58)	79
calc. 2	295	231	20	126	47	266	116	165	53	86
Gd	290	232		118	45	270	109	175		82
Tb	292	233		123	45	268	111	182	56	82
Dy	295	235		124	45	266	111	181		80
Но	297	239		127	47	267	114	176	61	83
Er	297	236	(21)	126	47	268	116	182	62	86
calc. 2	295	233	21	132	49	263	126	173	56	88
Tm	297	237	228^{a}	127	47	268	118	182	63	88
Yb	296		'	128	48	266	119	181		89
Ya	284	223	,	128	47	270		,		
calc. 3	296	240	39i	138	40	315 TO	137 TO	185 TO	45 TO	47
						360 LO	165 LO	211 LO	75 LO	
	Cs ₂ LiLnCl ₆	6 at 300 K, e2	scept ^a 20 K;	^b 85 K						
Pr			' '		48^{a}	262^{a}	111^{a}	219^{a}	59^{a}	89^{a}
Eu	288^{b}	212^{b}	(20)	132^{b}	(50)	263^{a}	119^{a}	(215)	(66)	95^a
calc. 1	288	211		138	ı	263	119			97
calc. 2	274	194	20	145	57	293	105	178	59	101
Er	285	219		140	52	261^{b}	124^{b}	209^{b}		102^{b}
Yb	288	ı	ı	144	56	259^{a}	129^{a}	215 ^a	,	109^{a}

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Ln	Unit cell gr	oup mode (S _i , i=1-10) (energy (cm ⁻¹	(1					
	$S_1 (v_1) \alpha_{1g}$	$S_2 (v_2) \epsilon_g$	$S_3(-)\tau_{1g}$	$S_4 (v_5) \tau_{2g}$	$S_5(-)\tau_{2g}$	$S_6 (v_3) \tau_{1u}$	$S_7(v_4)\tau_{1u}$	$S_8(-)\tau_{1u}$	$S_9(-)\tau_{1u}$	$S_{10} (v_6) \tau_{2u}$
Tm	289	220		146						1
M,A,Ln,X	M2ALnX ₆ a	und M2AYX ₆	Ln^{3+} at 300	K, except wł	here stated;	^a 20 K; ^b 85 K				
Cs,Na,Pr,Br	175	139	(15)	79	32^{a}	183^{a}	72 ^a	150^{a}	44^{a}	56^{a}
calc. 1	175	139	ı	79	ı	174	72	ı	I	56
calc. 2	178	143	13	76	35	197	72	135	39	50
Cs,Na,Nd,Br	174	137		74	38			1	I	ı
Cs,Na,Gd,Br	178	140		77	39			1	I	ı
Cs,Na,Tm,Br			15	ı	38^{b}	181^{b}	79 ^b	156^{b}	50^{b*}	55^{b}
Cs,Na,Ho,Br				ı	ı	178^{a}	80^{a}	154^{a}	ı	55^{a}
Cs,Na,Yb,Br	178	134	ı	84	43	180	94	150	I	53
Cs,Na,Y,Br	182	142	,	81	42	ı		ı	ı	ı
Cs,Na,La,Br	170	134		71	38	ı			ı	ı
Cs,Li,Tm,Br	185	140		98*		ı			ı	
Cs,Li,Tm,I	127	100		70*	ı				ı	
M,A,Ln	neat M ₂ AL	nF ₆ and M ₂	AYF ₆ :Ln ³⁺ at	: 300 K; ^a 120-	-10 K					
Cs,K,Pr	456^{a}	352^{a}	(50)	174 ^a	53^{a}	(370)	(137)	(170)	72 ^a	98^{a}
calc. 1	456	342	ı	152	ı	372	150	ı	I	108
calc. 2	457	355	49	172	52	376	154	201	63	16
Cs,K,Y:Eu				ı		372 ^a	139^{a}	174^{a}	ı	99^{a}
Cs,K,Gd	473	380		185		372	140	165	72	
Cs,K,Yb	490^{a}	370		195	54^{a}	413^{a}	153^{a}	174^{a}	72^{a}	115 ^a
Cs,K,La	443	334	,	ı	ı	357	130	170	65	ı
Cs,K,Y	476	382	,	194	ı	412	160	200	75	ı
calc. 4	363	270	ı	178	ı	305	190	ı	I	96
Rb,K,Y	470	,		210	60				ı	
Cs,Na,Tm	473	373	(50)	203	65 ^{a+}	401^{a}	173 ^a	249^{a}	92 ^{a+}	137 ^a
calc. 2	468	362	49	218	68	397	178	238	79	134
Cs,Na,Y:Eu	ı	ı		ı	65 ^a	373^{a}	162 ^a	252^{a}	55 ^{a+}	123 ^a

Table 2 (continued)										
Ln	Unit cell gr	roup mode	(S _i , i=1-10)	energy (cm ⁻	-1)					
	$S_1 (\nu_1) \alpha_{1g}$	$S_2 (v_2) \epsilon_g$	$S_3(-)\tau_{1g}$	$S_4 (v_5) \tau_{2g}$	$S_5(-)\tau_{2g}$	$S_6 (v_3) \tau_{1u}$	$S_7 (\nu_4) \tau_{1u}$	$S_8(-)\tau_{1u}$	$S_9(-)\tau_{1u}$	$S_{10} (v_6) \tau_{2u}$
Cs,Na,Y	467	363		200	69					ı
Cs,Na,Tb	468	362		194	69	ı		ı		ı
Rb,Na,Eu	ı	,	ı	ı	,	388	150	140^{*}	72	110
Rb,Na,Ho	498^{a}	396^{a}	50	205^{a}	75 ^a			ı		ı
Rb,Na,Tm	500	404	(20)	210	76	420	161	222	87	125
calc. 2	500	402	50	213	76	423	158	227	84	124
Values in parenthe tain experimental those given here; α dynamics calculati using the SBKJ pse	ses were assum- data. <i>calc</i> . 1 is <i>alc</i> . 2 is a 9-pari on [100]. TO tr udopotentials a	ed for the f a 5-parame ameter uni ransverse o ind extende	itting calcu eter Genera t cell group ptic mode; ed one-elect	lation. The c l Valence Fc calculation LO longituc ron basis sei	calculated v prce-Field employing final optic ts [101]	alues (<i>calc</i>), [74]. Some c a modified mode. i imé	of the fitted to General Vale aginary. <i>calc</i>	nearest inte frequencies nce Force-F 4 for YF ₆ ³	gers, are in i are slightly ield [76]; <i>cal</i> is at MP2 1	different from c. 3 is a lattice evel of theory

	120–10 k Cs ₂ NaPr	Cl ₆	120–10 I Cs ₂ NaPr	K Br ₆	120–20 l Cs ₂ LiEu	K Cl ₆	300 K Cs ₂ KPrF	36
	calc. 1	calc. 2	<i>calc</i> . 1	calc. 2	<i>calc</i> . 1	calc. 2	<i>calc</i> . 1	calc. 2
$egin{array}{c} K_1 \ K_2 \ k_1 \ H_1 \end{array}$	109.1 - 10.7 6.7	68.0 29.3 10.9 5.8	96.9 - 8.9 6.9	60.3 21.1 8.7 5.4	101.9 - 13.4 10.1	59.6 20.9 13.1 9.3	142.3 - 17.0 7.8	92.9 38.5 15.4 4.8

Table 3 Comparison of selected force constants (N $m^{-1})$ from the vibrational datafits to M_2ALnX_6

calc. 1 is a 5-parameter General Valence Force-Field [74]. Some of the fitted frequencies are slightly different from those given here; *calc.* 2 is a 9-parameter unit cell group calculation employing a modified General Valence Force-Field [76].

$$\lambda_i = (2\pi c \bar{\nu}_i)^2 \tag{6}$$

Tabulations have been given of the relevant **G** and **F** matrix elements [74, 76]. Some results from the General Valence Force Field (*calc.* 1) are compared with experimental observations in Table 2. The principal bond stretching (K_1) and bending (H_1) force constants both increase across the series of Cs₂NaLnCl₆ from Ce to Yb, and in Cs₂ALnX₆ from X=Br<Cl<F. Members of the series Cs₂LiLnCl₆ have higher values of H_1 (but lower values of K_1) for LnCl₆³⁻ than the corresponding ones in Cs₂NaLnCl₆, due to the constraint of the Cl⁻ nuclei by the polarizing Li⁺ cation. The self-consistent field (SCF) model, with refinements such as the inclusion of electron correlation effects at the second-order Møller-Plesset (MP2) level of theory, has also been employed for the calculation of vibrational frequencies of hexafluoroel-pasolites [101]. *Calc.* 4 in Table 2 lists these calculated frequencies for YF₆³⁻.

A more complete analysis of the vibrational spectra includes all of the unit cell vibrations, and some typical results (*calc.* 2) are included in Table 2. The fitted values of K_1 are only about 60% of those when considering the LnX_6^{3-} moiety alone, and also the X-Ln-X bending force constants are also slightly smaller (Table 3). The magnitudes of the Ln-X (*cis*-) bond-bond stretching interaction force constant (k_1) are generally similar in both analyses, being about 9–16% of the values of K_1 for Cs₂NaLnX₆ (X=Cl, Br), but rather greater for Cs₂LiLnX₆. The unit cell group analysis serves to show the importance of the mixing of the symmetry coordinates of internal and external vibrations. This is most noticeable for the four τ_{1u} modes, especially for S₇ and S₈ in hexafluoroelpasolites [76].

6 Lattice Dynamics

The unit cell group description of the normal modes of vibration within a unit cell, many of which are degenerate, given above is adequate for the interpretation of IR or Raman spectra. The complete interpretation of vibronic spectra or neutron inelastic scattering data requires a more generalized type of analysis that can handle 30N (*N*=number of unit cells) normal modes of the crystal. The vibrations, resulting from interactions between different unit cells, correspond to running lattice waves, in which the motions of the elementary unit cells may not be in phase, if $\mathbf{k} \neq 0$. Vibrational wavefunctions of the crystal at vector position ($\mathbf{r}+\mathbf{t}_n$) are described by Bloch wavefunctions of the form [102]

$$\Psi_{\mathbf{k}}^{\prime}(\mathbf{r}+\mathbf{t}_{\mathbf{n}}) = \exp\left(i\mathbf{k}\cdot\mathbf{t}_{\mathbf{n}}\right)\Psi_{\mathbf{k}}^{\prime}(\mathbf{r}) \tag{7}$$

where t_n is a general crystal lattice translation vector, and the wavevector k also describes the phase relationship between the Bravais cells, in addition to designating the lattice wave modes related to it. Due to the translational symmetry of the crystal, it is sufficient to consider all of the k within the first Brillouin zone of the reciprocal lattice. This is shown for the case of a cubic crystal in Fig. 5, in which the high-symmetry points Γ , Λ , L... are la-



Fig. 5 Two unit cells of the reciprocal lattice for the face-centred cubic lattice of Cs₂NaYCl₆, showing major symmetry points and directions (from [100] with permission)

belled. The unit cell group model thus refers to optical phonons of infinite wavelength, k=0, where the exponential factor becomes unity. When we carry out the crystallographic point-group, G_0 , operations on a k vector we generate the star of k. For a general k vector, the star has h wings (where *h*=point group G_0 order). The star has fewer wings if the k vector lies along a symmetry line or plane (since some of the symmetry operations then leave it unchanged), or if the k vector touches the zone boundary (some of the G_0 operators produce a k related to the original one by a reciprocal lattice vector, so that they are equivalent). The operations which leave \mathbf{k} invariant or equivalent comprise a subgroup P_k of the entire point group G_0 . All of the elementary operators related to elements of the point group $P_{\mathbf{k}}$ combined with the translation subgroup T_1 of the space group S describing all the symmetry of the crystal structure, give a subgroup S_k of the group S, called the group of the wave vector **k**. Under this group $S_{\mathbf{k}}$, some wave functions of $\Psi_{\mathbf{k}}^{i}$ (or other physical quantities) transform among themselves according to an irrep Γ of the group of **k**. This irrep Γ of the group S_k is also called a *small* representation of the space group S.

The appropriate symmetry group for the analysis of Fm3m crystal vibrational normal coordinates is the k group [102]. At k=0, all point-group $(G_0=O_h)$ operations leave this point invariant so that we can use the O_h point group operations. For a nonzero k-vector along the k_x-axis in reciprocal space (i.e. at the point Δ , Fig. 5) the symmetry is reduced to C_{4v} , and the symmetries $\Delta_1+\Delta_5$ (i.e. A_1+E) are compatible, for example, with the symmetry Γ_{4u} (T_{1u}) of the group O_h at k=0. Other compatibility relations exist for other special points in the reciprocal lattice, so that the symmetry is reduced from O_h at k=0 (Γ point) to C_{2v} at Σ , C_{3v} at Λ , D_{4h} at X, for example. The consideration of the crystal, rather than the unit cell, vibrations thus produces splittings of degeneracies of phonon modes, and the vibration frequency depends upon the irrep Γ corresponding to different points k of the reciprocal lattice. These phenomena are represented in dispersion curves by plotting the vibration frequency as a function of k in the first Brillouin zone (i.e. $-\pi/a \le k \le \pi/a$).

The lattice dynamics of several halogenoelpasolites has been modelled to include both short (nearest-neighbour) and long-range (electrostatic, due to ionic charges) interactions between rigid (unpolarizable) ions [100]. The results for Cs₂NaYCl₆ are shown in Fig. 6. Since the diagram is rather complicated, the irreps of modes at the point Γ are given, together with the energies, in Table 2, *calc.* 3. There are three gaps in the phonon density of states, roughly between 236–239, 274–284 and 297–309 cm⁻¹. The S₃ τ_{1g} mode is shown as an imaginary (negative) frequency. The τ_{1u} transverse (lower energy) and longitudinal (higher energy) acoustic phonons have energy 0 cm⁻¹ at the Γ point (the three acoustic phonons with **k**=0 correspond to in-phase translation of all unit cells, and therefore to translation of the crystal), but



Fig. 6 Calculated phonon dispersion curves for Cs₂NaYCl₆, with the irreps of vibrational modes denoted by line styles: short dashed lines Δ_1 , Z_1 , Σ_1 , Λ_1 ; dotted lines Δ_2 , Z_2 , Σ_2 , Λ_2 ; long dashed lines Δ_3 , Z_3 , Σ_3 ; dotted dashed lines Δ_4 , Z_4 , Σ_4 ; continuous lines Δ_5 , Σ_3 . (from [100] with permission)

show considerable dispersion for nonzero k in Cs₂NaYCl₆. The phonon dispersion curve region below 100 cm⁻¹ is very complex (Fig. 6). At highest energy, although the TO branch of S₆ (τ_{1u}) is fairly flat, the S₆ LO branch shows considerably more dispersion. We infer that the density of states per unit frequency interval for the TO mode is greater than for the LO mode, so that the spectral peak should be sharper. The calculated dispersion curves from [100] show some qualitative similarities to the dispersion curves for Cs₂UBr₆ [103], K₂ReCl₆ [104] and K₂NaAlF₆ [105]. The quantitative description of normal modes at the Γ point can be assessed from Table 2, *calc.* 3, by comparison with experimental data. Notably, the calculated energies of several modes (S₆, S₇) are rather high, and the S₁(α_{1g}) mode is calculated to be at higher energy than S₆(τ_{1u}). The energy of S₁₀(τ_{2u}) is too low. The calculated TO-LO splittings of τ_{1u} modes are rather large (e.g. 45 cm⁻¹ and 30 cm⁻¹ for S₆ and S₉, respectively), which arises from setting the ionic charges to those of the free ions.

The experimental investigation of the phonon dispersion curves of elpasolites has been rather limited, partly because features due to electronic inelastic scattering of neutrons occur with greater intensity than phonon peaks. The energy of the S₃ mode has been determined from neutron inelastic scattering data [40, 48]. The Γ -point minimum becomes more distinct in the dispersion relation of this mode as the temperature is lowered [40]. Bührer and Güdel [106] have measured and calculated the phonon dispersion curve for this Γ-point mode in Cs₂NaTmBr₆ along the Δ-direction, where it splits into an almost dispersionless (and unique) Δ_2 mode, and a doubly-degenerate (originally transverse rotatory mode) Δ_3 mode with strong dispersion. The energy spectra of neutrons scattered from Cs₂NaLa-Cl₆ at 8 K showed only one identifiable phonon peak at ca. 230 cm⁻¹, which corresponds to the S₂ mode [107]. Three peaks at ca. 48, 145 and 306 cm⁻¹ were attributed to phonon scattering in the inelastic neutron scattering spectrum of Cs₂NaLnBr₆ [60]. The first two of these features presumably correspond to S₅ and S₂, but assignment of the highest energy band is obscure. The measured phonon dispersion curves of Cs₂NaBiCl₆ along the directions Δ , Σ and Λ [108] are in qualitative agreement with Fig. 6.

7 One-photon 4f^N-4f^N Electronic Spectra

7.1 Electronic Hamiltonian and States of 4f^N Systems

The electronic states of rare earth ions in crystals are N-body localized states, since the N electrons of $4f^N$ are coupled strongly, and move around the corresponding ion core without extending far away. The semiempirical calculations for the $4f^N$ energy level systems employ a parametrized Hamiltonian H under the appropriate site symmetry for Ln^{3+} :

$$\mathbf{H} = \mathbf{H}_{AT} + \mathbf{H}_{CF} + \mathbf{H}_{ADD} \tag{8}$$

where H_{AT} comprises the atomic Hamiltonian, which includes all interactions which are spherically symmetric; H_{CF} is the operator comprising the nonspherically symmetric CF; H_{ADD} contains other interactions. The atomic Hamiltonian is expressed:

$$H_{AT} = E_{AV} + \sum_{k} F^{k} \mathbf{f}_{k} + \sum_{i} \zeta_{f} \mathbf{s}_{i} \cdot \mathbf{l}_{i} + \alpha \mathbf{L}(\mathbf{L}+1) + \beta \mathbf{G}(G_{2}) + \gamma \mathbf{G}(R_{7})$$
$$+ \sum_{s} T^{s} \mathbf{t}_{s} + \sum_{k} P^{k} \mathbf{p}_{k} + \sum_{j} M^{j} \mathbf{m}_{j}$$
(9)

where k=2,4,6; s=2,3,4,6,7,8; j=0,2,4. The first term E_{AV} (containing F^0) adjusts the configuration barycentre energy with respect to other configurations. The Slater parameters F^k represent the electron-electron repulsion interactions and are two-electron radial integrals, where the f_k represent the angular operator part of the interaction. The spin orbit magnetic coupling constant, ζ_{f_2} controls the interaction and the mixing of states from different *SL* terms with the same *J* manifold. These two parameters are the most im-

portant in determining the atomic energies. Note that the terms $\sum_{i=1}^{N} e_{4f}(i) =$

 Ne_{4f} involving the kinetic energy of the electrons and their nuclear attraction do not give rise to a splitting of the $4f^{N}$ levels and are contained in E_{AV} . The two-body configuration interaction parameters α , β , γ parametrize the second-order Coulomb interactions with higher configurations of the same parity. For f^{N} and f^{14-N} , N>2 the three body parameters T^{s} are employed to represent Coulomb interactions with configurations that differ by only one electron from f^{N} . With the inclusion of these parameters, the free ion energy levels can usually be fitted to within 100 cm⁻¹. The magnetic parameters M^{j} describe the spin-spin and spin-other orbit interactions between electrons, and the electrostatically correlated spin-orbit interaction. Usually the ratios $M^{0}:M^{2}:M^{4}$ and those of $P^{2}:P^{4}:P^{6}$ are constrained to minimize the number of parameters, which otherwise already total 20.

The H_{CF} operator represents the nonspherically symmetric components of the one-electron CF interactions, i.e. the perturbation of the $Ln^{3+} 4f^N$ electron system by all the other ions. The states arising from the $4f^N$ configuration are well-shielded from the oscillating crystalline field (so that spectral lines are sharp) but a static field penetrates the ion and produces a Stark splitting of energy levels. The general form of the CF Hamiltonian H_{CF} is given by

where the B_q^k are parameters and the $C_q^k(i)$ are tensor operators related to the spherical harmonics, see Eq. (19c); and the sum on *i* is over all electrons of the 4f^N configuration. Since the Hamiltonian is a totally symmetric operator, for the case of O_h site symmetry, only those values of *k* whose angular momentum irreps contain Γ_{1g} give nonzero B_q^k , i.e. k=4 and 6. The nonzero CF parameters for the O_h group reduce to $B_0^4, B_4^4, B_0^6, B_4^6$. The unit tensor normalized CF parameters $B_q^{(k)}$ (used by Richardson) are related to the spherical tensor CF parameters B_q^k (used by Wybourne) by

$$B_q^{(k)} = B_q^k \langle f || C^{(k)} || f \rangle = B_q^k (-7) \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$
(11)

so that $B_0^{(4)} = 1.128B_0^4$, and $B_0^{(6)} = -1.277B_0^6$. However, the B_4^k parameters are related to B_0^k , and in the Wybourne spherical tensorial notation [64] adopted herein, and in the cubic environment, $B_4^4 = B_0^4 (5/14)^{1/2}$ and $B_4^6 = -B_0^6 (7/2)^{1/2}$. Thus only 2 additional parameters are required to model the CF splittings of *J* terms by the octahedral CF, and this presents a more severe test for theory than for low symmetry systems where up to 27 parameters may be employed.

The labelling of electronic states of the rare earth ions in a CF differs from that of the transition elements with outer d-electrons where the CF is much larger. For the lanthanide ions, the spin-orbit interaction is larger than the CF acting upon Ln^{3+} . The comparison is misleading from the inspection of the relevant parameters, since ζ_f has the magnitude from 623 to 2903 cm⁻¹ for Ce³⁺ to Yb³⁺ in M₂ALnCl₆, whereas the largest of the CF parameters, B_0^4 , ranges from 2119 to 1471 cm⁻¹ in the same series [72]. However, the comparison is actually made by looking at the splitting of states, since the CF splitting is up to several hundred cm⁻¹ for these ions, whereas spin-orbit interaction produces a splitting of many thousands of cm⁻¹. Therefore we consider basis state wavefunctions of free ions first, which in the [*SL*] coupling scheme of the f^N electron system are written as combinations of $|\alpha'S'L'JM\rangle$ states:

$$\left| \mathbf{f}^{\mathrm{N}} \boldsymbol{\psi} J \boldsymbol{M} \right\rangle = \sum_{\boldsymbol{\alpha}' S' L'} C_{\boldsymbol{\psi}}(\boldsymbol{\alpha}' S' L') \left| \mathbf{f}^{\mathrm{N}} \boldsymbol{\alpha}' S' L' J \boldsymbol{M} \right\rangle \tag{12}$$

where $C_{\psi}(\alpha' S'L')$ are the intermediate coupling coefficients and α' represents extra quantum numbers that are necessary to describe the state completely. The state is usually specified by the symbol $\psi = [\alpha SL]$ since the term αSL makes the largest contribution to the eigenvector, and only *J* and *M* are good quantum numbers. The basis for the CF wavefunction for the irrep $\Gamma \gamma$ is expressed as linear combinations of $|JM\rangle$ kets:

$$\left| \mathbf{f}^{\mathrm{N}} \boldsymbol{\psi} J \boldsymbol{\Gamma} \boldsymbol{\gamma} \right\rangle = \sum_{M'} S_{J \boldsymbol{\Gamma} \boldsymbol{\gamma}} \left(M' \right) \left| \mathbf{f}^{\mathrm{N}} \boldsymbol{\psi} J M' \right\rangle \tag{13}$$

where the coefficients $S_{J\Gamma\gamma}(M')$ are given for example, in Table A19 of [68]. Several J' terms, with different $\psi'J'$ values but which correspond to the same symmetry irrep of the CF point group, can mix under the influence of the CF Hamiltonian as follows:

$$\left|\mathbf{f}^{\mathrm{N}}[\boldsymbol{\psi}J]\boldsymbol{\Gamma}\boldsymbol{\gamma}\right\rangle = \sum_{\boldsymbol{\psi}'J'} D_{\boldsymbol{\psi}'J'} \left|\mathbf{f}^{\mathrm{N}}\boldsymbol{\psi}'J'\boldsymbol{\Gamma}\boldsymbol{\gamma}\right\rangle \tag{14}$$

Taking $|f^N \alpha SLJM\rangle$ as matrix bases, and diagonalizing the Hamiltonian H in Eq. (8) to fit the experimental electronic energy levels, the values of the parameters in Eqs. (9) and (10), and of the mixing coefficients in Eqs. (12)–

(14) can be determined. Prof. M. Reid has written a suite of computer programs for this type of fitting.

7.2 Zero Phonon Lines and Vibronic Sideband

The energy levels of *SLJ*-multiplets of f^{N} configurations are depicted in many texts concerning lanthanide ions, in the form of Dieke diagrams. The intraconfigurational electronic spectra of Ln^{3+} comprise sharp lines, since the ion is shielded from external fluctuating electric fields by the full outer-shell electrons $5s^{2}5p^{6}$. The transition intensity between states *i* and *f* is measured independently of concentration by the oscillator strength [109], which for a cubic elpasolite crystal is given by [97]

$$P_{if} = 6.50 \times 10^{-19} \frac{a^3}{b} \int A(\bar{\nu}) d\bar{\nu}$$
 (15)

where a is the magnitude of the lattice parameter in pm, *b* is the crystal thickness in cm, and the integral is over absorbance $A(\bar{v})$ with respect to the energy in wavenumbers. For simplicity, in this equation and in the following, we assume that unpolarized radiation is incident upon an isotropic crystal. The measured oscillator strength of a ZPL (although more often, relative values are employed with respect to a certain transition) may be compared with the calculated value in order to confirm the assignment of a particular electronic transition. The oscillator strength of the transition may be defined with respect to the matrix element of the transition multipole moment, and is approximately given by [68]

$$P_{if} = \frac{8\pi^2 m \bar{\nu}_{if} c}{3hg_i} \left| M_{if} \right|^2 \tag{16}$$

where *m* is the electron mass, \bar{v}_{if} is the transition energy in cm⁻¹ and *c* is the velocity of light in cm s⁻¹. g_i is the degeneracy of the initial state, and this is frequently omitted from the definition, but (as well as η below), taken into account when comparing calculation and experiment [65]. In general the matrix element $|M_{if}|$ refers to vibronic states, which may be factored out by the Herzberg-Teller expansion [110, 111]:

$$|\mathbf{M}_{if}| = \langle \psi_f | \mathbf{M}_e | \psi_i \rangle \langle \chi_{fk} | \chi_{in} \rangle + \sum_{m} (\langle \psi_f | \mathbf{M}_e | \psi_m \rangle \langle \chi_{fk} | c_{mi} | \chi_{in} \rangle + \langle \psi_m | \mathbf{M}_e | \psi_i \rangle \langle \chi_{fk} | c_{mf}^* | \chi_{in}^* \rangle)$$
(17)

where ψ_f , ψ_i and ψ_m refer to final, initial and intermediate electronic state wave functions, and M_e contains the sum over f electrons only. The vibrational wave functions χ refer to *n* or *k* quanta and depend upon the nuclear

coordinates. One of the coefficients, c_{mi} , for a particular normal mode of vibration, Q_{ν} , is given by

$$c_{mi} = \frac{\langle \Psi_m | (\partial H / \partial Q_\nu)_{Q_0} Q_\nu | \Psi_i \rangle}{-(E_m - E_i)} = -\Delta E_{mi}^{-1} \langle \Psi_m | (\partial H / \partial Q_\nu)_{Q_0} Q_\nu | \Psi_i \rangle$$
(18)

where $(\partial H/\partial Q_{\nu})_{Q_0}$ is the change in potential energy with nuclear displacement, evaluated at the equilibrium nuclear geometry. The introduction of the phonon normal coordinate Q_{ν} leads to a change in phonon number between the initial and final electronic states.

When the first term is nonzero the electronic transition is allowed by a particular mechanism, whereas it is forbidden when zero. It contributes mainly zero phonon line intensity when the shift in equilibrium positions of the nuclei between the two states can be ignored, so that $\langle \chi_{fk} | \chi_{in} \rangle \neq 0$ only for the k=n case in Eq. (17). The second and third terms contribute mainly one-phonon sideband vibronic intensity to the transition. $|\langle \psi_f | M_e | \psi_i \rangle|^2$ is given by [68]

$$\begin{aligned} |\langle \psi_f | \mathbf{M}_e | \psi_i \rangle|^2 &= \left\{ \eta \sum_q |\langle \psi_f | \mathbf{D}_q^{(1)} | \psi_i \rangle|^2 + \eta' a \sum_q |\langle \psi_f | \mathbf{m}_q | \psi_i \rangle|^2 \\ &+ \eta'' b \sum_q |\langle \psi_f | \mathbf{D}_q^{(2)} | \psi_i \rangle|^2 \right\} \end{aligned}$$
(19a)

where the spherical tensor

$$\mathbf{D}_{q}^{(k)} = \sum_{i} r_{i}^{k} \mathbf{C}_{q}^{(k)}(\boldsymbol{\theta}_{i}, \boldsymbol{\phi}_{i}) \tag{19b}$$

 m_q is the magnetic dipole operator and

$$C_{q}^{(k)}(\theta_{i},\phi_{i}) = \sqrt{\frac{4\pi}{2k+1}} Y_{q}^{(k)}(\theta_{i},\phi_{i})$$
(19c)

where $Y_q^{(k)}$ is a spherical harmonic function of rank k. In Eq. (19a), a and b are constants expressed in terms of fundamental constants [68].

The three terms in brackets represent contributions from ED, MD and EQ transitions, respectively, and the matrix elements in terms of reduced matrix elements, 3-j and 6-j symbols are given elsewhere for MD [65, 112] and EQ [113, 114] transitions. The dimensionless factors η , η' , η'' [115] in Eq. (19a) correct the vacuum linestrengths to those appropriate for the crystal, by correcting the polarizability of the medium and/or the density of radiative modes. The ZPL (i.e. electronic origin) of a transition refers to the 0-0' transition, i.e. from the v=0 vibrational level of one state to the v'=0 level of the other in the case of absorption.

The selection rules of angular momenta S, L, J for the above transitions are listed in Table 1. The point group selection rule for an allowed transition

(in addition to the *S*, *L* and *J* etc., selection rules) is the same as Eq. (4). Examples are given in Table 1 for allowed transitions: of an even-electron f^N system, to terminal states from a nondegenerate Γ_{1g} initial state (column 6); and of an odd-electron f^N system (where the O^* double group is used [73]) from a Γ_{8g} initial state (column 7). The mechanism for the three types of transition in M₂ALnX₆ is shown schematically by the operator M_e in Fig. 7a, but it is noted that the ED process is forbidden due to the selection rule (Eq. 4), since Γ_0 corresponds to Γ_{4u} (Table 1) and Γ_i , Γ_f have the same parity for f-electron states.

More generally, it has been noted [116] that the oscillator strengths for fully allowed ED:MD:EQ transitions are in the approximate ratio of $1:10^{-5}:10^{-6}$, respectively. However, ED transitions are parity forbidden in the case of f-f intraconfigurational transitions, so that the mechanism which enables such transitions for rare earth ions is via crystal-field mixing of f^N wave functions with opposite parity wave functions such as $f^{N-1}d$ due to the odd terms $H'_{CF} = \sum_{i,t,p} B^t_p C^t_p(i)$ with t=1,3,5,7 (which are usually ignored when calculating energies) of the CF when the ion is situated at a noncentrosym-

calculating energies) of the CF when the ion is situated at a noncentrosymmetric site. Following Judd [117], this type of transition is called induced (forced) electric dipole in Table 1. The f^N wave function then becomes

$$\psi_i = |\mathbf{f}^{N}\psi_i\rangle + \sum_m c_{mi}|\mathbf{f}^{N-1}\mathbf{d}\psi_m^i\rangle \tag{20}$$

where

$$c_{mi} = \langle \psi_m^i | \mathcal{H}_{CF}^{'} | \psi_i \rangle / (E_i - E_m)$$
⁽²¹⁾

The mechanism is shown schematically in Fig. 7b, corresponding to the product of matrix elements of the type

$$\Delta E_{im}^{-1} \langle \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{f} | \mathbf{D}^{(1)} | \boldsymbol{\psi}_{m}^{i} \rangle \langle \boldsymbol{\psi}_{m}^{i} | \mathbf{H}_{CF}^{'} | \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{i} \rangle \tag{22}$$

where ψ_i and ψ_f denote the initial and final f^N states of the intraconfigurational transition, ψ_m^i denotes an opposite-parity state, and H'_{CF} is the CF operator connecting this state to the f^N state.

When the CF is centrosymmetric, as for Ln^{3+} in elpasolites, it is not $\text{H}_{CF}^{'}$ itself, but its increment $\sum_{\nu} \left(\frac{\partial \text{H}_{CF}^{'}}{\partial Q_{\nu}}\right)_{Q_{0}} Q_{\nu}$ caused by the odd-parity vibration Q_{ν} which introduces non-zero c_{mi} , and therefore induces an EDV transition.

Based upon an approximate assumption that all the energies E_m lie within a definite intermediate configuration, $4f^{N-1}5d$ for example, Judd [117] completed the summation over m, with closure over the operators $D^{(1)}$ and H'_{CF} to give the following formula:





















(ii)











$$\langle \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{f} J_{f} M_{f} | \mathbf{D}_{q}^{(1)} | \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{i} J_{i} M_{i} \rangle = \sum_{\lambda} \langle \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{f} J_{f} M_{f} | \mathbf{U}_{p+q}^{(\lambda)} | \mathbf{f}^{\mathbf{N}} \boldsymbol{\psi}_{i} J_{i} M_{i} \rangle$$
$$\times \left[\sum_{tp} (-1)^{p+q} [\lambda] \begin{pmatrix} 1 & \lambda & t \\ q & -(p+q) & p \end{pmatrix} A_{p}^{t} \Xi(t,\lambda) \right]$$
(23)

in which $\Xi(t,\lambda)$, $\lambda=2,4,6$) is a summation over intermediate configurations involving $\langle 4f||rC^{(1)}||5d\rangle\langle 5d||r^tC^t||5d\rangle$ etc., and average energies of these configurations; and $A_p^t = B_p^t/\langle 4f|r^t|4f\rangle$. Actually, Eq. (23) (which is the same as Eq. (133) given with detailed explanation in [65]) usually serves as a parametrization formula in which the $A_{tp}^{\lambda} = A_p^t \Xi(t,\lambda)$ are experimentally-fitted intensity parameters, since matrix elements of the unit tensor operators $U_{p+q}^{(\lambda)}$ can be calculated from [121], whilst the coefficients $C_{\psi}(\alpha'S'L')$ and $D_{\psi'I'}$ in Eqs. (12)–(14) for the initial and final CF states can be obtained from the CF fitting calculation.

Most publications have simply considered multiplet $\psi_i J_i$ to multiplet $\psi_j J_f$ transitions because the number of intensity parameters can be considerably decreased: to three. Approximately assuming that the populations of all CF states within the initial (ground) multiplet are equal, Judd gave a simple formula, as follows:

$$\sum_{\Gamma\gamma} \left| \langle \mathbf{f}^{\mathrm{N}} \psi_{f} J_{f} \Gamma_{f} \gamma_{f} | \mathbf{D}_{q}^{(1)} | \mathbf{f}^{\mathrm{N}} \psi_{i} J_{i} \Gamma_{i} \gamma_{i} \rangle \right|^{2} = \sum_{\lambda} \Omega_{\lambda} |\langle \mathbf{f}^{\mathrm{N}} \psi_{f} J_{f} \| \mathbf{U}^{(\lambda)} \| \mathbf{f}^{\mathrm{N}} \psi_{i} J_{i} \rangle |^{2}$$

$$\tag{24}$$

Fig. 7a-f Some mechanisms for f-f pure electronic (a-c) and vibronic (d-f) absorption transitions for Ln^{3+} systems: a MD, EQ pure electronic transitions (the operator M_{e} refers to the MD or EQ transition moment operators, Sect. 7.2); b Induced ED transition (one of the two mechanisms; H_{CF} is the CF operator connecting opposite parity configurations, $D^{(1)}$ is the electric dipole moment operator, Sect. 7.2); c Coulombic correlation of transient ED moments in the ligands by the EQ transition of the lanthanide ion [145] (one of the two mechanisms, with H' representing the metal quadrupole-ligand multipole moment operator, Sect. 7.2); d Judd vibronic mechanism, with H_{ν} representing the vibronic coupling operator; e Faulkner-Richardson [67] static (i), (ii) and dynamic (iii), (iv) coupling mechanisms. H' is a vibronic coupling operator, Eq. (37); f Stavola-Dexter two-centre vibronic transition, (i)–(iv) [175]. M_{Ln} and M_X are electric dipole transition moment operators and H_{Ln-X} represents the metal multipole-ligand multipole interactions, (Eqs. 48b-48e). b and c are not applicable also to centrosymmetric sites in M₂ALnX₆. Dotted lines represent vibrational energy levels, which are linked between Ln³⁺ and X⁻ in e to show that the vibration is that of the LnX_6^{3-} moiety, but unlinked in f where X⁻ is a vibrating ligand; horizontal bars represent correlated interactions; i, f are f^N states, m is an opposite-parity Ln^{3+} state; o is the ligand ground electronic state, u is a ligand opposite-parity state. The initial states are ground states in all cases, and final states are marked by semicircles

where

$$\Omega_{\lambda} = [\lambda] \sum_{tp} |A_{tp}^{\lambda}|^2 / [t]$$
⁽²⁵⁾

In this case, only Ω_2 , Ω_4 and Ω_6 (or only Ω_4 and Ω_6 for elpasolites) are fitting parameters, and the reduced elements of $U^{(\lambda)}$ in Eq. (24) can be calculated [121] and the coefficients $C_{\psi}(\alpha' S' L')$ obtained from energy level fitting.

The programs of Prof. Reid can also fit $4f^{N}-4f^{N}$ transition intensities to obtain A_{tp}^{λ} or Ω_{λ} , and the former intensity fitting is helpful to assign (and fit) CF energy levels.

The oscillator strength for entire multiplet-multiplet transitions enabled by the forced ED mechanism is in the region of 10^{-5} to 10^{-8} for Nd³⁺ at a C_s site [118]; 10^{-5} to 10^{-6} for Pr³⁺ at a C_s site [119]; or ca. 10^{-6} for Er³⁺ at an S_4 site [120].

We now arrive at the major factor which distinguishes the electronic spectra of centrosymmetric M₂ALnX₆ systems from those of most other lanthanide ion systems. This results from the vanishing of the second bracket of Eq. (22), since $\Gamma_m \times \Gamma_i$ is odd parity and $\Gamma(H'_{CF})$ is only even parity. Forced dipole pure electronic transitions are thus forbidden for these lanthanide systems.

Generally, the MD oscillator strengths are in the region 10^{-7} to 10^{-11} [122] for individual ZPL transitions of Ln³⁺. Considering M₂ALnX₆, the MD ZPL of transitions with $|\Delta J| = \pm 1$, such as the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er³⁺ in Cs₂NaErCl₆ and the ${}^{5}I_{8} \rightarrow {}^{5}I_{7}$ transition of Ho³⁺ in Cs₂NaHoCl₆, often dominate their respective spectral regions [112] since the vibronic transitions are generally weak. For the purpose of spectral assignments, the calculated MD relative intensities are generally in good agreement with experiment (e.g. [123]) as long as CF induced J-mixing is taken into account [112], except for cases where the composition of the wave function is especially sensitive to parameter values and inaccurately determined. Orbital reduction factors, which parametrize covalency contributions, have not been included in the calculations. MCD and MCPE have sometimes been employed to provide assignments of the irreps of terminal CF levels of MD transitions (e.g. [124]). Figure 8 shows the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ MCPE and emission spectra of Tb³⁺ in $Cs_2NaTbCl_{6}$, with the MD transitions between CF levels marked and shown in the energy level diagram. The selection rules identify that the MD intensity results from the contributions of both 7F_5 and 5F_5 to the final 7F_5 state, and of both ⁷F₄ and ⁵F₄ to the initial ⁵D₄ state. All bands shown in this figure are due to MD transitions. The ordinate I is the total emission intensity, whereas ΔI is the difference in emission intensity between left and right circularly polarized radiation. With some assumptions, ΔI_{fi} may be calculated from



Fig. 8 MCPE (ΔI) and emission (*I*) spectra for the ${}^{7}F_{5} \leftarrow {}^{5}D_{4}$ transition of Tb³⁺ in Cs₂NaTbCl₆ at 20 K with a magnetic field strength of 0.86 T. The individual crystal field transitions are labelled, and *vertical lines* in the energy level diagram show the MD transitions. The \leftarrow notation is as [124].

$$\Delta I_{fi} \propto B_i(T) \bar{\nu}_{if}^4 [|\langle \psi_i | \mathbf{m}_- | \psi_f \rangle|^2 - |\langle \psi_i | \mathbf{m}_+ | \psi_f \rangle|^2]$$
(26)

where $B_i(T)$ is a Boltzmann factor for the emitting state; $\bar{\nu}_{if}$ is the transition energy (cm⁻¹); and m_± are the MD operators for left and right circularly polarized radiation. In Fig. 8, the six prominent *A* terms [125] in the MCPE spectra were unambiguously assigned to six zero phonon lines [124]. When the CF interaction is larger than the magnetic interaction, then the first order Zeeman effect produces a symmetric splitting of Γ_4 and Γ_5 states, which is independent of the relative orientation of the crystal axis to the applied magnetic field. When the CF splitting is of the same order of magnitude as the Zeeman splitting, more complex second order effects occur such as the splitting of Γ_3 states and the appearance of forbidden transitions.

Care must be taken to avoid saturation effects when measuring the oscillator strengths of intense MD transitions [126]. It has been assumed that MD oscillator strengths are rather insensitive to the site symmetry of a particular rare earth ion [127], and this may be the case for some particular transitions. However, the ED contribution to the zero phonon line intensity of an ion at a noncentrosymmetric site may be comparable to, or greater than the MD contribution, so that the measured intensity arises from both contributions.

Some major differences between the electronic spectra of Ln³⁺ in a noncentrosymmetric system and in cubic elpasolites are evident from Fig. 9, where a



comparison is given of the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ spectra of YAlO₃:Er³⁺ and Cs₂AErCl₆ (A=Li, Na), with the pure electronic transitions being identified in each case. The SLJ energy levels of Er^{3+} in $Cs_2NaErCl_6$ are also shown for clarity. The site symmetry of Er^{3+} in YAlO₃ is C_s so that pure electronic transitions are allowed by the forced ED mechanism, Fig. 7b, in which the CF mixes 4f¹⁰5d¹ character into 4f¹¹ electronic states. All 15 features correspond to electronic transitions between Kramers doublet electronic states and the bands are relatively sharp even at 300 K. As mentioned above, the forced dipole pure electronic transitions are forbidden in cubic M₂ALnX₆ systems. Thus, by contrast, in Fig. 9a,b, there are fewer (5) zero phonon lines and their MD intensity contribution in the centrosymmetric system Cs₂AErCl₆ is overlapped and dwarfed by the broader, more intense vibronic structure. The spectra Fig. 9a,b become broad, with unresolved features at 300 K. In general, whereas the intensities of individual vibronic bands are quite small (oscillator strengths usually in the region of 10^{-10} to 10^{-8}), the summation of vibronic intensities for a particular transition between CF states can give a total sideband oscillator strength of up to 10^{-7} to 10^{-6} for the case of M₂ALnCl₆ [97, 128].

The EQ oscillator strengths are calculated to be between 10^{-10} to 10^{-13} [113] for individual ZPL transitions of Ln^{3+} in Cs_2NaMX_6 . Much attention has previously been paid to the relationship of hypersensitive and EQ transitions. It appears, however, that the spectra of many such transitions were usually recorded (in solution) at room temperature so that the distinction was not possible between vibronic and pure electronic structure (see for example [129–132]), with the total oscillator strengths being of the order 10^{-5} . Indeed, the only conclusive resolution of the electric quadrupole mechanism in contributing the entire ZPL intensity in a crystal concerns the uranyl ion.

Many theories concerning the origin of hypersensitivity explained the large changes in intensity for certain transitions of rare earth ions in different environments in terms of purely electronic effects (e.g. the inhomogeneous dielectric and dynamic coupling (ligand polarization) mechanisms [133, 134] including the screening of outer electron shells [135]; the anisotropic polarizability contributions [136]; and the role of linear CF terms [137]). One of the mechanisms of the coulombic correlation of transient

Fig. 9a–d 488-nm excited emission spectra of Er^{3+} in different crystal environments. 20 K spectra of: **a** Cs₂NaErCl₆ and **b** Cs₂LiErCl₆; **c** 300 K spectrum of YAlO₃:Er³⁺. The (one) emitting level in **a** and **b** is ${}^{4}S_{3/2}\Gamma_{8}$, whereas this splits into two Kramers doublets, labelled A and B, in YAlO₃:Er³⁺. This transition terminates upon the electronic ground state, where there are 5 CF levels in the cubic elpasolite systems (a,b, Γ_{8} , Γ_{7} , Γ_{6}), but 8 (labelled S through Z) for Er³⁺ at the C_{s} site in YAlO₃. (Adapted from [72] and unpublished data); **d** *SLJ* Energy levels of Er³⁺ in Cs₂NaErCl₆. The *semicircles* indicate terms from which luminescence has been observed for Er³⁺ in neat or diluted elpasolite hosts

electric dipole moments in the ligands by the EQ transition of the lanthanide ion is shown in Fig. 7c. Peacock [138] considered that the vibronic intensity mechanism is not important for molecular complexes. On the other hand, Henrie et al. [139], and also Judd [140], recognized the importance of the vibronic contribution to the intensity of hypersensitive transitions. Henrie et al. envisaged the occurrence of odd-parity vibrations via a covalency (charge transfer) model. Judd [140] noted that in the case of large Ln-X distances compared to the ligand displacements, all of the vibronic intensity should reside in the hypersensitive transitions, and subsequently gave an illustrative treatment for τ_{1u} vibrational modes [141].

The measured oscillator strength of the $({}^{6}H_{5/2})\Gamma_{7}\rightarrow\Gamma_{6}({}^{6}F_{1/2})$ pure EQ allowed transition of Sm³⁺ in Cs₂NaSmCl₆ [142], at 6355 cm⁻¹, is 3×10^{-10} (Fig. 10) in agreement with calculation [113, 143]. Using an oriented crystal, linear polarization measurements in different directions (in the absence of a magnetic field) of an MD allowed ZPL do not show a variation in intensity for the cubic M₂ALnX₆ systems. This is not the case for EQ ZPL, where the explicit polarization dependence has been given by Hellwege [144] for transitions between various CF levels in cubic systems.

The dynamic coupling mechanism (Fig. 7c) only makes a contribution to the intensity of an EQ transition for a system with point group symmetry



Fig. 10 295 K and 77 K absorption spectra of $Cs_2NaSmCl_6$ between 6000 and 7000 cm⁻¹. The $({}^{6}H_{5/2})\Gamma_7 \rightarrow \Gamma_6({}^{6}F_{1/2})$ pure EQ transition is marked, together with associated Stokes and anti-Stokes (*starred*) vibronic structure. (Adapted from [142])

such that one of the components of the ED operator transforms as the same irrep as one of the components of the EQ operator [145]. This is not the case for the O_h molecular symmetry point group, so that that the feature assigned to the EQ ZPL in the 300 K and 77 K spectra of Cs₂NaSmCl₆, Fig. 10, is much weaker than the associated vibronic structure. The electronic origin is identified by Stokes and anti-Stokes structure in the notation of Table 2. In conclusion it appears that nearly all of the intensity of hypersensitive transitions in M₂ALnCl₆ is vibronic in character. We have further observed that a noncentrosymmetric perturbation (for example, at crystal defect sites) introduces ED character into the pure electronic transition, which then becomes considerably enhanced.

7.3

Vibronic Spectra: Vibrational Progressions Caused by Displacement in Equilibrium Position

For an allowed transition, the intensity is distributed between the ZPL and vibrational progressions, since the first term in Eq. (17) can be nonzero for $k \neq n$ when the displacement in equilibrium position cannot be ignored, especially for the strong electron-phonon coupling case. This is quantified for Ln^{3+} electronic transitions by weak linear coupling (small Huang-Rhys parameter, S=0 inferring that all intensity is contributed by the electronic origin, the vibrational quantum v=0); or stronger linear coupling (e.g. S=w, where w (>0) phonons correspond to the intensity maximum of the sideband) [116]. The first situation corresponds to a very small displacement along the vibrational normal coordinate during the electronic transition (as in MD $f^N \leftrightarrow f^N$ transitions), whereas the second case is illustrated by a greater change, as in ED $f^{N} \leftrightarrow f^{N-1}d$ electronic transitions. In the absence of Jahn-Teller effects, considering the case at low temperature, when only the n=0vibrational level initial state is populated (i.e. $\Gamma(\chi_{in}) \equiv \Gamma_{1g}$), the symmetry selection rule for the first term of Eq. (17) to be nonzero for the first member k=1 of a given vibrational mode Q_v is that $\Gamma(\chi_{tk=1}) \times \Gamma(\chi_{in=0})$ contains Γ_{1g} . Thus the progression forming-mode is a totally-symmetric vibration.

The intensity ratio of the ZPL intensity $(I^{0,0})$ to that of the *p*-th member of the progression in the emission (Eq. 27) or the *q*-th in absorption (Eq. 28) spectra is given by

$$\frac{I^{0,p}}{I^{0,0}} = \left[\frac{E(ZPL) - p\bar{v}_1}{E(ZPL)}\right]^4 \left[\frac{R_{0,p}}{R_{0,0}}\right]^2$$
(27)

$$\frac{I^{q,0}}{I^{0,0}} = \left[\frac{E(ZPL) + q\bar{\nu}_1}{E(ZPL)}\right] \left[\frac{R_{q,0}}{R_{0,0}}\right]^2$$
(28)

respectively, where the wave function overlap integrals $R_{0,p}$ and $R_{q,0}$ can be related to the displacement ΔS of the minimum of the potential surface of the excited electronic state along the α_{1g} normal coordinate [146]. Furthermore, for the case of hexacoordinated species, the individual Ln-X bond length change, $\Delta r = \Delta S / \sqrt{6}$.

Totally symmetric vibrational progressions in the $\nu(\text{Ln} - \text{Cl})$ stretching mode have been reported very weak at the long wavelength tails of certain emission transitions, for example, for Pr³⁺ in the ${}^{3}\text{P}_{0} \rightarrow {}^{3}\text{H}_{4}$, ${}^{3}\text{H}_{5}$, ${}^{3}\text{F}_{2}$ transitions [147]; for Dy³⁺ in the ${}^{4}\text{F}_{9/2} \rightarrow {}^{6}\text{H}_{13/2}$ transition [123]; for Ho³⁺ in the ${}^{5}\text{F}_{5} \rightarrow {}^{5}\text{I}_{8}$ transition [148]; and for Yb³⁺ in the ${}^{2}\text{F}_{5/2} \rightarrow {}^{2}\text{F}_{7/2}$ transition [149]. The maximum bond length change along the α_{1g} coordinate is ca. 1.4 pm. Jahn-Teller effects are common in the spectra of d-block elements but are much less important for f^N systems, where progressions in nontotally symmetric modes have rarely been observed in 4f^N-4f^N electronic spectra [149].

7.4 Vibronic Spectra: One-phonon Sideband

The doped (guest) Ln^{3+} ion destroys the translational symmetry of the crystal and the 4f^N electronic states of Ln^{3+} are very localized, so that vibronic states are classified according to irreps of the site group. The vibrational irreps have been described as those of the LnX_6^{3-} complex ion point group, or more accurately as those of the Ln^{3+} site group contained in the space group. The second and third terms of (17) refer to the vibrational sideband structure of the transition caused by the electron-phonon coupling Hamiltonian $\left(\frac{\partial H}{\partial Q_\nu}\right)_{Q_0} Q_\nu$, and they are nonzero when [110, 150]

$$\Gamma(\psi_f^*) \times \Gamma(\mathbf{M}_e) \times \Gamma(\psi_m)$$
 contains Γ_{1g} (29a)

$$\Gamma(\chi_{fk}^*) \times \Gamma(Q_\nu) \times \Gamma(\chi_{in})$$
 contains Γ_{1g} (29b)

and

$$\Gamma(\psi_m) \times \Gamma(Q_\nu) \times \Gamma(\psi_i)$$
 contains Γ_{1g} (29c)

The vibrational states χ_{fk} and χ_{in} differ by one quantum of Q_v , i.e. the two $4f^N$ vibronic states differ by one quantum of a vibration. Usually M_e is the ED operator, so that the Q_v has odd-parity for centrosymmetric systems, and ψ_m corresponds to an opposite-parity ($4f^{N-1}5d$) intermediate state.² Based on Eq. (29), from the k=0 unit cell vibrations identified in Table 2, the symmetry species of vibrational modes enabled in specific EDV transitions between the CF levels of $4f^N$ rare earth ions in elpasolite lattices are therefore

² Both theoretically [151] and experimentally (e.g. [152]) it is evident that MD vibronic intensity contributions are small for M_2ALnX_6 systems.

$\Gamma_i \Gamma_f$	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
$ \begin{array}{c} \Gamma_1 \\ \Gamma_2 \\ \Gamma_3 \\ \Gamma_4 \\ \Gamma_5 \end{array} $	$ au_{1\mathrm{u}}$	$ au_{2\mathrm{u}} \ au_{1\mathrm{u}}$	$\tau_{1u} + \tau_{2u}$ $\tau_{1u} + \tau_{2u}$ $\tau_{1u} + \tau_{2u}$	$\begin{array}{l} \alpha_{1\mathrm{u}} + \epsilon_{\mathrm{u}} + \tau_{1\mathrm{u}} + \tau_{2\mathrm{u}} \\ \alpha_{1\mathrm{u}} + \epsilon_{\mathrm{u}} + \tau_{1\mathrm{u}} + \tau_{2\mathrm{u}} \\ \text{All u} \\ \text{All u} \\ \text{All u} \end{array}$	$\begin{array}{l} \alpha_{1u} + \epsilon_{u} + \tau_{1u} + \tau_{2u} \\ \alpha_{1u} + \epsilon_{u} + \tau_{1u} + \tau_{2u} \\ \text{All } u \\ \text{All } u \\ \text{All } u \\ \text{All } u \end{array}$
$\Gamma_i \backslash \Gamma_f$	Γ_6			Γ_7	Γ_8
Γ_6 Γ_7 Γ_8	$\alpha_{1u} + \epsilon_{u}$	$+\tau_{1u}+\tau_{2u}$		$\alpha_{1u} + \epsilon_u + \tau_{1u} + \tau_{2u}$ $\alpha_{1u} + \epsilon_u + \tau_{1u} + \tau_{2u}$	All u All u All u

Table 4 k=0 Selection rules for one-phonon sideband structure of the $i \rightarrow f$ transition in the EDV spectra of octahedral symmetry compounds (from [110]). The M₂ALnX₆ unit cell group modes contain $\tau_{1u} + \tau_{2u}$, but not ϵ_u or α_{1u}

subject to the selection rules given in Table 4, in which only τ_{1u} type (S₆= v_3 and S₇= v_4) and τ_{2u} type (S₁₀= v_6) are active moiety modes. The oscillator strengths of entire vibronic sidebands of Cs₂NaYCl₆:Ln³⁺ do not vary significantly with the concentration of Ln³⁺ in the crystal, although some individual vibronic origins do exhibit minor changes attributed to the change in mixing of vibrational symmetry coordinates with change in Ln-Cl bond distance with concentration [153, 154]. The vibronic sideband intensity at temperature *T*, *I*(*T*) shows a coth law dependence with temperature [155]:

$$I(T) = \sum_{i} I_i(0) \coth(\mathrm{h}c\bar{\nu}_i/2k_BT)$$
(30)

where the sum is over all the component vibrations v_i in the sideband, and k_B is the Boltzmann constant.

The model which has been most widely applied to the calculation of vibronic intensities of the Cs₂NaLnCl₆ systems is the vibronic coupling model of Faulkner and Richardson [67]. Prior to the introduction of this model, it was customary to analyse one-phonon vibronic transitions using Judd closure theory, Fig. 7d, [117] (see, for example, [156]) with the replacement of the $T_{\lambda}^{electronic}$ (which is proportional to the above Ω_{λ}) parameters by $T_{\lambda}^{vibronic}$, which include the vibrational integral and the derivative of the CF with respect to the relevant normal coordinate. The selection rules for vibronic transitions under this scheme therefore parallel those for forced electric dipole transitions (e.g. $|\Delta J| \leq 6$; and in particular when the initial or final state is J=0, then $|\Delta J|=2, 4, 6$).

Because the general features of the Faulkner-Richardson model are representative and convey a simple physical picture, and it is the only model that has been extensively and fairly successfully applied to the interpretation of the vibronic spectra of Cs₂NaLnCl₆ systems, it will be described in slightly modified form in more detail herein. It is assumed that the Ln^{3+} ion and six ligands X⁻ interact by Coulomb, and not exchange forces. Only the (oddparity) LnX_6^{3-} vibrations, the so-called moiety modes, are considered to be responsible for vibronic perturbations. The Hamiltonian for the complete system is partitioned into three parts: free ion (H_A^0), ligand (H_B^0) and lanthanide ion-ligand interaction. Each charge distribution is expanded as a multipolar series about the appropriate centre. The latter lanthanide ion-ligand part of the Hamiltonian is then further partitioned into operators representing electrostatic interactions between the metal ion multipoles and the monopoles (static coupling operator, V) and higher multipoles (dynamic coupling operator, U) of the ligands. Both operators are expanded in the normal coordinates Q_{ν} about the equilibrium geometry, and retaining the linear terms in Q_{ν} , the vibronic Hamiltonian is

$$H = H_A^0 + H_B^0 + V^0 + U^0 + \sum_{\nu} V'_{\nu} Q_{\nu} + \sum_{\nu} U'_{\nu} Q_{\nu}$$
(31)

where the ' signifies differentiation with respect to Q_{ν} at the equilibrium position.

The operators U^0 and V^0 are expressed in terms of the interaction potential:

$$\mathbf{V}^{0} = \sum_{X} \sum_{l_{Ln}} \mathbf{V}_{X}(l_{Ln}, \mathbf{0}) = \sum_{X} \sum_{l_{Ln}} \sum_{m_{Ln}} \mathbf{T}_{m_{Ln}, \mathbf{0}}^{(l_{Ln}, \mathbf{0})}(X) \mathbf{D}_{m_{Ln}}^{(l_{Ln})}(Ln) \mathbf{D}_{\mathbf{0}}^{(0)}(X)$$
(32)

$$\mathbf{U}^{0} = \sum_{X} \sum_{l_{Ln}} \sum_{m_{Ln}} \sum_{m_{X}} \mathbf{T}_{m_{Ln},m_{X}}^{(l_{Ln},1)}(X) \mathbf{D}_{m_{Ln}}^{(l_{Ln})}(Ln) \mathbf{D}_{m_{X}}^{(1)}(X)$$
(33)

with

$$T_{m_{Ln},m_{X}}^{(l_{Ln},l_{X})}(X) = \frac{(-1)^{l_{X}+m_{X}+m_{Ln}}}{R_{X}^{l_{Ln}+l_{X}+1}} \cdot \frac{[(l_{Ln}+l_{X}+m_{Ln}+m_{X})!(l_{Ln}+l_{X}-m_{Ln}-m_{X})!]}{[(l_{Ln}+m_{Ln})!(l_{Ln}-m_{Ln})!(l_{X}+m_{X})!(l_{X}-m_{X})!]} C_{-(m_{Ln}+m_{X})}^{(l_{Ln}+l_{X})}(\Theta_{X},\Phi_{X})$$
(34)

where *l* is the rank of the multipole and *m* specifies its component; (R_X, Θ_X, Φ_X) are the ligand X⁻ coordinates with respect to the rare earth ion Ln³⁺. The $D_0^{(0)}(X) = q_X$ in Eq. (32) is the net charge on X, and the U⁰ in Eq. (33) is approximated by only taking $l_X=1$ terms, the dipole $D_{m_X}^{(1)}$ ones, from the sum over $l_X \ge 1$. Differentiation gives

$$V'_{\nu} = \sum_{l_{Ln}, m_{Ln}} \left[\sum_{X} \left(\frac{\partial T_{m_{Ln}, 0}^{(l_{Ln}, 0)}(X)}{\partial Q_{\nu}} \right)_{0} q_{X} \right] D_{m_{Ln}}^{(l_{Ln})}(Ln)$$
(35)
$$\mathbf{U}'_{\nu} = \sum_{l_{Ln}, m_{Ln}} \left[\sum_{X, m_X} \left(\partial \mathbf{T}^{l_{Ln}, 1}_{m_{Ln}, m_X}(X) / \partial Q_{\nu} \right)_0 \mathbf{D}^{(1)}_{m_X}(X) \right] \mathbf{D}^{(l_{Ln})}_{m_{Ln}}(Ln)$$
(36)

For the centrosymmetric elpasolite systems, the last three terms of Eq. (31) (denoted in brief by U^0 , V_1 and U_1) are chosen as the perturbation Hamiltonian (H') upon the zeroth order Hamiltonian operator. Then V_1 is a vibronic coupling operator, arising from the interactions between the f-electrons of Ln^{3+} and the vibrating point-charge distributions of the ligands. Since U_0+U_1 involves higher multipoles (approximately only the dipole is considered here) of the ligand charges, it involves dynamic coupling between Ln^{3+} and X^- . The last two perturbation operators (V_1 and U_1) produce the EDV intensity, with the participation of opposite-parity lanthanide ion states, abbreviated as Ln_m , and ligand excited states X_u .

The ground-state $|Ln_{00}X_0\rangle$ wavefunction is utilized as the zeroth order basis set (using rounded kets), and using the singly- and doubly-excited state functions, the perturbed wavefunctions of the LnX_6^{3-} system are written to first order in H'. Then the EDV transition moment for the $|Ln_{00}X_0\rangle \rightarrow |Ln_{f1}X_0\rangle$ transition is given by

$$M_{00,f1}(Q) = (Ln_{00}X_0|D^{(1)}|Ln_{00}X_0)(Ln_{f1}X_0|H'|Ln_{00}X_0)/(E_{f1}) -\sum_{m\neq f}'(Ln_{m0}|D^{(1)}|Ln_{00})(Ln_{m0}X_0|H'|Ln_{f1}X_0)^{\dagger}/(E_{m0} - E_{f1}) -\sum_{m}'Ln_{f1}|D^{(1)}|Ln_{m1}(Ln_{00}X_0|H'|Ln_{m1}X_0)^{\dagger}/(E_{m1}) +\sum_{u}'(X_u|D^{(1)}|X_0)(Ln_{00}X_u|H'|Ln_{f1}X_0)^{\dagger}\left[\frac{2E_u}{(E_{f1})^2 - (E_u)^2}\right]$$
(37)

of which the first term is zero for a centrosymmetric system, and the dipole strength is

$$D_{00,f1} = |M_{00,f1}|^2 \tag{38}$$

The vibronic wave functions for the LnX_6^{3-} system are written as Herzberg-Teller products of harmonic oscillator wave functions and electronic wave functions. We consider an absorption transition from the zeroth vibrational level of the electronic ground state to the *f*-th electronic excited state accompanied by the excitation of one quantum of the *v*-th odd-parity normal mode Q_v (i.e. the occupation number k(v)=1). The vibrational wavefunctions are then χ_{00} and χ_{f1} for the ground and *f*-th excited electronic state, respectively. The EDV transition element of the *q*-th component of the moment $M_{00,f1}$ in Eq. (37) for the $00 \rightarrow f1$ transition can be written in terms of static and dynamic coupling parts:

$$M_{00,f1;q} = \sum_{\nu} \left[\langle \chi_{00} | M_{0f;q}^{(s)}(Q_{\nu}) | \chi_{f1} \rangle + \langle \chi_{00} | M_{0f;q}^{(d)}(Q_{\nu}) | \chi_{f1} \rangle \right]$$
(39)

This partitioning gives rise to the occurrence of interference terms between the static and dynamic coupling contributions in the expression for the dipole strength Eq. (38), Eq. (46).

The vibrational integral is separated

$$M_{00,f1;q} = \langle \chi_{00} | Q_{\nu} | \chi_{f1} \rangle \sum_{l_{Ln}, m_{Ln}} [A'_{\nu}(l_{Ln}, m_{Ln}) Z^{(s)}_{0f;q}(l_{Ln}, m_{Ln}) + B'_{\nu}(l_{Ln}, m_{Ln}; q) Z^{(d)}_{0f;q}(l_{Ln}, m_{Ln})]$$
(40)

where

$$A'_{\nu}(l_{Ln}, m_{Ln}) = \sum_{X} q_{X} \left[\partial T^{(l_{Ln}, 0)}_{m_{Ln}, 0}(X) / \partial Q_{\nu} \right]_{0}$$
(41)

$$B'_{\nu}(l_{Ln}, m_{Ln}; q) = \sum_{X} \bar{\alpha}_{X}(\nu_{f}) \left[\partial T^{(l_{Ln}, 1)}_{m_{Ln}, q}(X) / \partial Q_{\nu} \right]_{0}$$
(42)

in which $\bar{\alpha}_X(v_f)$ is the average ligand polarizability,

$$Z_{0f;q}^{(s)}(l_{Ln}, m_{Ln}) = -\sum_{m}^{\prime} \{ (Ln_0 | \mathbf{D}_q^{(1)} | Ln_m)^{\dagger} (Ln_m | \mathbf{D}_{m_{Ln}}^{(l_{Ln})} | Ln_f)^{\dagger} / E_{fm} - (Ln_f | \mathbf{D}_q^{(1)} | Ln_m) (Ln_0 | \mathbf{D}_{m_{Ln}}^{(l_{Ln})} | Ln_m)^{\dagger} / E_{m0} \}$$
(43)

$$Z_{0f}^{(d)}(l_{Ln}, m_{Ln}) = (Ln_0 \big| \mathcal{D}_{m_{Ln}}^{(l_{Ln})} \big| Ln_f)^{\dagger}$$
(44)

The electronic multipolar factor $Z_{0f;q}^{(s)}$ in Eq. (43) may be evaluated in terms of reduced matrix elements and 3-j and 6-j symbols following the closure arguments of Judd [117] mentioned before. The vibrational integral is given by

$$\langle \chi_{00} | Q_{\nu} | \chi_{f1} \rangle = \sqrt{\frac{\hbar}{4\pi c \bar{\nu}_{\nu}}} \tag{45}$$

where \bar{v}_v is the harmonic wavenumber of the *v*-th normal mode. The evaluation of the vibronic coupling factors $A'_v(l_{Ln}, m_{Ln})$ and $B'_v(l_{Ln}, m_{Ln}; q)$ was carried out by numerical differentiation. The first of these quantities depends upon the X⁻ charge, q_X , and the ligand positional displacements of the *v*-th normal mode. The second quantity depends upon the ligand polarizability, $\bar{\alpha}_X(v_f)$, and positional displacements.

The evaluation of the electronic factors, by way of the 3-j and 6-j symbols, leads to selection rules for the vibronic spectra. In the formula for $\Xi(l_{Ln},\lambda)$

Transition	Dipole strength ^a	Relative intensity	7
		Calculated	Observed ^b
$\Gamma_{1g} \rightarrow \Gamma_{3g} + \nu_3$	2.4	0.88	0.82
$\Gamma_{1g} \rightarrow \Gamma_{3g} + \nu_4$	2.7	1.0	1.0
$\Gamma_{1g} \rightarrow \Gamma_{3g} + \nu_6$	0.6	0.22	0.19
$\Gamma_{1g} \rightarrow \Gamma_{5g} + \nu_3$	3.0	1.0	1.0
$\Gamma_{1g} \rightarrow \Gamma_{5g} + \nu_4$	2.1	0.7	0.56
$\Gamma_{1g} \rightarrow \Gamma_{5g} + \nu_6$	1.2	0.4	с

Table 5 EDV dipole strengths and relative intensities for the ${}^7F_0 \rightarrow {}^5D_2$ transition of Eu³⁺ in Cs₂NaEuCl₆ (from [67])

^a In units of 10⁻⁴³ e.s.u.² cm². The total electric dipole strength is calculated (observed) to be 12 (48); ^bMeasurement error ±20%; ^cOverlapped by other bands

in the approximate Judd expression for $Z_{0f;q}^{(s)}(l_{Ln}, m_{Ln})$ the values of l_{Ln} and λ are limited (λ =2, 4, 6; $l_{Ln}=\lambda\pm1$); and there are triangle conditions limiting the intermediate Ln³⁺ configuration to an opposite parity $f^{N-1}d$ or $f^{N-1}g$ configuration (with only the latter if $l_{Ln}=7$). For the $Z_{0f}^{(d)}(l_{Ln}, m_{Ln})$ in Eq. (44), the value of $l_{Ln}=2,4,6$. Also, other selection rules on *S*, *L* and *J* from the Faulkner-Richardson model are given in Table 1.

The Faulkner-Richardson vibronic intensity model has been used to rationalize the vibronic sidebands in many LnCl₆³⁻ systems [157–164]. The radial integral and $\Xi(l_{Ln},\lambda)$ parameter values were not fitted, but taken from the literature. Generally, the agreement with experimental vibronic intensities has been of a semiquantitative nature, but the relative magnitudes of the ED vs MD contributions to the total dipole strengths of multiplet-multiplet transitions are fairly well-reproduced. In some cases, for example Eu³⁺ in Cs₂NaEuCl₆ [67], the agreement of both absolute and relative intensities is remarkable (Table 5). Furthermore, the vibronic intensities of several hypersensitive transitions (e.g. ${}^{4}I_{15/2} \rightarrow {}^{2}H_{11/2}$, ${}^{4}G_{11/2}$ of Er^{3+} in $Cs_2NaErCl_6$, [163] and ${}^{4}G_{7/2} \rightarrow {}^{4}I_{11/2}$ of Nd³⁺ in Cs₂NaYCl₆:Nd³⁺ [158]) are calculated to be very large, due to transition quadrupole (Ln³⁺)-transition dipole (Cl⁻) interactions incorporated in the dynamic coupling part of the intensity model. More generally, one of the main features of the model has been that the static coupling (SC) and dynamic coupling (DC) terms usually make comparable contributions, and that signed interference terms may play an important role in determining vibronic intensities:

$$D_{00,f1} = |M_{00,f1}(SC)|^2 + M^*_{00,f1}(SC) \times M_{00,f1}(DC) + M^*_{00,f1}(DC) \times M_{00,f1}(SC) + |M_{00,f1}(DC)|^2$$
(46)

The sign of the interference terms in Eq. (46) has been the subject of discussion which has been clarified by Xia and Reid [165].

Some further modifications have been suggested since the first use of the model, although no detailed calculations have been forthcoming. In the Faulkner-Richardson model, the vibronic factor $A'_{v}(l_{Ln}, m_{Ln})$ was calculated by numerical partial differentiation. In a manuscript focusing upon the vibronic structure of EQ transitions, Judd [141] subsequently pointed out that this can be avoided by using the appropriate bipolar expansions. In addition, Judd included a further mechanism in the static coupling term, not only to account for the interaction between metal ion multipoles and ligand charges, but also the induced charges on the ligands (which are polarized by Ln³⁺). The dynamic coupling mechanism, represented by the last term of Eq. (37) where the 4f^N electrons polarize the ligands, which then interact with the radiation field, was represented by Judd in an alternative manner where the radiation field induces dipoles in the ligands which then re-radiate and interact with the 4f^N electrons. A factor was also introduced in the dynamic coupling term to account for the screening of the quadrupole fields by the fifth shell electrons of Ln³⁺. Stewart [166] further modified the dynamic coupling term by including polarizability derivatives as well as anisotropic polarizabilities and found that these terms were important for the vibronic structure of the hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺. On the same subject, Malta [167] utilized a ligand field model and included the dependence of the effective charges and polarizabilities upon the Ln³⁺-Cl⁻ distance.

More general calculations have not been forthcoming from the above refinements due to lack of knowledge about some of the parameters involved. An alternative more general parametrization approach was presented by Reid and Richardson for vibronic intensities [168], based upon linear vibronic coupling, but independent of the detailed nature of the Ln³⁺-ligandradiation field interactions under the electric dipole approximation. The general parametrization scheme for vibronic intensities, which also includes the contributions from vibrational progressions to the vibronic intensity, utilizes the point group notation of Butler. An electronic operator called the effective vibronic transition operator is introduced for one-phonon electric dipole vibronic processes. It contains rank 2, 4 and 6 unit tensor operators which act within the 4f^N configuration, and parameters $A_{t-c*v*}^{\lambda^+}(dv*)$ which represent the vibronic mixing of CF states with opposite-parity configurations. For the LnCl₆³⁻ moiety, the parameters are derivatives with respect to the 3 odd-parity normal modes, with up to 11 parameters each for the τ_{1u} modes and 10 for τ_{2u} . The parameters may be reduced in number when expressed in terms of the intrinsic parameters of the superposition model, \bar{A}_{t}^{λ} , where each Ln-Cl interaction is cylindrically symmetric and independent. The Herzberg-Teller formalism is applied to calculate the electric dipole



Fig. 11 Comparison of calculated and observed vibronic oscillator strengths for absorption transitions from the $({}^{4}I_{15/2})a\Gamma_{8}$ level of Er^{3+} in Cs₂NaErCl₆. (Data from [128])

strength of the vibronic transition by using the initial and final 4f^N electronic wavefunctions with the effective vibronic transition operator, including the product with the vibrational integral. The latter assumes a harmonic force-field. The results of calculated and experimental oscillator strengths for the v_3 , v_4 and v_6 vibronic intensities in the electronic absorption spectra of Er³⁺ in Cs₂NaErCl₆ are shown in Fig. 11, where 68 vibronic transitions were fitted [128]. The signs of the derived intensity parameters were taken to indicate the importance of both the static and dynamic coupling mechanisms. The agreement with experimental data is good, although a large number (18) of parameters were employed and the descriptions of physical mechanisms are not forthcoming. More recently [169], it has been found that different sets of parameter values may provide a similar goodness-of-fit to the experimental vibronic intensities, due to the presence of multiple local minima in the nonlinear fitting process. Furthermore the parameter signs may not be uniquely determined because intensities depend upon the squares of these values.

An attempt to elucidate the physical mechanisms of vibronic transitions and to avoid excessive parametrization has been made in the vibronic intensity calculations of Acevedo et al. [97, 170–173] which have been performed for individual vibronic transitions between CF states, with and without the Judd closure approximation, following the point group symmetry notation of Griffith [174]. Particular care has been given to the vibrational analysis of the moiety modes, which was largely based upon the normal coordinate analyses of solid pyridinium complexes in the studies of Richardson and co-workers. However, the direct calculations have only employed the major ${}^{2S+1}L_J$ components of states, and a selected intermediate state. This is probably the reason for the rather poor agreement with calculation in some cases, due to the delicate balance and interference between the signed contributions from dynamic and static coupling terms. The agreement for overall multiplet-multiplet vibronic intensities is found to be generally good.

It is relevant here to mention the treatment of vibronic intensities by the two-centre theory of Stavola and Dexter [175, 176], which leads to the expression for the ED transition matrix element for the vibronic absorption of a coupled rare earth-ligand system. In the present case of M_2ALnX_6 the ligand is monatomic, but more generally, we consider the case where X is not monatomic in Ln^{3+} -X⁻ (e.g. X=OH, NO₂, etc). Following Stavola and Dexter, the ED strength for the *q*-th polarized component of the transition in which the Ln^{3+} ion undergoes an intraconfigurational $4f^N$ transition, $Ln_i \rightarrow Ln_{f_5}$ and one quantum of vibration within ligand X⁻ is simultaneously excited i.e. $X_0 \rightarrow X_1$, is

$$D_{Ln_{i}X_{0},Ln_{f}X_{1}} = \left| \langle Ln_{i}X_{0} | \mathbf{M}_{Ln}^{q} + \mathbf{M}_{X}^{q} | Ln_{f}X_{1} \rangle \right|^{2}$$
(47)

where M_{Ln} and M_X operate over the coordinates of Ln and X respectively. Dropping the superscript q in the following, assuming that Ln_0 and X_0 refer to ground states with reference energy zero, and denoting lanthanide and ligand (opposite parity) intermediate states by the subscripts m and u, respectively, the matrix element in Eq. (47) is expanded, with rounded kets denoting zeroth-order states [175]:

$$\langle Ln_0 X_0 | \mathbf{M}_{Ln} + \mathbf{M}_X | Ln_f X_1 \rangle = (Ln_0 X_0 | \mathbf{M}_{Ln} + \mathbf{M}_X | Ln_f X_1)$$
 (48a)

$$-\sum_{m \neq f} (Ln_m | \mathbf{M}_{Ln} | Ln_f) (Ln_0 X_0 | \mathbf{H}_{Ln-X} | Ln_m X_1) (E_{Ln_m} + E_{X_1})^{-1}$$
(48b)

$$-\sum_{u\neq 1} (X_u | \mathbf{M}_X | X_1) (Ln_0 X_0 | \mathbf{H}_{Ln-X} | Ln_f X_u) (E_{Ln_f} + E_{X_u})^{-1}$$
(48c)

$$-\sum_{m \neq f} (Ln_0|\mathbf{M}_{Ln}|Ln_m) (Ln_m X_0|\mathbf{H}_{Ln-X}|Ln_f X_1) (E_{Ln_f} + E_{X_1} - E_{Ln_m})^{-1}$$
(48d)

$$-\sum_{u\neq 0} (X_0|\mathbf{M}_X|X_u) (Ln_0 X_u|\mathbf{H}_{Ln-X}|Ln_f X_1) (E_{Ln_f} + E_{X_1} - E_{X_u})^{-1}$$
(48e)

The first term (Eq. 48a) is nonzero in the presence of odd CF terms (but zero in the present case for Ln^{3+} at an O_h site). By including several assumptions, such as the neglect of terms at Eqs (48c) and (48e), and of in-

terference effects when squaring matrix elements, and the restriction of the Ln-X interaction Hamiltonian H_{Ln-X} to dipole-dipole coupling interactions; and approximations such as the averaging over polarization directions and over *SLJ*-multiplet states of Ln^{3+} , a simple expression for the dipole strength of the cooperative absorption $Ln_0X_0 \rightarrow Ln_fX_1$ was derived [175].

Modifying the diagrams of Dexpert-Ghys and Auzel [177], it is instructive to compare the mechanisms of vibronic transitions enabled by the Faulkner-Richardson [67] and Stavola-Dexter mechanisms. Figure 7e shows the static (i), (ii) and dynamic (iii), (iv) coupling mechanisms of Faulkner and Richardson [67], involving the excitation of one quantum of a certain LnX_6^{3-} moiety mode in an f^N excited state. Notice that the mechanism is vibronic and not electronic in nature. In the Stavola-Dexter mechanism, Fig. 7f, the vibration is excited within a (separate) ligand and the excitation at the lanthanide ion, M_{Ln} , is purely electronic dipolar. The $Ln^{3+}-X^-$ interaction is ligand dipole-metal dipole or ligand dipole-metal quadrupole.

All of the above vibronic intensity calculations of M₂ALnX₆ systems have employed the LnX₆³⁻ moiety model. By contrast, the earlier studies of the electronic spectra of rare earth ions interpreted the vibronic sidebands in terms of crystal, rather than moiety mode or unit cell vibrations. This is because more than one elementary excitation occurs in vibronic spectroscopy, so whereas the conservation of wavevector restricts the sum of the momenta of the electronic and vibrational excitations: $k_{photon} = k_e + k_{vib} = 0$, then \mathbf{k}_{e} or \mathbf{k}_{vib} can be nonzero [110]. This means that $\mathbf{k}\neq 0$ vibrational modes (i.e. due to dispersion, with consequent reduction in symmetry and maybe also degeneracy, and with change in energy) can produce vibronic intensity. This is particularly so for acoustic modes (which have zero energy at k=0) which show greater dispersion than optical modes (Fig. 6). Although all vibrational modes can therefore contribute to the intensity of a vibronic band, only those points of high density of vibrational states in fact produce sufficient spectral intensity [178], and these points lie near special points of the Brillouin zone (Fig. 5). The method for obtaining the vibronic selection rules at points other than k=0 has been the focus of several studies [for example, 179–182]. In conclusion, it is observed that the major spectral features in a vibronic sideband can be explained under k=0 selection rules, sometimes particularly well [183], but the interpretation of fine structure requires a more detailed lattice dynamics model [184], and we return to this in the next section. The description of the vibrational states of the guest ion in the crystal is not made in terms of a single k vector (running or plane wave) but in terms of linear combinations (standing waves) since the translational symmetry is destroyed.

Finally, it is noted that for transitions such as $\Gamma_1 \rightarrow \Gamma_i + \nu_3(\tau_{1u})$, where *i*=3, 4 or 5, in the absence of electron-vibrational interaction, the terminal vibronic state irreps are degenerate. In fact, various experimental studies have shown that the splitting of these states is <1 cm⁻¹ for Ln³⁺ systems. The major broadening mechanisms of the linewidths of ZPL transitions to the electronic ground state (e.g. Fig. 9b, $\Gamma_8 \rightarrow a\Gamma_8$), are (i) inhomogeneous broadening due to random microscopic crystal strain, and (ii) homogeneous broadening due to ion-ion interactions, as well as Raman broadening within the excited state. Doppler and lifetime broadenings are very much smaller. Vibrational sequences can also contribute to line broadening, due to the slight change in vibrational frequencies between the ground and excited states. Other pure electronic transitions in Fig. 9b are additionally broadened by the short lifetimes of the terminal electronic states. This effect is more evident in Fig. 9c. The vibronic transitions in Fig. 9b are also additionally broadened due to the phonon dispersion and to the shorter lifetimes of terminal vibronic states.

7.5 Interpretation and Assignment of 4f^N-4f^N Spectra

The electronic spectra of M_2ALnX_6 systems are particularly complex because they are mainly vibronic, and many transitions overlap. So how can the spectral features be reliably assigned? First, the electronic origin of each transition needs to be identified. Selection rules foretell if the transition is MD or EQ allowed, and the MD selection rules are rather less restrictive for odd-electron systems (Table 1). If the band is MD allowed, its oscillator strength (or intensity ratio) can be compared with calculation. For absorption transitions from nondegenerate ground states, the splitting of ZPL for earlier members of the Cs₂NaLnCl₆ series below T_c (see above), not apparent in Cs₂NaYCl₆:Ln³⁺, can indicate the presence of a degenerate excited state.

If the ZPL is weak, then variable temperature studies can identify its location from hot electronic and vibronic structure, with the latter illustrated in Fig. 10. The vibronic structure can be used to identify certain symmetry types of transition, for example Γ_1 - Γ_2 (Table 4). One viewpoint has been put forward that the spectral interpretation is confused by phonon dispersion in the vibronic sidebands of transitions. However, this complexity of the vibronic structure can in fact be utilized to provide a fingerprint to identify the location of the electronic origin. Where possible, it is more certain to compare both emission and absorption (or excitation) spectra for a particular transition in order to locate the electronic origin. Otherwise, transitions from different emissive states (with different state irreps) can be employed to confirm the symmetries and locations of terminal levels. Whereas other neat systems such as PrCl₃ show additional features not present in the electronic spectra of the diluted crystal (LaCl₃:Pr³⁺) due to interactions between Pr^{3+} ions [183], this is generally not the case for M₂ALnX₆ systems because the Ln³⁺-Ln³⁺ separation is large (>ca. 0.7 nm).

The problem of resolving an individual transition from overlapping emission transitions, or of populating a certain electronic state of Ln^{3+} in M_2ALnX_6 may in some cases be simplified by quenching the emission from a certain state by doping with another lanthanide ion. Thus the infrared emission of Yb³⁺ has been studied by doping Cs₂NaLnCl₆ (Ln=Ho, Nd) with Yb³⁺ [149]; the emission transitions from the Ho³⁺ ⁵S₂ level have been quenched [185]; and the ⁵I₄ level of Ho³⁺ has been populated in Cs₂ NaHo_{0.99}Er_{0.01}Cl₆ [186].

We turn now to the use of vibronic fine structure in aiding spectral assignments. Dilution of Cs₂NaLnCl₆ into the transparent host crystal Cs_2NaYCl_6 leads to a closer approximation to k=0 selection rules, with the disappearance of certain features which are present in the vibronic spectra of Cs₂NaLnCl₆. By contrast, the guest Cs₂NaLnCl₆ modes lie within the bands of host Cs₂NaGdCl₆ modes, so that the vibronic spectra of Cs₂NaGdCl₆:Ln³⁺ and Cs₂NaLnCl₆ are very similar except for minor energy shifts of features. This phenomenon is observed more clearly for the later members of Cs₂NaLnCl₆ which retain the cubic structure at low temperature, for example, the ${}^{5}S_{2} \rightarrow {}^{5}I_{7}$ emission spectra of Ho³⁺ in (a) Cs₂NaYCl₆:Ho³⁺ and (b) Cs₂NaGdCl₆:Ho³⁺ are displayed in Fig. 12 [185]. The Ho^{3+ 5}S₂(Γ_3) level is at 18365 cm⁻¹. Several transitions to the ⁵I₇ CF levels (located between 5118-5270 cm⁻¹) overlap in the spectral region 13300-12800 cm⁻¹, but we do not discuss these in detail [185], and focus on the individual vibronic band shapes. The band marked 0–0 is the electronic origin ${}^{5}S_{2}(\Gamma_{3}) \rightarrow {}^{5}I_{7}(a\Gamma_{4})$. The v_6 vibronic origin (labelled 6) of this transition has a more prominent high energy shoulder (6') in the Cs₂NaGdCl₆ host. Similarly, v_4 (4) also has a more prominent low energy shoulder (4'), and v_3 [(3)—also shown in the lowest energy band, $\Gamma_3 \rightarrow b\Gamma_4 + v_3$] has two accompanying bands (3' and 3") in the Cs₂NaGdCl₆ host. The characteristic (changes in) band shapes thus aid the assignments of vibronic structure. By contrast, the electronic spectra of Cs₂LiLnCl₆ and Cs₂NaLnCl₆ show considerable differences in the displacement energies of vibronic structure from a particular electronic origin (Fig. 9a,b) because the LnCl₆³⁻ vibrational frequencies are rather different, particularly for S_8 (Table 2). Since these systems differ only by changes in the Ln³⁺ third-nearest neighbour, the changes in the electronic energy levels of Er³⁺ are minor. Thus, chemical modification techniques have been used to locate and identify electronic energy levels by subtle differences in vibronic fingerprints. The comparison of analogous vibronic structure in the luminescence and absorption spectra of Cs₂NaLnX₆ (X=Cl, Br, F) has also been employed to aid spectral assignments (see, for example, [185, 187]). Vibronic intensity calculations have seldom been used to assign electronic transitions, but rather for comparison of their agreement with observed spectral intensity assignments.

The actual assignment of *individual* fine structure within vibronic peaks in the spectra of M_2ALnX_6 is by no means clear at present. Comparison of the vibronic spectra of Cs₂NaYbCl₆ (Fig. 4d) and Cs₂NaErCl₆ (Fig. 9a) shows that more detailed structure is observed in the former case, due to greater phonon dispersion. Chodos and Satten calculated the dispersion curves and phonon density of states for Cs₂UBr₆, and used these to model the Γ_{4u} (T_{1u}) and Γ_{5u} (T_{2u}) vibronic sidebands. It is interesting to compare the results for this system [184, 188] with the elpasolite dispersion curves [100] and vibronic spectra, because both systems crystallize in the Fm3m space group and comprise LX₆ units. However the electron-phonon coupling for the actinide system is about an order of magnitude greater than for the lanthanide system. Bron [189] has pointed out that in general, intraconfigurational f^Nf^N transitions are coupled to nonlocalized vibrations as well as to localized vibrations. The τ_{1u} vibrational fields are longer range than τ_{2u} , (or α_{2u} , ϵ_{u} [190]) so that the model of Chodos and Satten confined the τ_{2u} field to motions of the 6 nearest Br and 8 next-nearest Cs nuclei. First, we consider the similarities between the results for Cs₂UBr₆ and the vibronic spectra of elpasolites, with Cs₂NaYbCl₆ as an example. At high energy, in Fig. 4c,d, the features at 258, 277 cm⁻¹ correspond to TO and LO modes, with the latter exhibiting greater dispersion. Weak bands at 209, 219 cm⁻¹ in Fig. 4c, d are similar to the weak double-hump in Cs_2UBr_6 from the k=0 ϵ_g mode at points Z_1 , W_2' . There are three major features both in Cs_2UBr_6 and $Cs_2NaYbCl_6$ in the region of v_4 . The highest energy band (130 cm⁻¹) has previously been assigned to the LO mode, but the calculated LO-TO splitting is rather smaller [191] and the band can gain intensity from the k=0 v_5 mode at special points in the reciprocal lattice. The major peak in the τ_{2u} projected density of states in Cs_2UBr_6 has four components, with the lowest energy of these being associated with the k=0 mode in [184]. In the elpasolite vibronic sideband, the v_6 k=0 band has been assigned to the stronger peak, which has a prominent low energy shoulder. This weakens in the Cs₂NaYCl₆:Ln³⁺ systems, but becomes stronger in systems which undergo the phase transition to C_{4h}^{5} . The major problem in the assignment of structure is whether the peaks in the vibronic spectra correspond to k=0 modes, with the work of Satten concluding that this is not the case. The assignments of the v_4 and v_6 vibrations in Table 2, from the vibronic spectra of Cs₂NaLnCl₆ would be ca. 5 cm⁻¹ and 8 cm⁻¹ too high, respectively if we follow the model assignments of Chodos and Satten.

Some differences in the vibronic sidebands of $Cs_2NaLnCl_6$ and Cs_2UBr_6 are the sharp peak at 290 cm⁻¹ in the former spectrum (Fig. 4c,d) which corresponds to the flat v_1 mode at special points, and the weak feature at 178 cm⁻¹ due to third shell motion. The low-vibrational-energy shoulder on v_3 (at 245 cm⁻¹, Fig. 4c,d and 3' in Fig. 12) is characteristic of $Cs_2NaLnCl_6$ systems and could correspond to τ_{1u} modes at special points such as X_4^- , X_5^- . The assumption has been made that the vibronic sideband is one-pho-



Fig. 12 488 nm excited 12–15 K luminescence spectra of $Cs_2NaYCl_6:Ho^{3+}$ (*top*) and $Cs_2NaGdCl_6:Ho^{3+}$ (*bottom*) between 13,300 and 12,800 cm⁻¹. The zero phonon lines are marked 0–0. The numbers i=3,4,6 indicate the vibrational modes v_i in the sidebands. (Adapted from [185])

non in nature [179]. Otherwise, the 245 cm^{-1} band could be associated with several two-phonon modes.

Finally, the assignment of electronic energy levels from $f^{N}-f^{N}$ electronic spectra can strengthened by techniques such as the vibronic Zeeman effect [192], MCD, MCPE, and the use of high pressure, but these have not been systematically employed. ESA measurements could be employed to locate (congested) levels at energies >20,000 cm⁻¹. Ground state term energies have been determined from complementary techniques such as electronic Raman spectra [91], inelastic scattering of neutrons [60, 106, 107], magnetic measurements [28, 193, 194], electron spin resonance [42, 195, 196], nuclear magnetic resonance [44, 197] and electron spin-lattice relaxation [198] for comparison with the results from electronic spectroscopy. TP spectroscopy (see Sect. 10) has proved to be a valuable tool in extending the energy level datasets of rare earth ions. Generally, the assignment of energy levels goes hand-in-hand with the refinement of the energy level calculations.

8 Electronic Raman Spectra

At room temperature, the Raman spectra of cubic lanthanide elpasolites comprise four bands, corresponding to the S_1 , S_2 , S_4 and S_5 modes of vibration. On cooling, the very broad, unresolved features due to electronic transitions between CF levels of Ln^{3+} , sharpen and reveal the locations of $4f^N$ excited states. The first studies of the electronic Raman spectra therefore focused upon the determination of the CF levels of the lower multiplet terms



Fig. 13 35 K Raman spectrum of $Cs_2NaCeCl_6$ using argon ion laser excitation. Note the change of scale for the 2661 cm⁻¹ band. (Adapted from [92])

of Ln^{3+} in the elpasolite lattices, and the fitting of these levels by CF theory [88, 93, 94, 147, 199–201]. Figure 13 shows the usefulness of the electronic Raman technique in completely and unambiguously identifying the f¹ energy level structure of Ce³⁺ in Cs₂NaCeCl₆ [92] (shown in Table 6 and subse-

Transition	Energy	Electronic Raman scattering intensity ^a						
trom ² F _{5/2} l ² ₇	(cm ⁻¹)	Observed	Theoretical	JOA-1	JOA-2	Direct		
${}^{2}F_{5/2}\Gamma_{8}$	562,580	4.2±0.5	$0.2449 F_2 ^2+0.2073 F_1 ^2$	4.2	4.2	4.2		
${}^{2}F_{7/2}\Gamma_{7}$	2161	0.16 ± 0.01	$0.0078 F_1 ^2$	0.00	0.04	0.25		
${}^{2}F_{7/2}\Gamma_{8}$	2662	0.86±0.07	$0.0227 F_2 ^2+0.0058 F_1 ^2$	0.39	0.31	1.52		
${}^{2}F_{7/2}\Gamma_{6}$	3050	1.00	$0.0181 F_2 ^2$	0.31	0.22	1.27		

Table 6 Experimental and calculated electronic Raman transition intensity ratios for Ce^{3+} in $Cs_2NaCeCl_6$

Data taken from [203] and [91]. JOA-1, standard Judd-Ofelt-Axe calculation using F_1 =0.00, F_2 =4.13; JOA-2, standard JOA calculation using F_1 =2.38, F_2 =3.5; Direct, direct calculation

quently discussed in Fig. 17), since all intraconfigurational electronic Raman transitions are allowed from the Γ_7 electronic ground state. Note that although Cs₂NaCeCl₆ undergoes the phase transition at 178 K [41], no vibrational splittings are observed at 35 K, and only the electronic level ${}^2F_{5/2}$ Γ_8 exhibits a resolved splitting into two Kramers doublet levels.

More recent interest has focused upon the interpretation of the relative intensities of the electronic Raman transitions. The theory of electronic Raman spectroscopy has been well-summarized elsewhere [63, 202], and the electronic Raman scattering amplitude from an initial $|\psi_i\rangle$ to a final $|\psi_f\rangle$ vibronic state (where the phonon states are the same, and usually zero-phonon (i.e. electronic) states) is given by $\langle \psi_f | \alpha_{\rho\sigma} | \psi_i \rangle$. In this expression, the cartesian polarizations of the incident photon $(hc\bar{v})$ and the scattered photon $(hc\bar{v}_s)$ are σ and ρ , respectively. The Cartesian electronic Raman scattering tensor is written as

$$\alpha_{\rho\sigma} = -\sum_{r} \left[\frac{\mathbf{D}_{\rho}^{(1)} |\psi_{r}\rangle \langle \psi_{r} | \mathbf{D}_{\sigma}^{(1)}}{hc(\bar{v}_{r} - \bar{v})} + \frac{\mathbf{D}_{\sigma}^{(1)} |\psi_{r}\rangle \langle \psi_{r} | \mathbf{D}_{\rho}^{(1)}}{hc(\bar{v}_{r} + \bar{v}_{s})} \right]$$
(49)

where ψ_r is a vibronic state [63] with opposite-parity to the f^N states ψ_i and ψ_f , usually taken from the $4f^{N-1}5d$ and $4f^{N-1}5g$ configurations. The Cartesian tensor is expressed as a linear combination of spherical tensors, which in turn may be expressed in terms of unit tensors and scattering parameters [91]. By invoking the Judd closure approximation in the Judd-Ofelt-Axe formalism, the relative electronic Raman scattering intensities can be expressed in terms of just two parameters, F_1 and F_2 , which are further inter-related if the intensity is entirely contributed by the $4f^{N-1}5d$ configuration. Based upon this simple model, the relative intensities of electronic Raman bands were calculated for various $Cs_2NaLnCl_6$ systems (Ln=Ce, Pr, Eu, Er, Tm and Yb). The observed and calculated relative intensities for Ln=Ce are shown in Table 6 and are reasonably well-fitted by the two parameters. The experimental values are from integrated band intensities using polycrystalline ma-

terial, so that the calculated intensities are averaged over all polarizations. For some other Ln^{3+} elpasolite systems, the electronic Raman band relative intensities were considerably over-estimated, and this was attributed to the matching of the energy gap between the upper level ψ_f and the next lower f^N level with (multiple) quanta of phonons of the appropriate symmetry [91]. Fast multiphonon relaxation can then occur which shortens the excited state lifetime.

Other features of interest in the electronic Raman spectra of these systems [91] are the occurrence of an excited-state electronic Raman transition in $Cs_2NaTmCl_6$ when the excited state is thermally populated; and of *D*-term [63] resonance electronic Raman scattering.

The validity of the Judd closure approximation, where an entire configuration degeneracy is taken, with an effective energy barycentre, is more stringently tested in the electronic Raman calculations than in the conventional electric dipole intensity calculations because only two variable parameters are employed. However, the use of this approximation serves as a 'black box' approach and does not give insight into the intensity mechanisms of electronic Raman transitions. The direct calculation, presented first for TmPO₄ by Xia [204], utilizes the detailed energy eigenvectors and eigenvalues of intermediate CF states, and the results for the electronic Raman relative intensities of Ce³⁺ are somewhat improved from the JOA calculation [203] (Table 6). However, the performance of the direct calculation suffers from the problem that the opposite parity intermediate states have not yet been well-characterized for Ln³⁺ systems. A strategy has therefore been employed in which, for example for Pr^{3+} in $Cs_2NaPrCl_6$ [205], the direct products of the CF 4f¹ core states and 5d¹ CF states are employed, but the electrostatic interaction between the 4f¹ core and the 5d¹ electron is neglected. The appropriate energies may be estimated from the CF levels of Ce³⁺ in Cs₂NaCeCl₆. Some serious discrepancies between experimental and calculated intensities remain when using this approach [205], which are more likely to be due to the inaccurate wave functions employed for the 4f¹5d¹ intermediate states, rather than to the failure to include states from 4f¹5g¹. Neglecting the latter configuration, then for the electronic Raman transitions from the ${}^{3}H_{4}\Gamma_{1g}$ electronic ground state of Pr^{3+} , it follows from the consideration of the selection rule for the ED allowed transition to the intermediate state Γ_r (i.e. $\Gamma_{1g} \times \Gamma_{4u} \times \Gamma_r$ contains Γ_{1g}) that the r is one or more of the 18 Γ_{4u} 4f¹5d¹ CF states. A detailed energy level calculation of the 4f¹5d¹ configuration which includes electrostatic interactions [206] shows that the large CF leads to more extensive mixing of SLJ states than is the case for the 4f² configuration [207]. However, when utilizing these more accurate intermediate state wave functions for some transitions, specific intensity sources can be pinpointed for certain electronic Raman transitions [208].

9 Electron-phonon Mixing of States

Chodos [103] said that the electron-phonon interaction can be thought of as the changing crystalline field due to the neighbouring nuclear vibrations. Thus, Henderson and Imbusch [116] write the electron-phonon interaction as the first term in the power series the crystal strain, and show how it modifies a $4f^N$ electron wavefunction by introducing opposite-parity ones. Actually, the electron-phonon coupling takes part in many phenomena, including the shapes and widths of spectral lines, and relaxation rates, in addition to vibronic sidebands. However, the vibronic coupling between the lanthanide ion and the lattice is generally weak [116].

Malta [167] has described the case when a vibronic state is in resonance with a pure electronic state, and it was found that depending upon the strength of the vibronic interaction, the admixture between these levels can lead to nearly equal spectral intensities. In fact this phenomenon was observed previously in the ${}^{3}P_{0}(\Gamma_{1}) \rightarrow {}^{3}F_{2}$ luminescence spectra of $PrCl_{6}{}^{3-}$ [147], where an apparent doubling of features occurred. It is also responsible for the anomalous behaviour in the Raman spectrum of Cs₂NaYbCl₆ [91]. We consider here only the Cs₂NaTmCl₆ system, where it has contributed to the disputed assignments of the ${}^{3}H_{6}$ ground term of Tm³⁺ in TmCl₆³⁻, so that the experimental and calculated energy level schemes were apparently in disagreement [209–213].

The experimentally measured ${}^{3}H_{6}$ energy levels are located (in cm⁻¹) at 0, 56, 108, 148, 261, 370 and 394 (Fig. 14a) from the low temperature TmCl_6^{3-} luminescence spectra of transitions terminating upon the electronic ground state. The two energy levels (measured at 10 K at 108 and 148 cm⁻¹) are in fact derived from the resonance of the ${}^{3}H_{6}a\Gamma_{5}$ (T_{2g}) CF level, through electron-phonon coupling with the vibronic level ${}^{3}H_{6}\Gamma_{1} + v_{5}(\tau_{2g})$. This resonance can be turned on or off by the action of heat [91] or pressure [214]. At room temperature, the energy of v_5 is 132 cm⁻¹. At 120 K, the band in the Ar⁺ ion laser excited Raman spectrum at 128 cm⁻¹ develops a high energy shoulder at 144 cm⁻¹ [91], and on further cooling these features become more widely separated and clearly resolved. The simplest model of the interaction of the $a\Gamma_5$ electronic and $\Gamma_1 + v_5$ vibronic states utilizes first order perturbation theory (a more accurate theoretical treatment of these phenomena is given in [215]) and the corrected electronic energy at 10 K is shown at 123 cm^{-1} in Fig. 14a, with the experimental energies as dotted lines. The interaction matrix element is some tens of cm⁻¹ [91]. This interaction has also been probed by the use of high pressure at ambient temperature [214], but in this case only one band is observed-for example, at 2.7 GPa, the blue-shifted $\Gamma_1 + v_5(\tau_{2g})$ coupled mode is at 143 cm⁻¹. The lower-energy coupled mode, mainly of electronic character, is line-broadened at room temperature and not resolved from the background. Figure 14b shows the shifts to high ener-



Fig. 14a–c Electron-phonon coupling in $Cs_2NaTmCl_6$: a energy levels of Tm^{3+} at 10 K (see Sect. 9); b 295 K Raman spectra at stated pressures; c integrated areas of moiety mode Raman bands as a function of pressure. (Adapted from [214])

gy of the three Raman-active moiety modes of TmCl_6^{3-} as the pressure is increased. The integrated areas of the bands at different pressures are plotted in Fig. 14c, and the band areas of the $v_2(\epsilon_g)$ and $v_1(\alpha_{1g})$ modes do not show a noticeable change. The area of the coupled $\Gamma_1+v_5(\tau_{2g})$ mode decreases at 11–

12 GPa, but then increases at 13 GPa. This has been attributed to a redistribution of intensity between the resonant vibronic and electronic states when the electron-phonon coupling is greater (between 11–12 GPa), followed by the commencement of decoupling of the electronic and vibronic states, at 13 GPa. A further example of the resonance between pure electronic and vibronic states has been found for the ${}^{3}\text{H}_{4}\Gamma_{4}$ CF level of this system, which couples with ${}^{3}\text{H}_{4}\Gamma_{5}+\nu_{2}(\epsilon_{g})$ [213].

Further examples of the coupling of vibronic states involving gerade moiety modes with CF states have been found in studies of the TP spectra of $Cs_2NaTbCl_6$ [216].

10 One and Two Colour Two-photon 4f^N-4f^N Spectra

The CF energy levels of some M_2ALnX_6 systems become congested above ~20,000 cm⁻¹, so that the overlapping of electronic and vibronic transitions in the ultraviolet absorption spectrum makes assignments ambiguous in many cases. The use of TP excitation in several cases, using spectral regions where one-photon excitation corresponds to an open window, has enabled detailed energy level datasets to be assigned. The assignments are especially clarified by the use of single crystals with plane-polarized radiation and applied magnetic fields.

TP transitions within a $4f^N$ configuration involve intermediate states belonging to opposite parity configurations, such as $4f^{N-1}5d$, $4f^{N+1}4d^9$, $4f^{N-1}5g$ configurations, etc., but usually only the first of these is considered because it lies at a much lower energy than any other opposite parity configuration.

In general for two-colour TP transitions, where $hc\bar{v}_1$ and $hc\bar{v}_2$ are the photon energies, with cartesian polarizations ρ and σ , the relevant second- (i.e. the lowest), third- and fourth-order terms for the transition elements M_{if} between the ground state and the final state are as follows respectively [217– 220]:

$$-\sum_{n}\left[\frac{\langle\psi_{f}|\mathbf{D}_{\rho}^{(1)}|\psi_{n}\rangle\langle\psi_{n}|\mathbf{D}_{\sigma}^{(1)}|\psi_{i}\rangle}{hc(\bar{v}_{n}-\bar{v}_{2})}+\frac{\langle\psi_{f}|\mathbf{D}_{\sigma}^{(1)}|\psi_{n}\rangle\langle\psi_{n}|\mathbf{D}_{\rho}^{(1)}|\psi_{i}\rangle}{hc(\bar{v}_{n}-\bar{v}_{1})}\right]$$
(50)

$$\sum_{m,n} \left[\frac{\langle \psi_f | \mathbf{D}_{\rho}^{(1)} | \psi_m \rangle \langle \psi_m | V' | \psi_n \rangle \langle \psi_n | \mathbf{D}_{\sigma}^{(1)} | \psi_i \rangle}{(hc)^2 (\bar{\mathbf{v}}_m - \bar{\mathbf{v}}_2) (\bar{\mathbf{v}}_n - \bar{\mathbf{v}}_2)} + \frac{\langle \psi_f | \mathbf{D}_{\sigma}^{(1)} | \psi_m \rangle \langle \psi_m | V' | \psi_n \rangle \langle \psi_n | \mathbf{D}_{\rho}^{(1)} | \psi_i \rangle}{(hc)^2 (\bar{\mathbf{v}}_m - \bar{\mathbf{v}}_1) (\bar{\mathbf{v}}_n - \bar{\mathbf{v}}_1)} \right]$$
(51)

$$-\sum_{l,m,n} \begin{bmatrix} \frac{\langle \psi_{f} | \mathbf{D}_{\rho}^{(1)} | \psi_{l} \rangle \langle \psi_{l} | \mathbf{V}'' | \psi_{m} \rangle \langle \psi_{m} | \mathbf{V}' | \psi_{n} \rangle \langle \psi_{n} | \mathbf{D}_{\sigma}^{(1)} | \psi_{l} \rangle}{(hc)^{3} (\bar{v}_{l} - \bar{v}_{2}) (\bar{v}_{n} - \bar{v}_{2})} \\ + \frac{\langle \psi_{f} | \mathbf{D}_{\sigma}^{(1)} | \psi_{l} \rangle \langle \psi_{l} | \mathbf{V}'' | \psi_{m} \rangle \langle \psi_{m} | \mathbf{V}' | \psi_{n} \rangle \langle \psi_{n} | \mathbf{D}_{\rho}^{(1)} | \psi_{l} \rangle}{(hc)^{3} (\bar{v}_{l} - \bar{v}_{1}) (\bar{v}_{n} - \bar{v}_{1}) (\bar{v}_{n} - \bar{v}_{1})} \\ + \frac{\langle \psi_{f} | \mathbf{D}_{\rho}^{(1)} | \psi_{l} \rangle \langle \psi_{l} | \mathbf{V}' | \psi_{m} \rangle \langle \psi_{m} | \mathbf{V}' | \psi_{n} \rangle \langle \psi_{n} | \mathbf{D}_{\sigma}^{(1)} | \psi_{l} \rangle}{(hc)^{3} (\bar{v}_{l} - \bar{v}_{2}) (\bar{v}_{n} - \bar{v}_{2})} \\ \frac{\langle \psi_{f} | \mathbf{D}_{\sigma}^{(1)} | \psi_{l} \rangle \langle \psi_{l} | \mathbf{V}' | \psi_{m} \rangle \langle \psi_{m} | \mathbf{V}'' | \psi_{n} \rangle \langle \psi_{n} | \mathbf{D}_{\rho}^{(1)} | \psi_{l} \rangle}{(hc)^{3} (\bar{v}_{l} - \bar{v}_{1}) (\bar{v}_{n} - \bar{v}_{1})} \end{bmatrix}$$

$$(52)$$

In these expressions, $|\psi_i\rangle(i=l,m,n)$ refer to intermediate states within the 4f^{N-1}5d configuration; and $hc\bar{v}_i$ (*i*=*l*, *m*, *n*) are the energies of these states above the ground state energy; V' and V'' can be the spin-orbit or the CF operator, acting between intermediate states.

The mechanism of the TP transition, which is principally a second-order process, involves an ED transition from the initial state to an intermediate state (with or without resonance), and thence another from the intermediate state to the final state [221]. However, the states and energies in Eqs. (50)–(52) are only eigenstates and eigenvalues of the zero-order Hamiltonian H_0 in a stationary perturbation treatment, in which the complete Hamiltonian is

$$H = H_0 + V' + V'' + \dots$$
(53)

where H₀ includes the central field Hamiltonian and the Coulomb interaction between the 4f electrons, V=V'+V''+... is the perturbation Hamiltonian which includes the spin-orbit and CF interactions, and the electrostatic interaction between the (N-1) 4f electrons and the 5d electron which is often ignored. The Judd-Pooler [218] type perturbation calculation (50, 51) and Judd-Pooler-Downer [220] type perturbation calculation (50-52), both use eigenstates of the zeroth-order Hamiltonian H₀ within the 4f^{N-1}5d configuration, but the relevant energies $hc\bar{v}_i$ (*i=m*, *l...*) are approximately taken to be degenerate, somehow like using the closure approximation. By contrast, in the direct calculation, the intermediate eigenstates $|\phi_N\rangle$ and eigenvalues $hc\bar{v}_N$ of the complete Hamiltonian, H, are used within the 4f^{N-1}5d configuration, as well as within the 4f^N configuration, and only the second-order expression (obtained from Eq. 50 by changing $|\psi_n\rangle$ and $hc\bar{v}_n$ to be $|\phi_N\rangle$ and $hc\bar{v}_N$, respectively) needs to be evaluated.

The *SLJ* selection rules for the second-order Axe process are listed in Table 1. Note that by the contraction of the expression at Eq. (50) using Judd closure, the transitions of the type $\Gamma_{1g} \rightarrow \Gamma_{1g}$ become forbidden. Inclusion of the CF operator in the third-order expression $[V'=H_{CF}$ (Eq. 51)] widens the *SLJ* selection rule to $\Delta S=0$; $|\Delta J| \leq 6$; $|\Delta L| \leq 6$, whereas for $V'=H_{SO}$ in (51), $\Delta S=1$; $|\Delta J| \leq 2$; $|\Delta L| \leq 3$. The 4th-order expression at Eq. (52) leads to the selection rules $\Delta S=1$; $|\Delta J| \leq 6$; $|\Delta L| \leq 6$.

Thus far, the experimental investigations of TP spectra of M₂ALnX₆ have utilized the more sensitive technique of excitation spectra rather than ab-



Fig. 15a, b Two-photon excitation spectra of a single crystal of $Cs_2NaTbCl_6$ at ca. 6 K: **a** in two linear polarizations making the angle indicated to [100]; **b** in the presence of a 4.5 T field along [110]. The *inset* shows the ⁵D₄ energy level scheme of Tb³⁺ in this system. (Adapted from [223])

sorption spectra, and have used one colour. Nevertheless, unlike the onephoton spectra of these cubic systems, studies employing TP excitation can distinguish the symmetry of the terminal state in a particular transition. In the case of a nondegenerate Γ_{1g} electronic ground state, transitions are allowed to Γ_{1g} , Γ_{3g} and Γ_{5g} terminal states for one-colour TP excitation (Table 1), with additional transitions to Γ_{4g} excited states for the two-colour case [221, 222]. Using one-colour radiation along the *z* axis, linearly polarized along the *x* axis, $\Gamma_{1g} \rightarrow \Gamma_{1g}$ transitions do not show a polarization dependence; $\Gamma_{1g} \rightarrow \Gamma_{5g}$ transitions are forbidden, and $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transitions exhibit maximum intensity. With *xy* polarized radiation, the intensity of $\Gamma_{1g} \rightarrow \Gamma_{5g}$ is at a maximum, whereas that of $\Gamma_{1g} \rightarrow \Gamma_{3g}$ transitions decreases by a factor of four. Figure 15a shows the experimental polarization dependence of the $(^7F_6)\Gamma_{1g} \rightarrow (^5D_4)\Gamma_{1g}$, Γ_{3g} , Γ_{5g} one-colour TP transitions of Tb³⁺ in Cs₂NaTbCl₆ [223]. Although $\Gamma_{1g} \rightarrow \Gamma_{2g}$ transitions are forbidden, the hot transitions such as those from Γ_{4g} initial states of the ground multiplet term to Γ_{2g} states are allowed, and in variable temperature studies the relevant states can be populated. Figure 15b shows that the application of a magnetic field can confirm the degeneracy of excited states (first order Zeeman effect) and introduce intensity into transitions that are forbidden in the absence of the magnetic field (second order Zeeman effect) [221]. For even-electron systems, first-order Zeeman splittings only occur in Γ_4 and Γ_5 states. The second-order effect is sensitive to the orientation of the crystal axes relative to the magnetic field direction [224]. When second-order interactions are small, experimental g-values can be used to distinguish between states of the same symmetry [224].

From Fig. 15 it is evident that the TP spectra of M_2ALnX_6 consist of a few sharp lines, due to transitions between CF states, which are uncluttered by vibronic structure. This situation is distinct from, and complementary to, one-photon studies. Sztucki [225, 226] has presented a theory of TP vibronic transitions and anticipated the observation of some weak lines in TP spectra induced by even-parity vibrations in the case of ED-ED TP absorption, and odd-parity vibrations for ED-MD TP transitions. The observation of the former is clear from the studies of Denning et al. [212, 216, 227-230], but the observation of the latter is less certain [231]. Certainly, the appearance of vibronic structure can complicate the assignments of spectral features in TP spectra, especially when resonances occur between vibronic and pure electronic levels, as discussed in the previous section [216]. When polarization or Zeeman studies cannot be performed, it may be difficult to assign the bands in TP spectra because they lack the confirmatory vibronic fingerprints of one-photon spectra. Furthermore, since the excitation spectral technique is utilized, absorption by an impurity ion might occur and subsequently lead to emission in the (broad) spectral range being monitored. In fact, the impurity ion might otherwise transfer the excitation to the majority species by ET. Alternatively, ESA might occur at the pump energy. Such problems have been encountered in the TP excitation spectra of Cs₂NaYCl₆:Sm³⁺ [229], Cs₂NaTbCl₆ [216] and Cs₂NaYCl₆:Tm³⁺ [212], where some spectral features are unexplained.

The first studies of the TP spectra of M_2ALnX_6 systems were carried out on neat $Cs_2NaGdCl_6$, since the energy level scheme of the f^7 ion Gd^{3+} has a transparent window up to almost 32000 cm⁻¹ [232–234]. This was followed by more extensive studies of Cs_2NaTbX_6 (X=F, Cl, Br) [216, 223, 227, 230], $Cs_2NaEuCl_6$ and $Cs_2NaYF_6:Eu^{3+}$ [228], $Cs_2NaYCl_6:Sm^{3+}$ [229] and $Cs_2NaYCl_6:Tm^{3+}$ [212] by Denning's group.

The theoretical calculation of TP intensities has been called unreliable [224], but semiquantitative agreement with experiment has recently been achieved. A particular difficulty was experienced with $\Gamma_1 \rightarrow \Gamma_1$ transitions since the calculated intensity is zero under second-order treatments. Ceulemans and Vandenberghe [71, 235, 236] considered the third and fourth-order analyses of TP transitions in cubic lattices, and utilized a fourth-order

scheme incorporating spin-orbit coupling and CF interactions to analyse the $^7F_6{\rightarrow}^5D_4$ transition of Tb^{3+} in $Cs_2NaTbCl_6.$ Subsequently it was proposed from a direct calculation that the $({}^{7}F_{6})\Gamma_{1} \rightarrow ({}^{5}D_{4})\Gamma_{1}$ TP transition is actually a third-order rather than a fourth-order process [237], and the calculated line strength was found to be sensitive to the location of the intermediate levels. Reid et al. [238] have previously demonstrated the equivalence of direct and Judd-Pooler -type perturbation calculations for calculating TP transition intensities, provided that the appropriate eigenstates and eigenvalues are employed. In the direct calculation of the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition intensity [237] the pure Russell-Saunders multiplets for the initial and terminal state wavefunctions were employed (thereby neglecting the SL- and J- admixtures), and only the lowest-energy intermediate states of $4f^{7}5d^{1}$ were considered. Ligand-metal couplings were not included [239, 240]. More recently, a secondorder direct calculation of 18 TP transitions of Tb³⁺ in Cs₂NaTbCl₆ has been performed, and closer agreement with experiment was obtained for the intensity of the $\Gamma_{1g} \rightarrow \Gamma_{1g}$ TP transition, because CF wavefunctions were used for the 4f⁸ states, and rather exact wavefunctions for 4f⁷5d states [241]. The wavefunctions of the initial and final states of the 4f⁸ system were expressed in terms of Russell-Saunders coupled wavefunctions, with one f-electron coupled to the 4f⁷ core. For the 4f⁷5d intermediate configuration, the free ion and CF wavefunctions of 4f⁷ (Gd³⁺) were employed, and combined with the CF wavefunctions of the excited 5d¹ configuration of Ce³⁺, to give direct product type intermediate state wavefunctions. This treatment neglects the electrostatic interaction between the 4f⁷ core and the 5d-electron. The results of this calculation for the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition are shown in Table 7, which compares the calculated transition linestrengths for two polarizations with the experimental values. It is observed that a considerable difference exists for the calculations using free ion and CF wavefunctions for the 4f⁷ core configuration, with the latter giving better agreement.

In previous calculations [235, 237] only the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition channel was considered, but other wavefunctions are admixed (to small extents) into ${}^{7}F_{6}$ and ${}^{5}D_{4}$, so that *other* channels ${}^{7}F_{6} \rightarrow {}^{7}F_{4}$, ${}^{5}F_{4}$, ${}^{3}F_{4}$; ${}^{5}G_{6} \rightarrow {}^{5}D_{4}$, ${}^{7}F_{4}$, ${}^{5}F_{4}$, ${}^{3}F_{4}$; and ${}^{7}F_{4} \rightarrow {}^{5}D_{4}$, ${}^{7}F_{4}$, ${}^{5}F_{4}$, ${}^{3}F_{4}$ may contribute to the intensity. In fact, the dominant contributions are found to be ${}^{7}F_{4} \rightarrow {}^{7}F_{4}$ and ${}^{7}F_{6} \rightarrow {}^{7}F_{4}$, and *not* the nominal ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$. As mentioned above for the vibronic intensity calculations, the accuracy of the wavefunctions and energies employed is the key factor in obtaining agreement between theory and calculation.

The direct calculation method has also been applied to the calculation of transition linestrengths and intensity ratios of the $({}^{7}F_{0})\Gamma_{1g} \rightarrow ({}^{5}D_{2})\Gamma_{3g}$, Γ_{5g} and $({}^{7}F_{0})\Gamma_{1g} \rightarrow ({}^{5}L_{6})\Gamma_{1g}$, $a\Gamma_{5g}$ TP transitions of Eu³⁺ in the cubic Cs₂NaYF₆ host [70, 243]. The calculated relative intensities for the former transition were in reasonable agreement with experiment and the neglect of *J*-mixing in the initial state only had a minor effect. However, the neglect of spin-orbit

Table 7 Cá	alculated and ϵ	experimental two	-photon transitic	on intensities fo	or the ${}^{/}F_{6} \rightarrow {}^{3}D_{4}$ t	ransition of	Tb ³⁺ in Cs ₂	NaTbCl ₆ (from [241])
⁵ D ₄ final state ^a	Energy (cm^{-1})	Calculated (rel	ative) transition	linestrength ^b		Observed along [10	intensities 1 0]	or incident radiation propagating
		Using free-ion for 4f ⁷ configu	wavefunctions ration	Using CF wav for 4f ⁷ config	e-functions uration	Relative ^c		Polarization orientation averaged, corrected for depolarization ^d
		$\theta=0^{\circ}$	$\theta = 45^{\circ}$	$\theta = 0^{\circ}$	$\theta = 45^{\circ}$	$\theta=0^{\circ}$	$\theta = 45^{\circ}$	Absolute (×10 ⁵)
Γ_{lg}	20,470	60(11.0)	60(11.0)	77(11.0)	77(11.00)	11.0	11.0	11.0
Γ_{3g}°	20,500	2.89(0.53)	0.73(0.13)	77(11.0)	20(2.86)	1.87	1.10	2.1
Γ_{5g}	20,553	0(0.0)	26(4.77)	0(0.0)	8(1.14)	0.33	0.99	1.5
^a The initi	al state is $(^7F_6$) Γ_{1g} in all cases						

^b In units of $(10^{-14} \text{ cm}^2/4\text{f}|r|5d)^4/h^2c^2)$. θ is the angle that the radiation electric vector makes with [001]

^c Measured by integration of the hard copy spectra in [242]. These results are semi-quantitative

^d Intensities tabulated in [242]

couplings within the initial and terminal states drastically reduced the transition linestrengths, but did not significantly change the transition intensity ratios. In the case of the latter $({}^{7}F_{0})\Gamma_{1g} \rightarrow ({}^{5}L_{6})\Gamma_{1g}$, $a\Gamma_{5g}$ TP transitions, it is necessary to use intermediate states built from 5d¹ CF states and 4f⁵ core CF (rather than free ion) states in order to obtain satisfactory agreement with experiment.

11 4f^N-4f^{N-1}5d Electronic Spectra

In contrast to intraconfigurational $f^{N}-f^{N}$ transitions of Ln^{3+} , the interconfigurational $f^{N}-f^{N-1}d$ electronic transitions are ED allowed in the first order, with the selection rules given in Table 1. There have been relatively few reports of the f-d electronic spectra of Ln^{3+} although the characterization of $4f^{N-1}5d^{1}$ states, in terms of eigenvalues and eigenvectors is essential for accurate calculations of vibronic, electronic Raman scattering and TP transition intensities. Following earlier studies of the absorption spectra of lanthanide hexahalides [244, 245], Ionova et al. [246] systematized the energies of f-d and charge transfer transitions of LnX_6^{3-} species, with the lowest energies (determined from broad spectral bands of these species in solution at ambient temperatures) for the transitions of $LnCl_6^{3-}$ being shown in Fig. 16.

Theoretical developments [250], the requirements for vacuum ultraviolet phosphors, the search for blue and ultraviolet solid-state lasers, coupled with improvements in the construction of vacuum ultraviolet spectrometers [251] and the easier access to synchrotron radiation, have led to a recent upsurge of interest in $4f^{N}-4f^{N-1}5d^{1}$ spectra of rare earths. Just as in the case of $4f^{N}-4f^{N}$ spectra [207], the $4f^{N}-4f^{N-1}5d^{1}$ spectra of lanthanide ions in octahedral symmetry environments comprise much more detailed structure than in the case of low symmetry systems.

The elpasolite system which has received the most attention is Ce³⁺, and the results of this simplest 5d¹ system are now reviewed. Unlike the 4f configuration, the 5d configuration experiences a CF interaction that is considerably larger than the 5d spin-orbit coupling. In octahedral (O_h) symmetry, the CF splits the 5d¹ configuration into two levels, a triply degenerate $T_{2g}(\Gamma_{5g})$ lower state and a doubly degenerate $E_g(\Gamma_{3g})$ upper state. With the inclusion of the spin-orbit interaction, the splitting of the T_{2g} and E_g states is as shown in Fig. 17. Schwartz and Schatz [252] reported the absorption and MCD spectra of octahedral Ce³⁺ (in the Cs₂NaYCl₆ host) at 6 K. Two electronic transitions were observed in the region between 28,150 to 31,000 cm⁻¹, assigned, in order of increasing energy, to (${}^{2}F_{5/2}$) $\Gamma_{7u} \rightarrow \Gamma_{8g}({}^{2}T_{2g})$ and (${}^{2}F_{5/2}$) $\Gamma_{7u} \rightarrow \Gamma_{7g}({}^{2}T_{2g})$. The transition to the 5d¹(${}^{2}E_{g}$) state was not detected up to 50,000 cm⁻¹, so that $\Delta=10Dq \ge 20,000$ cm⁻¹. van't Spijker et al. [253] did not comment upon these results in their more recent study of Ce³⁺-



Fig. 16 Lowest f-d, charge transfer π -f and π -d transition energies of LnCl_6^{3-} (Adapted from [246]). The *crosses* for Ce, Pr, Nd and Tb represent the lowest 4f^{N-1}5d electronic state in the crystalline elpasolite lattices. (Data from [206, 247–249])

doped elpasolites using room-temperature X-ray excitation, where two room-temperature bands at 48,780 cm⁻¹ and 46,512 cm⁻¹ in Cs₂NaLu-Cl₆:Ce³⁺ were assigned to absorption to the 5d¹(²E_g) state. Features were reported at similar energies in Cs₂NaLnCl₆:Ce³⁺ (Ln=Gd, Y) [254]. Since the state ²E_g transforms as a Kramer's quartet, Γ_{8g} , in O_h symmetry, these bands presumably correspond to the unresolved electronic transitions from the ground ²F_{7/2} and excited ²F_{5/2} terms. Otherwise one of the bands does not correspond to single Ce³⁺ ions in octahedral symmetry. The assignment of higher energy structure, and of features in the synchrotron excitation spectra of Cs₂LiLnCl₆ (Ln=Y, La) [255–257] is not clear. Broad features have been observed in the absorption and emission spectra of Ce³⁺ doped into hexafluoroelpasolites [258, 259], attributed to the presence of several Ce³⁺ sites.



Fig. 17 Energy levels of Ce³⁺ in a Cs₂NaLnCl₆ host crystal (Adapted from [248])

Recently, Laroche et al. [260] have obtained the $4f^{N-1}5d^1 \rightarrow 4f^N$ emission spectra of Cs₂NaYCl₆:Ce³⁺ and Pr³⁺ at 77 K by pumping the ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$ f²-electron absorption bands of Pr^{3+} . The absorption and $({}^{2}T_{2g})\Gamma_{8g}$ emission spectra at 10 K have recently been reported [248] and are shown in Fig. 18a. The electronic origin is coincident in both spectra, but is strongly self-absorbed in the emission spectrum. The lack of mirror-image symmetry between absorption and emission is due to the presence of further transitions, as marked, in emission and absorption. The spectra differ considerably from the $4f^{N}-4f^{N}$ spectra of M₂ALnCl₆ and each transition consists of two strong vibrational progressions (see Sect. 7.3), which in the absence of Jahn-Teller effects, from Table 1 must correspond to totally symmetric modes. The first progression is in the v_1 (Ln-Cl) breathing mode (299±2 cm⁻¹). The second is in a mode of energy 48 ± 2 cm⁻¹, and comparison with the f-d spectra of other systems shows that the energy does not change greatly in the spectra of Cs₂NaTbCl₆, Cs₂NaYCl₆:U³⁺ or Cs₂LiYCl₆:Ce³⁺. This energy is similar to that of the $S_5(\tau_{2g})$ mode, so that the motion is mainly of the second shell LnCs₈.

The bond length change in the f-d excitation process can be calculated for the Ln-Cl and Ln-Cs coordinates by application of Eqs. (27) and (28). It is not clear whether or not to subtract the broad underlying continuum when integrating spectral features (e.g. in Fig. 18a, the maximum for the nv_1 replicas on the zero phonon line is at n=1, but the peak intensity of the groups of bands is at n=2). With subtraction of the continuous background from the spectrum, the bond length change along the Ce-Cl coordinate from



Fig. 18a, b 10 K f-d absorption and emission spectra of Cs_2NaYCl_6 doped with: a Ce^{3+} ; b Pr^{3+} . Refer to Fig. 17 for the identification of the Ce^{3+} transitions. Only the lowest energy absorption and highest energy emission transitions are marked for Pr^{3+} . (Adapted from [206, 248])

the f-electron ground state to the 5d-electron ${}^{2}T_{2g}$ state is calculated to be 0.06 Å, which is <2% of the bond distance. An ab initio calculation based upon the CeCl₆³⁻ cluster [248] gives a similar value, 0.05 Å, and it predicts a bond length contraction in the ${}^{2}T_{2g}$ state.

Ν	SLJ	Irrep	Energy (cm ⁻¹)		
			Expt	Calculated	
				$4f^{2}$	4f²/4f6p
1	${}^{3}H_{4}$	Γ_1	0	38	8
2	$^{3}H_{4}$	Γ_4	242	257	247
3	$^{3}H_{4}$	Γ_3	422	408	411
4	$^{3}H_{4}$	Γ_5	702	683	721
5	$^{3}H_{5}$	$a\Gamma_4$	2300	2310	2297
6	$^{3}H_{5}$	Γ_5	2399	2413	2395
7	$^{3}H_{5}$	Γ_3	2645	2625	2650
8	$^{3}H_{5}$	$b\Gamma_4$	2763	2718	2750
9	$^{3}H_{6}$	Γ_3	4386	4406	4373
10	$^{3}H_{6}$	aΓ ₅	4437	4456	4429
12	$^{3}H_{6}$	Γ_2	4591	4643	4616
13	$^{3}H_{6}$	$b\Gamma_5$	4807	4798	4809
14	$^{3}H_{6}$	Γ_4	4881	4867	4887
11	$^{3}H_{6}$	Γ_1	4942	4897	4922
15	${}^{3}F_{2}$	Γ_3	5203	5224	5195
16	${}^{3}F_{2}$	Γ_5	5297	5282	5305
17	³ F ₃	Γ_4	6616	6634	6605
18	³ F ₃	Γ_5	6621	6628	6621
19	³ F ₃	Γ_2	6682	6686	6703
22	³ F ₄	Γ_1	6902	6913	6909
20	${}^{3}F_{4}$	Γ_3	6965	6994	6982
21	³ F ₄	Γ_4	7012	6967	6979
23	³ F ₄	Γ_5	7278	7260	7265
24	${}^{1}G_{4}$	Γ_1	9847	9766	9841
25	${}^{1}G_{4}$	Γ_4	9895	9852	9897
26	${}^{1}G_{4}$	Γ_3	9910	9901	9921
27	${}^{1}G_{4}$	Γ_5	10,327	10,441	10,328
28	${}^{1}D_{2}$	Γ_5	16,666	16,705	16,670
29	${}^{1}D_{2}$	Γ_3	17,254	17,209	17,248
30	³ P ₀	Γ_1	20,625	20,611	20,611
31	${}^{1}I_{6}$	Γ_1	21,166	21,163	21,169
32	³ P ₁	Γ_4	21,218	21,225	21,218
33	${}^{1}I_{6}$	Γ_4	21,255	21,263	21,254
34	${}^{1}I_{6}$	aΓ ₅	(21,343 ^a)	21,380	21,360
35	${}^{1}I_{6}$	Γ_2	21,788	21,793	21,777
36	${}^{1}I_{6}$	$b\Gamma_5$	21,967	21,971	21,975
37	${}^{1}I_{6}$	Γ_3	22,035	22,024	22,032
38	${}^{3}P_{2}$	Γ_5	22,367	22,387	22,375
39	${}^{3}P_{2}$	Γ_3	22,494	22,491	22,500
40	¹ S ₀	Γ_1	(>39,017 ^a)	45,759	44,880

Table 8 Energy level calculations for Pr^{3+} in the $Cs_2NaPrCl_6$ elpasolite lattice [207]

^a From Cs₂NaYCl₆:Pr³⁺

It is interesting that the emission from the 5d¹ ²E_g state of Ce³⁺ (Fig. 17) has never been reported, and was not observed (near 47,000 cm⁻¹) upon ultraviolet excitation of Cs₂NaYCl₆:Ce³⁺ [248]. However, a group of bands was observed in (neat) Cs₂NaErCl₆ which has been assigned to the ²E_g→²F_{5/2}, ²F_{7/2} transitions of Ce³⁺ impurity [248]. One possibility [248] is that the emission is quenched by transfer to killer sites (such as by transfer to f^{N-1}d electronic states of Nd³⁺ or Pr³⁺ ions) in Cs₂NaYCl₆, which are not as numerous in Cs₂NaErCl₆. Otherwise, it could be that the excited Ce³⁺ ion is oxidized to Ce⁴⁺ by transfer of an electron to the host conduction band. Presumably this does not occur for the trace concentration of Ce³⁺ present in the Cs₂NaErCl₆ host.

In contrast to Ce³⁺, the first bands in the 10 K f-d emission and absorption spectra of Pr³⁺ [206] are separated by more than 1000 cm⁻¹, and the band maxima by 2724 cm⁻¹, Fig. 18b. In this case, the lowest excited f¹d¹ state, Γ_{3u} (of mainly ${}^{3}F_{2}$ and ${}^{3}H_{4}$ character [206, 261]), is not accessible by absorption or emission from/to the (${}^{3}H_{4}$) Γ_{1g} f² ground state. The assignment of the labelled transitions in Fig. 18b: (f¹d¹) $\Gamma_{3u} \rightarrow$ (f²) Γ_{4g} (emission) and (f²) $\Gamma_{1g} \rightarrow$ (f¹d¹) Γ_{4u} , is evident from the f² energy levels of Pr³⁺ (Table 8) and the selection rules in Table 1. Transitions from Γ_{3u} are allowed to terminal Γ_{4g} and Γ_{5g} CF states only, whereas transitions from Γ_{1g} are allowed only to the 18 Γ_{4u} levels of f¹d¹. The 4f¹5d¹ \rightarrow 4f² emission spectra are extensive over a wide spectral range because transitions are observed from the (f¹d¹) Γ_{3u}



Fig. 19 First four groups of bands in the 252.7-nm excited 10 K emission spectrum of $Cs_2NaY_{0.99}Pr_{0.01}Cl_6$. The progressions in v_1 and in the lattice mode are indicated. Zerophonon lines are assigned to terminal *SLJ* states, and the electronic transitions are indicated by *horizontal bars* above the spectra. The *inset* shows the first (*circled*) group of bands in greater detail, with the displacements from the $\Gamma_{3u} \rightarrow \Gamma_{4g}$ origin marked. (Adapted from [206])

state to the ladder of f^2 levels in Table 8. The first groups of bands are shown in Fig. 19, with the inset enlarging the initial $\Gamma_{3u} \rightarrow \Gamma_{4g}({}^{3}H_{4})$ structure. The relative intensities of these ED transitions were evaluated by the first term in Eq. (17), taking into account the mixing of the f^2 and f^1p^1 configurations [206, 207, 261] and are in reasonable agreement with experiment.

The first $4f^3 \rightarrow 4f^25d$ bands of Nd³⁺ in Cs₂NaYCl₆:Nd³⁺ have been investigated by ground-state absorption, as well as by excited-state absorption from the $({}^{4}F_{3/2})\Gamma_{8}$ level at 11,348 cm⁻¹ [247]. The onset of absorption in the former spectrum is above 45,600 cm⁻¹, with the first maximum at 47,600 cm⁻¹. However, unlike the cases of Ce³⁺ and Pr³⁺, no d-f emission is observed for Nd³⁺ in hexachloroelpasolite hosts, because the lowest 4f²5d level is rapidly depopulated by nonradiative relaxation to the f³ levels directly below. This situation differs from YPO₄:Nd³⁺ [262–264] and MYF₄:Nd³⁺ [246, 265, 266] where $4f^25d \rightarrow 4f^3$ emission is observed.

12 Variation Across the Lanthanide Series of Energy Level Parameter Values

One of the outcomes of the spectral analyses is an energy level dataset, as in Table 8, column 'Expt.'. Clearly the most important criterion for the energy level dataset is that no incorrect assignments are included, which lead to spurious parameter values and possibly a poor datafit. Systematic errors between different energy level datasets have often been due to the calibration from "standard air" wavelengths to vacuum wavelengths. These errors are small in the infrared spectral region, but are up to 10–15 cm⁻¹ in the ultraviolet. Since the symmetry representations of energy levels are frequently illdefined, often an experimentally-determined energy level is matched with the closest calculated energy level, and this is more permissible when all levels of a given multiplet term have been identified. However, different fits have often switched certain symmetry irreps for levels of incompletely-assigned terms. The second criterion for the energy level dataset is completeness. Extensive datasets have been presented for a few other systems, such as for the garnets and LaX₃:Ln³⁺, where about 100 levels have been fitted, but it has been pointed out that the assignments have not always been secure [267]. In the energy level parametrizations of Cs₂NaLnCl₆, neglecting Yb³⁺ and Ce³⁺, only 7-30 (in 1980, [268]), 19-45 (in 1985, [269]), and 23-61 (in 1994, [72]) CF levels were fitted. The data for other M₂ALnX₆ systems has generally been scarce. More recently, the use of TP excitation spectroscopy [216, 227-230] and ultraviolet emission and absorption spectroscopy [35, 207, 213, 270] have enabled more complete energy level datasets to be tested. Taking into account the high degeneracies (up to 3) of many of the energy levels, in several cases the datasets are now among the most extensive of those available for Ln^{3+} systems. Table 9 lists some of the previous energy

System (N:s)	Ref.	Comments
Cs ₂ NaLnCl ₆ ; Ln=Ce(5:1),Pr(30:19),	[268]	g-values and MD linestrengths
Nd(7:9),Eu(16:13),Tb(27:8)		also calculated
Cs ₂ NaLnCl ₆ ; Ln=Ce (5:1), Pr (33:16), Nd (32:25), Sm	[269, 271]	Mixed datasets of Cs ₂ NaLnCl ₆
(28:9), Eu (19:12), Tb (27:11), Dy (42:17),		and Cs ₂ NaYCl ₆ :Ln ³⁺ . SCCF fits
Ho (45:18), Er (35:23), Tm(22:21), Yb (5:40)		for Sm, Dy, Ho. Superposition model analysis
$Cs_2NaPrCl_6$ (27:15):	[272]	SCCF fits also carried out
$C_{s_2}NaYX_{\epsilon}:Pr^{3+}, X=Cl (27:14), Br (24:16)$	[_/_]	
$Cs_2NaHoX_6, X=Cl (61:15,14), Br (34:7)$	[273]	Fits with and without SCCF; mixed datasets with diluted
Cs ₂ NaDyCl ₆ (43:14)	[123]	Mixed dataset with
Cs ₂ NaGdCl ₆ :Nd ³⁺ (41:15)	[274]	$3 \text{ levels from } Cs_2NaNdCl_6$
C_0 NoLpCl $(I_{p-C_0}(5,0))$ Dr (20.20) NJ (22.21)	[72]	Mixed detects with diluted
Cs_2 NaLIICI6: LII=Ce (5:0), Pf (26:59), Nu (55:21), Ex (27:12), Cd (25:25), Th. (22:0), Dr. (40:15)	[/2]	witten datasets with diluted
Eu (2/:12), Gd (35:25), 1D (23:8), Dy (40:15),		systems
Ho (61:13), Er (41:18), Im (30:33), Yb (5:19);		
$Cs_2NaYCl_6:Ln^{-1}: Ln=Pr (25:26), Sm (25:10); Eu (19:12);$		
$Cs_2NaGdCl_6:Ln^{3+}:Ln=Nd$ (41:15), Ho (33:5)		
$Cs_2LiErCl_6$ (29:14)		
Cs ₂ NaLnBr ₆ Ln=Pr (24:39); Ho (37:6); Tm (22:40); Yb		
(5:43)		
Cs_2KPrF_6 (4:6); $Cs_2KYF_6:Eu^{5+}$ (9:9); Rb_2NaEuF_6 (9:10)		
Cs ₂ NaLnCl ₆ Ln=Er (35:21); Nd (33:25); Tm (25:32)	[275, 276]	Relativistic crystal field
$Cs_2NaLnBr_6$: Ln=Ce (2), Pr (4); Nd (3); Tb (3);	[60]	<i>C</i> _{4<i>h</i>} symmetry Hamiltonian
Dy (5); Ho (5); Er (5); Tm (3); Yb (3)		
$Cs_2NaErCl_6$ (40:10)	[277]	SCCF fit
$Cs_2NaPrCl_6$ (27:10, 27:8); $Cs_2NaYCl_6:Pr^{3+}$ (27:9,27:7)	[278]	With and without SCCF
$Cs_2NaYCl_6:Tm^{3+}$ (36:55, 36:28)	[212]	With and without SCCF
Cs ₂ NaYCl ₆ :Sm ³⁺ (67:21; 67:20); Cs ₂ NaEuCl ₆ (77:19;77:16);	[216, 279]	With and without SCCF
Cs ₂ NaYF ₆ :Eu ³⁺ (57:27;57:23); Cs ₂ NaTbX ₆ : X=Cl		
(100:19;100:18);		
Br (91:21; 91:15)		
Cs ₂ NaTbX ₆ X=F (86:26); Cl (125:22;125:20);	[223]	Chloride with
Br (28:12)		and without SCCF
Cs ₂ NaEuCl ₆ (77:16); Cs ₂ NaYF ₆ :Eu ³⁺ (57:22)	[228]	
$Cs_2NaYCl_6:Sm^{3+}$ (67:17)	[229]	
Cs_2NaTbX_6 ; X=F (90:27); Cl (100:19); Br (90:19)	[227, 280,	
	281]	
Cs2NaPrCl ₆ (38:38.38:14); Cs2LiPrCl ₆ (32:34,32:15);	[207]	With and without CI
$Cs_2NaYCl_6:Pr^{3+}$ (36:39,36:14)		
Cs ₂ NaTmCl ₄ : (38:55:38:11)	[213]	With and without CI
Cs ₂ NaErCk; (58:20;58:17,	[35]	With and without modified
- <u>-</u>	L - 1	matrix element
CsaNaErCl ₄ : (75:20:75:11)	[282]	With and without CI
	r1	and an and a state of the state

Table 9 Selected energy level parametrizations of M_2ALnX_6 and $M_2AM'X_6$: Ln^{3+} systems^a

^a The standard deviation, s (cm⁻¹), is defined in [269] as $[\Sigma(E_{calc.}-E_{expt.})^2/(N-p)]^{0.5}$, where $E_{calc.}$ and $E_{expt.}$ are the calculated and experimental energies, N is the number of energy levels fitted, and p is the number of parameters. Values are rounded to the nearest integer. Values in italics represent the mean deviation, which does not take into account the number of parameters employed (p=0). Bold values refer to SCCF or CI fits. The underlined value refers to the inclusion of a multiplying factor for the matrix element $\langle^2 H(2) || U^4 ||^2 H(2) \rangle$ level parametrizations for M_2ALnX_6 systems but is not exhaustive. The number of levels fitted, and the resulting standard deviation, are also included in the table. Apparently very good energy level fits in some cases may result from over-parametrization, omission of energy level outliers in the fit, inclusion of incorrect assignments, or from the fit of only one or two *SLJ* terms. The standard deviations of the fits are generally not as good as those obtained in the analysis of Ln^{3+} at low symmetry sites, since the presence of a much larger number of CF parameters in the latter case can absorb some of the deficiencies in the model [271].

Often the energy level fitting process is performed by first fitting the energy level *SLJ* baricenters, and then fitting the CF parameters to the splitting of the *J* levels [283, 284]. Certain parameter values can vary wildly if not constrained in the early stages of fitting [207, 230].

12.1 Atomic Hamiltonian Parameters

Figure 20 shows a plot of the Slater parameters against atomic number, with data from the most extensive fits of each lanthanide ion in the series $Cs_2NaLnCl_6$. Most of the parameters from the fit of 77 energy levels for Eu [228] are far from the general trend (as marked for the F^4 graph, for example). The lower points for Eu (not labelled) in the F^k plots are from the 27-level fit [72]. The ratios F^2/F^4 and F^4/F^6 are 1.36±0.10 and 1.48±0.08, respectively, and are fairly close to those expected for a Coulomb field. The log-log plot of the spin-orbit coupling constant, ζ_{f_5} against atomic number, Z, shows a slight curvature (Fig. 21), and from the plot of ζ_f against Z, the empirical relationship between these two quantities is

$$\zeta_f = (18,704 \pm 614) - (725 \pm 19)Z + (7.13 \pm 0.15)Z^2; R^2 = 0.9999$$
(54)

The parameter α generally lies in the range 15–25 cm⁻¹, with apparently anomalous values in the fits of Eu³⁺ [228] and Gd³⁺, Tm³⁺ [72], and does not exhibit a clear trend. The parameter β generally lies between -500 to -800 cm⁻¹, and γ generally needs to be constrained in the fits, to within a reasonable range. In some of the energy level fits, the parameters M^j , P^k or T^i were constrained, but there are no clear trends for these parameter values across the series Cs₂NaLnCl₆.

The effects upon the free ion parameters through the replacement of Na by Li, or Ln by Y or Gd, are negligible. There are small, systematic differences in the energy level schemes of these systems which, within the experimental errors, do not translate into significant parameter differences for the Cs₂ALnCl₆ systems studied [72, 207]. Even the replacement of the first nearest neighbour Cl in LnCl₆³⁻ by Br leads to the following four (Br/Cl) parameter ratios near unity for four different Ln³⁺ systems [72, 223]: F^2 0.999±0.005; F^4 1.015±0.030; F^6 1.010±0.035; ζ_f 0.999±0.003. The data are



Fig. 20 Plots of Slater parameters F^k against atomic number for Cs₂NaLnCl₆, from Pr (Z=59) to Tm (Z=69). (Data from [35, 72, 207, 213, 216, 223, 229, 270])

scarce for M₂ALnF₆ systems [72, 223], but the ratios (Cl/F) are found to be: $F^2 0.995 \pm 0.006$; $\zeta_f 0.997 \pm 0.006$.

12.2 One-electron Crystal Field Parameters

The fourth and sixth degree CF parameters from some previous energy level fits for $Cs_2NaLnCl_6$ systems are plotted against atomic number of Ln in Fig. 22, and it is evident that considerable data scatter results. Indeed, it has been realized for some time for the system $Cs_2NaLnCl_6$ [147] that the CF parameters exhibit a *SLJ*-term dependence (see Sect. 12.3), so that different



Fig. 21 Plot of log(spin-orbit coupling constant, ζ_{f_2} in cm⁻¹) against log(atomic number) for Cs₂NaLnCl₆. (Data as in Fig. 20)



Fig. 22 Plots of fourth and sixth degree crystal field parameters against atomic number from Ce (Z=58) to Tm (Z=69) for Cs₂NaLnCl₆. (Data as in Fig. 20)

values are obtained when fitting different numbers of levels, different multiplets, or by differently weighting the levels in the fits. The linear regression lines (not shown) for Fig. 22 are

$$B_0^4 = (4701 \pm 479) - (45.8 \pm 7.5)Z; R^2 = 0.674$$
(55)

$$B_0^6 = (992 \pm 150) - (12.3 \pm 2.4)Z; R^2 = 0.601$$
(56)

Generally, but with notable exceptions, the CF parameters are greater for larger lattice parameters, as for the earlier members of the lanthanide series in $Cs_2NaLnCl_6$. The most comprehensive comparison of CF parameters for Cs_2NaLnX_6 systems has been made for Ln=Tb, X=halide. The approximate values (in cm⁻¹) of B_0^4 were 3163, 1718, 1383; and of B_0^6 were 242, 180, 121 for F, Cl, Br, respectively [223, 230]. In this case, the CF parameters are smaller for increasing lattice parameter in Cs_2NaTbX_6 .

The comparison of the energy level datafits with those for other systems should take into account the fact that only two CF parameters have been employed for M_2ALnX_6 , whereas the number is considerably greater for other systems where Ln^{3+} is doped, for example: 9 for $Y_3Al_5O_{12}$ (YAG) and LaF_3 ; 6 for CsCdBr₃ and Cs₃Lu₂X₉ (X=Cl, Br). As an example, the CF parameters from the Cs₂NaErCl₆ datafit [35] are compared with those for Er³⁺ in several lattices in Table 10, using the CF strength, S^k, which is a spherical parameter independent of the crystal symmetry:

$$S^{k} = \left[7/(2k+1) \begin{pmatrix} 3 & 3 & k \\ 0 & 0 & 0 \end{pmatrix}^{2} \sum_{q=-k,k} (B_{q}^{k})^{2}\right]^{1/2}$$
(57)

The comparison is made with respect to uncorrected CF parameters, i.e. without empirical correction or correlated CF (CCF) contributions. The inclusion of this second-order CF effect does not, at least in the studies of oth-

System	Ref.	Site symmetry	N ^a	S^4	S ⁶
YAG	285	D_2	9	337	207
YVO ₄	286	D_{2d}	Not stated	184	92
LaCl ₃	287	C_{3h}	4	38	76
LaF ₃	288	C_{2v}	9	123	153
CsCdBr ₃	289	C_{3v}	6	238	31
Cs ₃ Lu ₂ Br ₉	290	C_{3v}	6	251	44
Cs ₃ Lu ₂ Cl ₉	291	C_{3v}	6	257	48
Cs ₂ NaErCl ₆	277	O_h	2	272	61
Cs ₂ NaErCl ₆	35	O_h	2	287	60

Table 10 Fourth- and sixth-order crystal field strength, S^k (in cm⁻¹), from various energy level fits for Er^{3+} in crystals (from [35])

^a Number of crystal field parameters fitted

er systems which are quoted here, change significantly the values of the CF strength parameters which describe a first-order CF effect. For instance, the changes in the magnitude of the k=4 CF strength amount to 1, 8 and 0% for garnets [285], CsCdBr₃ [289] and Cs₃Lu₂Cl₉ [291], respectively. For the compounds with Cs⁺ cations in Table 10, the k=4 and 6 CF strengths show an increasing trend from Br to Cl nearest neighbours of Er³⁺. The expected trend from Cl to F is observed in LaX₃. The CF strengths for the dimeric system Cs₃Lu₂Cl₉ (where three Cl atoms are shared by two Er³⁺, each of which are 6-coordinate) and the system Cs₂NaErCl₆ are fairly similar, proving that their environments are not very different, as considered in more detail in [35].

12.3

Refinements to the Energy Level Parametrization

In the conventional CF analyses of lanthanide ion systems, the CF splittings of certain multiplet terms (e.g. $Ho^{3+3}K_8$; $Pr^{3+1}D_2$; $Nd^{3+2}H(2)_{11/2}$) were poorly modelled. The SLJ-dependence of the CF parameters, and their irregular behaviour on crossing the lanthanide series, prompted the introduction of further phenomenological parameters into the CF Hamiltonian. CF parameters which accurately model low-lying multiplets give poor fits for higherenergy multiplet terms. The one-electron CF model assumes that the CF potential experienced is independent of the properties of the remaining electrons, despite their strong electrostatic correlation [223]. Correlation CF corrections to the Hamiltonian have been proposed by Newman and Judd, which take into account the different interactions with the ligand field of multiplet terms with different orbital angular momenta (orbitally-correlated CF) as well as the different interactions of multiplet terms with different spin (spin-correlated CF). The two-electron correlation terms introduce up to 637 parameters for systems with C_1 site symmetry, which reduce down to 41 parameters for O_h symmetry [284]. The spin-correlated CF has received most attention. It is argued that because spin-parallel electrons are subject to an attractive exchange force they are expected to occupy orbitals with a more compact radial distribution than spin-antiparallel electrons. Thus, spin-anti-parallel (minority spin) electrons should be subject to stronger CF interactions [292]. Most of the earlier CF analyses for M_2ALnX_6 systems were carried out on limited datasets pertaining to maximum multiplicity states, so that the importance of this hypothesis could not be evaluated fairly.

The practice in modifying the CF Hamiltonian to include spin-correlation has been to replace the one-electron $CF \sum B_q^k C_q^k(i)$ by

$$\sum_{i} \left[B_q^k C_q^k(i) + b_q^k \mathbf{S} \cdot \mathbf{s}_i C_q^k(i) \right]$$
(58)

where the sum runs over the 4f electrons. Although the simplicity of the additional term suggests the inclusion of a pseudo-one-body operator, it actually involves a two-body operator since $S = \sum s_j$. Usually, the ratio $c_k =$

 b_q^k/B_q^k is taken to indicate the importance of the spin-correlated CF. For terms of maximum multiplicity, the spin-correlated CF is proportional to the one-electron CF, so that it is important to include non-maximum multiplicity terms to determine the b_q^k parameters. It has been argued [269] that the 'sudden drop' in sixth-rank CF parameters in the second-half of the lanthanide series is due to the fact that the matrix elements of the one-electron operators in Eq. (10) change sign, whereas the matrix elements of the two-electron contributions add in the first half of the series and cancel in the second half. However, whether there is actually a 'sudden drop' is not clear from Fig. 22.

The earlier attempts to improve the CF analyses of M_2ALnX_6 systems by incorporating terms of the type in Eq. (58) were not very successful in greatly reducing the mean deviation (for example, [272, 273]) although the term dependence of the ratio B_0^4/B_0^6 was removed. Subsequently, a simplified ' δ function' model, which assumes that the dominant contributions to the correlation CF interactions come from paired electrons within the same angular orbital (with opposite spin), was used to fit the Pr^{3+} energy level scheme in $Cs_2NaPrCl_6$ [293]. Two problematic terms in this case, using a one-electron CF Hamiltonian, are 1D_2 and 1G_4 (Table 8). In fact, the calculated energies [293], using the δ -function model, were 9810 cm⁻¹ for level 24 (Γ_1) and 10522 cm⁻¹ for level 27 (Γ_5), both of 1G_4 , which are far from the experimental values (Table 8).

With the advent of more extensive datasets, further impetus was placed in the application of the spin-correlated CF model, with rank 4 and 6 operators [223, 267, 279, 281, 294]. The improvement in the standard deviation of the CF analysis for 91 levels of Cs₂NaTbBr₆ with the inclusion of these two additional parameters is 27%, but rather less for Cs₂NaYCl₆:Sm (1.4%), Cs₂NaEu-Cl₆ (14.1%), Cs₂NaYF₆:Eu (15.4%) and Cs₂NaTbCl₆ (8.4%). The improvement for the Cs₂NaTbX₆ systems is more marked for X=Br than X=F, since the ⁵D, ⁵G and ⁵H CF levels are poorly fitted in the former case [267]. It was suggested that these results, and the signs of c_k parameters for several systems, show the importance of the orbitally correlated CF [223], and of ligand polarization and covalency in determining the correlation CF [212, 223, 267, 279, 281]. However, to conclude from the most recent CCF fits, there is no 'magic fix' CCF parameter which significantly improves the standard deviation of energy level fits and 'rehabilitates the rogue multiplets' [280].
The calculated splitting of the ${}^{2}H(2)_{11/2}$ levels in Er^{3+} [295] (and Nd³⁺ [296]) compounds is always smaller than experimental splitting. An empirical correction has been proposed which includes a multiplying factor for the fourth-order diagonal reduced CF matrix element $\langle {}^{2}H(2)||C^{4}||^{2}H(2)\rangle$. The correction is efficient for ${}^{2}H(2)_{11/2}$ and ${}^{2}H(2)_{9/2}$ and for those levels which are coupled to them by spin-orbit interaction, such as ${}^{4}I_{9/2}$, ${}^{4}F_{9/2}$ and ${}^{4}G_{11/2}$. With the multiplying factor 1.717, the mean deviation in fitting 58 levels of Cs₂NaErCl₆ was decreased by 18% [35]. This correction has approximately the same effect as the $g^{4}_{10,A}$ operator of the correlation CF.

It is, however, more pleasing to have a physically intuitive model which improves the fitting process. Denning [267] has pointed out that the correlation CF effective operator arises from terms of the type

$$H_{CCF} = -(1/\Delta E) \left[\sum_{m} \langle \psi_i | \mathbf{G} | \psi_m \rangle \langle \psi_m | \mathbf{H}_{CF} | \psi_f \rangle + \sum_{m} \langle \psi_i | \mathbf{H}_{CF} | \psi_m \rangle \langle \psi_m | \mathbf{G} | \psi_f \rangle \right]$$
(59)

where G is the Coulomb operator, and the sum is over the states ψ_m of the same parity configuration that differs from f^N by two electrons. An alternative fitting process employs first-order CF matrix elements between the states of the f^N configuration and interacting states of other configurations. This is a more natural way of correcting the energies of f^N CF states because no new hypotheses need to be included, but the CF model is extended to include relevant states whose symmetries permit interaction with f^N states. Faucher and Garcia have successfully employed this model to the refinement of the energy level structure of PrCl₃ and other systems, by including interactions with the 4f^{N-1}5d configuration via odd-rank CF parameters [297, 298]. In other cases, however, the configuration interaction of 4f^N with 4f^{N-1}6p via even-rank CF parameters was found to be most effective in reducing the fitting errors [299-301]. Indeed, this type of configuration interaction has been found to be the case in centrosymmetric systems [302] where the CF interaction of f^N states with $f^{N-1}d$ is forbidden by symmetry. In Table 8 the energy level fits for Pr³⁺ in Cs₂NaPrCl₆, with and without the inclusion of 4f6p configuration interaction, are compared. The mean deviation of the energy level fit is reduced by a factor of 2.9 (from 32.7 cm^{-1} to 11.6 cm⁻¹), and the CF splittings of ${}^{1}D_{2}$ and ${}^{1}G_{4}$ are well-modelled [207]. The additional parameters introduced into the fit are required to describe the excited configuration 4f6p and its interaction with 4f². These were the interconfiguration parameters, R^k ; the spin-orbit coupling parameter, ζ_p ; and the CF parameter $B_0^4(f,p)$, so that 13 (instead of 10) parameters were varied freely. In the case of Pr^{3+} , and especially for the ${}^{1}D_{2}$ and ${}^{1}G_{4}$ states, it is observed that the configuration interaction is primarily due to certain large CF matrix elements between the two configurations, and the expression for

their calculation has been given in [207]. The extent of interaction is reflected in the eigenvectors of the CF states, for example, for the f^2 level at 10327 cm⁻¹, the wavefunction is

$$\begin{split} (f^2)^1 G_4(a\Gamma_5) = & 64.09\%^1 G_4(f^2) + 32.09\%^3 F_4(f^2) + 1.60\%^3 H_4(f^2) \\ & + 0.36\%^1 G_4(fp) + 0.25\%^1 F_3(fp) \end{split} \tag{60}$$

The quality of the CF fit for Pr³⁺ in Cs₂NaPrCl₆, including configuration interaction, is not sensitive to the variation of the energy gap between the $4f^2$ and 4f6p configurations. This is not the case for Tm^{3+} systems, and in addition the perturbing configuration is found to be of the type $f^{13}p^5$ [303] rather than f¹¹p. For example, the mean deviation in fitting 38 (out of a possible 40) energy levels of Tm^{3+} in Cs₂NaTmCl₆ is reduced from 55.4 cm⁻¹ to 10.9 cm⁻¹ by including the $f^{12}p^6/f^{13}p^5$ configuration interaction. The nature of the f¹³p⁵ configuration is of interest. Since the gap between 4f¹² and this configuration is fitted to be at $38,500 \text{ cm}^{-1}$ (rather than the expected ca. 200,000 cm^{-1} for 4f¹³5p⁵), and Ionova et al. [246] have assigned charge transfer bands at ca. 48,000 cm⁻¹ in the spectra of TmCl_6^{3-} , it is assumed that the p-orbital hole is not in the Tm^{3+} 5p orbital but within the chloride ligand 3p orbital [213]. Further evidence for the interaction of the f^N configuration with a charge transfer configuration comes from the fit of 75 levels of Er³⁺ in Cs₂NaErCl₆ with a mean deviation of 10.5 cm⁻¹, compared to that of 19.8 cm⁻¹ in the standard one-electron model [282]. The p electrons involved originate from the 3p⁶ chloride orbitals, which are in part projected onto the central Er³⁺ coordinate system as a unique orbital with p-character [282]. The preferred interaction of $4f^N$ configurations with $4f^{N-1}4p^1$ at the beginning of the lanthanide series, and with 4f^{N+1}3p⁵ at the end of the Cs₂NaLnCl₆ series, follows the respective tendencies of Ln³⁺ ions to oxidation and reduction. Furthermore, these trends in the mixing of ligand p-orbital character into f^N configurations can explain the variation of electronphonon coupling strengths across the lanthanide series, since these are strongest at the beginning and at the end of the series. The appreciable ligand orbital admixture is also expected to be important in energy transfer processes.

In studies of low-symmetry systems, the inclusion of a second-order correlation CF effect does not change significantly the values of the CF parameters which describe the first-order CF effect [35]. More sensitive changes might be anticipated with the use of only two first-order CF parameters for M_2ALnX_6 systems. It is found that the inclusion of two correlation CF parameters increases the value of $B_0^4(B_0^6)$ by 2.2% (10.4%) in Cs₂NaPrCl₆ [272], but decreases the respective values by 23.8% (16.1%) in Cs₂NaYCl₆:Tm³⁺ [212]. These changes in parameter values are outside the fitting errors of the first-order CF parameters. However, the outcome is even more dramatic when the values from fits with and without the inclusion of configuration in-



Fig. 23 Plot of ${}^{1}D_{2}$ barycentre energy against ${}^{3}P_{0}$ nondegenerate level energy for Pr^{3+} in various systems. (Data from [207]). The *best fit line* is drawn through the points

teraction are compared. For Cs₂NaPrCl₆, the value of $B_0^4(B_0^6)$ without the inclusion of configuration interaction increases by 72% (172%) [207], whereas the corresponding values show a decrease of 59% and an increase of 210% for Cs₂NaTmCl₆ [213]. Clearly, the values of CF parameters for different Ln³⁺ should be compared with caution.

A criterion for evaluating incorrect energy level assignments has recently been proposed [304]. The barycentre energies of ${}^{2S+1}L_J$ terms are plotted against one another for a series of systems containing the relevant Ln³⁺ ion, and the deviation from linearity is taken to indicate an incorrect assignment in a particular system. When the barycentre data for ${}^{3}P_{0}$ and ${}^{3}P_{1}$ are plotted against one another, the data point from Cs₂NaPrCl₆ sits upon the straight line fit. However, Fig. 23 shows that considerable scatter occurs in the plot of the ${}^{1}D_{2}$ barycentre energy against ${}^{3}P_{0}$. This may not only represent the possibility of incorrect assignments, but alternatively, of cases where the ${}^{1}D_{2}$ levels are perturbed by configuration interaction. Thus the Cs₂NaPrCl₆ data point in Fig. 23 lies about 50 cm⁻¹ away from the best-fit line.

13 Energy Transfer in M₂ALnX₆ Systems

Much of the motivation for the study of the electronic, vibrational and vibronic properties of M_2ALnX_6 systems is towards the understanding of ET phenomena. ET can involve the radiationless transfer of energy from the site of its absorption in a crystal by a donor (sensitizer), over distances greater than interatomic separations, to an acceptor (activator) without collision or conversion to thermal energy. The transfer is resonant if the energy transferred matches the difference in electronic energy between levels of both the donor and acceptor systems. More often, nonresonant ET involves the creation or annihilation of phonons at the donor and/or acceptor sites. Radiative ET from a donor to an acceptor involves a photon, and the donor lifetime is unchanged unless it is the same species as the acceptor.

The f^N excited states of Cs_2NaLnX_6 systems are long-lived (Table 11). Lifetimes of $f^{N-1}d$ states are listed in Table 12. Although ET can be very efficient in these crystals their softness and hygroscopic properties make them unsuitable for optical applications. However, due to the high site symmetry of Ln^{3+} , these materials serve as model systems for understanding ET processes of lanthanide ions.

Neglecting effects due to stimulated emission and reabsorption of emitted light, for one type of emitting centre in a M_2ALnX_6 system, the (natural) lifetime τ of a particular state is related to the population or emission intensity of a transition from that state, *I*, at time *t*, following pulsed excitation at *t*=0, by

$$I(t) = I(0) \exp(-kt)$$
, where $k = 1/\tau$ (61)

where k is the sum of the radiative (k_r) and nonradiative (k_{nr}) decay processes. Some of the tabulated lifetimes (Table 11) are approximate due to deviations from exponential behaviour. However, it is clear that the lifetimes are longer than for Ln^{3+} at lower symmetry sites. For example, compare the ⁴F_{9/2}, ⁴I_{9/2} lifetimes of Er^{3+} in $\text{LaF}_3:\text{Er}^{3+}$ (0.1 mol%): 0.75, 0.15 ms [349], CaF₂: Er^{3+} (0.2 mol%): <0.98, 0.02 ms [350], YVO₄: Er^{3+} (1 mol%): 10, 10 μ s [286] (where the Er^{3+} site symmetries are C₂, tetragonal and D_{2d}, respectively) with those listed in Table 11. The variation in measured lifetimes from sample to sample (Table 11) is due to the crystal quality, since M₂ALnCl₆ systems in particular are moisture sensitive. Excited states are then quenched by the ET to trap sites such as those with oxychloride or hydroxide species coordinated to Ln³⁺.

Studies in the 1970s by Weber [351], Watts [352] and others have shown that three regimes occur for ET when the donor (i.e. sensitizer, D) concentration is increased: (i) when the concentration of donors is small, direct (one-step) relaxation from an excited donor (D^*) to an acceptor (i.e. activator, A) without diffusion occurs (giving nonexponential donor decay, followed by exponential decay); (ii) at higher donor concentrations, fast migra-

Ln ³⁺	Host (dopant conc. mol%)	Lumines- cent <i>SLJ</i> term	Temp. (K)	Lifetime ^b	Reference
Pr	Cs ₂ NaPrCl ₆	³ P ₀	80 [10]	53±9* [140±4*]	[147]
	$Cs_2NaPrCl_6$	${}^{3}P_{0}$	80 [20]	43* [108*]	[305, 306]
	Cs_2NaYCl_6 (10)	$^{3}P_{0}$	300	118*	[260]
	Cs_2NaYCl_6 (~1)	³ P ₀	300 [80] 10	141±20* [273±15*] 413+2*	[147]
	Cs_2NaYCl_6 (0.1)	$^{3}P_{0}$	80 [20]	277* [473*]	[305, 306]
	Cs ₂ NaYBr ₆	${}^{3}P_{0}$	300 [80] 10	87±7* [266±30*] 575±50*	[147]
	Cs ₂ NaYBr ₆	³ P ₁	300 [80]	87±7* [49±2*]	[147]
Nd	Cs ₂ NaNdCl ₆	⁴ D _{3/2}	300	75**	[247]
	Cs ₂ NaNdCl ₆	⁴ F _{3/2}	300 [77]	1.2 [5]	[307, 308]
	$Cs_2NaLnCl_6$ (1) (Ln=Y, La)	⁴ F _{3/2}	300 [77]	4.1 [11]	[307, 308]
	Cs ₂ NaYCl ₆ (0.5,1,5)	⁴ D _{3/2}	300	100*, 90*, 70*	[247]
	$Cs_2NaGdCl_6(1)$	⁴ F _{3/2} ; ⁴ G _{7/2}	300 [80]	4.3 [6.4]; 30±4* [74±6*]	[274]
	Cs ₂ NaYbCl ₆ (99)	⁴ F _{3/2}	300	700*	[274]
	Rb ₂ KNdF ₆	⁴ F _{3/2}	300	318*	[309]
	Cs ₂ KNdF ₆	⁴ F _{3/2}	300	717*	[309]
	Cs ₂ KLaF ₆ (10, 40)	⁴ F _{3/2}	300	3.2, 1.4	[309]
	$Rb_2NaYF_6(1)$	${}^{4}F_{3/2}$	4, 77, 300, 568	6, 10.7, 4.4, 2.85	[259]
Sm	Cs ₂ NaSmCl ₆	⁴ G _{5/2}	10 [300]	86* [3.2*]	[310-312]
	Cs_2NaYCl_6 (0.5)	⁴ G _{5/2}	10	17	[310, 313, 314]
	$Cs_2NaGdCl_6$ (0.1)	⁴ G _{5/2}	10 [300]	17 [9.3]	[311, 315–318]
Eu	Cs ₂ NaEuCl ₆	⁵ D ₀	295 [80]	0.65 [68*]	[319]
	Cs ₂ NaEuCl ₆	⁵ D ₀	12	5.6±0.7	[320, 321]
	Cs2NaEuCl6	⁵ D ₁	293 [80]	(66±3)* [0.53±0.03]	[320, 322]
	$Cs_2NaEuCl_6$	⁵ D ₂ ; ⁵ D ₁ ; ⁵ D ₀	300 [80]	80* [520*]; 0.16 [0.71]; 2.0 [2.7]	[323]
	$Cs_2NaYCl_6(1)$	⁵ D ₁ ; ⁵ D ₀	12	7.4±0.5;11.1	[320, 322]
	Cs ₂ NaTbCl ₆ (1–15)	⁵ D ₁	293 [80]	24±1* [1.3±0.1]	[324-326]
	Cs ₂ NaGdCl ₆	⁵ D ₁	80	8.3	[317]
	Cs ₂ NaYF ₆ (0.1, 20)	⁵ D ₁ ; ⁵ D ₀	295	$1.24 \pm 0.05, 0.22 \pm 0.01;$ $15 \pm 1, 13 \pm 1$	[25]
	Cs_2NaYF_6 (0.1, 20)	⁵ D ₂ ; ⁵ D ₁ ; ⁵ D ₀	4	84±4*, 49±3*; 2.7±0.1, 2.5±0.1; 15±1, 15±1	[25]
Gd	$Cs_2NaGdCl_6$	⁶ P _{7/2}	4.2	13±2	[327]
	$Cs_2NaGdCl_6$	⁶ I _{7/2}	4.2	3.1±0.2	[327]

 Table 11
 Natural lifetimes of 4f^N CF levels in M2ALnX6 systems^a

tion between donors before ET from D^* to A gives an exponential decay of donor emission; and (iii) at low A concentrations, diffusion-limited decay occurs (with a time-dependent change from non-exponential to exponential donor decay). Case (ii) may be analysed by a hopping mechanism, which

		st (dopant Lumines- nc. mol%) cent <i>SLJ</i> term			Reference	
Tb	Cs ₂ NaTbCl ₆	⁵ D ₃ ; ⁵ D ₄	8	45*; 9.5	[242]	
	Cs ₂ NaTbCl ₆	⁵ D ₄	293 [80]	6.6±0.2 [9.4±0.2]	[324]	
	$Cs_2NaYCl_6(1)$	⁵ D ₄	293 [80]	6.9±0.2 [9.9±0.4]	[324]	
	Cs ₂ NaTbF ₆	⁵ D ₃ ; ⁵ D ₄	77 [10]	4* [14*]; 16.9 [17.3]	[328]	
	Cs ₂ KInF ₆ (0.1–10)	⁵ D ₃ ; ⁵ D ₄	16	8; 18	[329]	
	Cs ₂ NaTbBr ₆	⁵ D ₃ ; ⁵ D ₄	77 [10]	32* [110*]; 5.9 [4.0]	[230, 330]	
Ho	Cs ₂ NaHoCl ₆	⁵ I ₇	85	50	[122]	
	Cs ₂ NaHoCl ₆	⁵ I ₅	300 [85]	48 [108]	[331]	
	Cs ₂ NaHoCl ₆	⁵ F ₃ ; ⁵ F ₅	20	1.2±0.5; 15	[148, 332]	
	Cs ₂ NaHoCl ₆	⁵ F ₅	300 [80] 10	4.5 [5.5] 6.9	[323, 333]	
	Cs ₂ NaHoCl ₆	⁵ F ₅	300 [85]	7 [10]	[186]	
	Cs ₂ NaHoCl ₆	⁵ I ₇ ; ⁵ I ₅ ; ⁵ F ₅	300	27±9; 48; 7	[185]	
	Cs ₂ NaHoCl ₆	⁵ I ₇ ; ⁵ I ₅ ; ⁵ F ₅	85	35±15; 107; 10	[185]	
	Cs ₂ NaHoCl ₆	⁵ I ₄ ; ⁵ F ₅ ; ⁵ F ₃	15	75; 12±3; 1.2±0.5	[185]	
	Cs_2NaYCl_6 (0.01)	⁵ F ₅	295 [80]	5.5 [14.7]	[334]	
	Cs ₂ NaYCl ₆ (1, 20)	⁵ F ₅	300 [80]	5.9 [6.5], 6.1 [6.6]	[323, 333]	
	Cs_2NaYCl_6 (0.7)	⁵ F ₃ ; ⁵ S ₂	15-20	9.3±2; 40±2	[148, 185]	
	Cs ₂ NaSmCl ₆ (98)	⁵ F ₅	300 [80]	70* [50*]	[333]	
	Cs ₂ NaYbCl ₆ (99)	⁵ F ₅	300 [80]	35* [20*]	[333]	
	Cs ₂ NaYbCl ₆ (99)	⁵ F ₅	300 [85]	300* [140*]	[149]	
	Cs ₂ NaYbCl ₆ (1)	⁵ F ₃ ; ⁵ S ₂	20	9±2; 44±15	[185]	
	Cs ₂ NaGdCl ₆ (1)	⁵ F ₃ ; ⁵ S ₂ ; ⁵ F ₅	300	2.8±0.1; 6±2; 7	[185]	
	$Cs_2NaGdCl_6$ (1)	⁵ F ₃ ; ⁵ S ₂ ; ⁵ F ₅	85	5.7±0.1; 19.9±0.6; 22.5±1.5	[185]	
	$Cs_2NaGdCl_6(1)$	⁵ F ₃ ; ⁵ S ₂ ; ⁵ F ₅	20	8.5±1.5; 38±3; 28±5	[185, 148]	
	Cs ₂ NaTmCl ₆ (99)	⁵ F ₃ ; ⁵ F ₅	20	270*; 2	[332]	
	$Cs_2NaErCl_6$ (99)	⁵ F ₅	300 [85]	0.2-1 [0.1-0.6]	[186]	
	Cs ₂ NaHoBr ₆	⁵ F ₅	300-30	0.6-1.1	[187]	
	Cs ₂ NaHoBr ₆	⁵ F ₃	20	80*	[187]	
	Cs ₂ NaHoBr ₆	⁵ I ₅	300 [85]	11 [16]	[187]	
	Cs ₂ NaYBr ₆ (dilute)	⁵ F ₃ ; ⁵ F ₅ ; ⁵ I ₅	300 [85]	1 [3.3]; 4.4 [14]; 66 [102]	[187]	
Er	Cs ₂ NaErCl ₆	⁴ I _{9/2} ; ⁴ F _{9/2} ; ⁴ S _{3/2} ; ² G _{9/2}	85	18.9±1.3; 7.5; 4.6±0.5; 4.4±1.0	[335]	
	Cs ₂ NaErCl ₆	⁴ I _{13/2} ; ⁴ I _{11/2} ; ⁴ I _{9/2} ; ⁴ F _{9/2} ; ⁴ S _{3/2}	300 [77]	22 [-]; - [4.7]; 6.5 [21]; 3.8 [8.5]; 0.5 [0.5]	[336, 337]	
	Cs ₂ NaErCl ₆	${}^{4}F_{9/2}$	1.2	9.1	[338]	
	Cs ₂ NaErCl ₆	⁴ S _{3/2} ; ⁴ I _{9/2}	50-300	Graphical form	[339]	
	Cs ₂ NaYCl ₆ (0.1–100)	⁴ S _{3/2} ; ⁴ F _{9/2} ;	10-300	Graphical form	[340, 341]	
	Cs ₂ NaYCl ₆ (0.1, 100)	⁴ I _{9/2} ⁴ S _{3/2}	80	8.2, 4.0	[342]	
	Cs ₂ NaYCl ₆ (2, 10)	⁴ S _{3/2} ; ⁴ I _{11/2}	15	11.2, 11.0; 83.6, 45	[343]	
	$\mathrm{Cs_2NaEr_{0.2}Yb_{0.4}Y_{0.4}Cl_6}$	${}^{4}I_{11/2}; {}^{4}I_{9/2};$ ${}^{4}F_{9/2}; {}^{4}S_{2/2}$	300	4.1; 32.5; 8.6; 0.37	[337, 339]	

Table 11 (continued)

Ln ³⁺	Host (dopant conc. mol%)	Lumines- cent <i>SLJ</i> term	Temp. (K)	Lifetime ^b	Reference
Tm	Cs ₂ NaTmCl ₆	${}^{3}H_{4}$	300 [20]	1 [1.6]	[332]
	$Cs_2NaTmCl_6$	${}^{3}P_{2}$	300	59*	[344]
	Cs ₂ NaTmCl ₆	$^{3}H_{4}$	300	4*	[345]
	Cs ₂ NaYCl ₆ (1, 5, 25)	¹ D ₂ ; ¹ G ₄ ; ³ H ₄	300	71*, 60*, 54*; 380*, 300*, 130*; 990*, 930*, 580*	[345]
	$Cs_2NaGdCl_6(1)$	¹ G ₄ ; ³ H ₄	20	6; 20–50	[332]
	Cs ₂ NaGdCl ₆ (0.1)	${}^{1}G_{4}$	10	4.5	[346]
	Cs ₂ NaGdCl ₆ (0.1, 1, 10)	¹ D ₂ ; ¹ G ₄ ; ³ F ₃ ; ³ H ₄	300	101*, 95*, 51*; 1.92, 1.30, 145*; 243*, 194*, 75*; 3.9, 4.1, 3.3	[344, 347]
	$Cs_2NaHoCl_6(1)$	³ F ₃	20	2	[332]
Yb	$Cs_2NaHoCl_6(1)$	$^{2}F_{5/2}$	300 [30]	6 [13]	[149]
	Cs ₂ NaHoCl ₆ (50)	${}^{2}F_{5/2}$	300	1	[149]
	$Cs_2NaNdCl_6$ (60)	² F _{5/2}	300–13 [13–12]	150? [5.3]	[348]

Table 11 (continued)

^a The variations are due to changes in crystal quality, absorption of moisture and the presence of concentration gradients in crystals

 $^{\rm b}$ Values are in ms except starred values: * in μ s; ** in ns

also predicts an exponential donor decay, but which leads to a different dependence upon donor concentration and interaction parameters.

Generally, CF levels within a given multiplet term are in thermal equilibrium (i.e. they have the same lifetime). A slow relaxation rate (k') from an upper to a lower multiplet term (shown in Fig. 24a) produces a noticeable rise-time in the decay of emission from the lower state, following pulsed excitation:

$$I(t) = I(0) \exp(-kt) + I'(0)[k'/(k-k')][\exp(-k't) - \exp(-kt)]$$
(62)

where I'(0) is the population of the upper state at t=0.

Ln ³⁺	Host (dopant conc. mol%)	opant Luminescent ol%) <i>SLI</i> term		Lifetime (ns)	Reference	
		11 m	. ,		[2:0]	
Ce	Cs_2NaYCl_6 (10)	$d^{1} T_{2g}$	300	~30	[260]	
	$Cs_2LiLaCl_6(1)$	$d^1 T_{2g}$	300	36.4±0.3	[256]	
	$Rb_2NaYF_6(1)$	$d^1 T_{2g}$	300	70-90	[258]	
	$Cs_2NaYF_6(1)$	$d^1 T_{2g}$	300	42	[258]	
Pr	Cs ₂ NaPrCl ₆	$f^{1}d^{1} {}^{3}F_{2}$	8	13	[206]	
	$Cs_2NaYCl_6(1)$	f ¹ d ¹ ³ F ₂	8	18	[206]	
	Cs_2NaYCl_6 (10)	$f^{1}d^{1}$ $^{3}F_{2}$	300	~20	[260]	

Table 12 Lifetimes of 4f^{N-1}5d CF levels in M₂ALnX₆ systems



Fig. 24a–j Energy transfer mechanisms in M_2ALnX_6 systems: a multiphonon relaxation; b migration; c cross-relaxation; d ET upconversion; e second-order two-body ED, ED-ED, ED ET; f diagonal one-phonon-assisted ET; g nondiagonal one-phonon-assisted ET; h TP absorption; i excited state absorption terminating upon electronic and vibronic levels; j photon avalanche upconversion. D,A represent Donor and Acceptor, respectively. *Horizontal or slanted links* represent various coupling mechanisms. *Wavy arrows* represent phonon emission or absorption. *Dashed arrows* represent the laser pump. *Dashed energy levels* are vibronic states. In most cases, only one illustration of the several possible diagrams is given. *i*, *l*, *f* represent f^N states, and *m* is an opposite-parity state. Where applicable, *semicircles* represent the final D and A states. Refer to Sect. 13 for explanations

Single-ion nonradiative decay for Ln^{3+} diluted into transparent host elpasolite crystals, where the energy gap is greater than the Debye cutoff, is primarily due to multiphonon relaxation (with rate k_{mp}). In some cases, first order selection rules restrict phonon relaxation between states, such as between Γ_{1g} and Γ_{4g} , or between Γ_{2g} and Γ_{5g} , CF states for MX₆³⁻ systems. The dependence of the multiphonon relaxation rate, k_{mp} , upon the energy gap to the next-lowest state (ΔE) has been investigated for other systems and is given by a relation such as [353, 354]

$$k_{mp} = \beta[\exp\left(-\alpha\Delta E\right)] \tag{63}$$

where α and β are constant for a particular host lattice. From a survey of the luminescent and non-luminescent states of M2ALnCl6 systems it has been observed that as long as a state is populated, then in the absence of concentration quenching effects or restrictive selection rules, the state should be luminescent provided that ΔE is spanned by five or more phonons [355]. For M_2ALnCl_6 systems, since the highest energy phonon is 279–296 cm⁻¹ for Ce-Yb (Table 1), this means that ΔE >ca. 1120–1180 cm⁻¹. Thus, for example in the Cs₂NaLnCl₆ series, weak luminescence occurs from the $({}^{6}F_{5/2})\Gamma_{7}$ level of Dy^{3+} ($\Delta E=1270 \text{ cm}^{-1}$), and from the $({}^{4}G_{7/2})\Gamma_{8}$ level of Nd³⁺ ($\Delta E=1374 \text{ cm}^{-1}$) [355]. M^cCaw has pointed out that the lifetimes of states of Cs₂NaTbX₆ systems decrease for the heavier halides, which he accounted for by the increase in k_r (due to more intense vibronic sidebands associated with higher ligand polarizability) [330]. Although this seems to be the case for the ${}^{5}D_{4}$ state (Table 11), the lifetime of the ⁵D₃ state shows the reverse trend. A simple trend is not evident from other systems (e.g. Table 11: Cs₂NaYX₆:Ln³⁺, X=Cl, F). Slower multiphonon relaxation rates due to lower vibrational frequencies would lead to longer lifetimes for systems with the heavier halides. However, additional factors, such as the crystal quality and ease of hydrolysis of M₂ALnX₆, also play roles in determining the experimental lifetimes of neat systems.

13.1 Resonant Energy Transfer

In this section, the transfer of excitation energy from the donor to the acceptor, with no energy mismatch involved, by the ET mechanism, is discussed. Other possible transfer mechanisms, such as radiative transfer [356] and photoconductivity, are not considered here. Nonradiative ET between adjacent Ln^{3+} ions involves only a one-step process which requires the direct coupling of the ions by various electric (ED-ED, ED-EQ, EQ-EQ), and/or magnetic (MD-MD) interactions; by exchange interactions if their wavefunctions overlap [357] (not considered to be important since the Ln^{3+} separation in Cs_2NaLnX_6 is large, $a/\sqrt{2}\sim0.75$ nm, Fig. 1a); or by superexchange interactions involving intervening ions. The donor-acceptor separations for the elpasolite system $Cs_2NaTmCl_6$ are listed in Table 13 for the *n*th (*n*=1...6) nearest neighbour shells.

Examples of two-body ET are shown in Figs. 24b,c. Migration, Fig. 24b, represents the case when the donor and acceptor are the same species. However, it can also occur nonresonantly since there may be a slight energy mismatch from the donor to the acceptor site, which can be compensated by acoustic phonons. In the second cross-relaxation mechanism, Fig. 24c, the emission from level f' is quenched, and level i' is populated. If the acceptor level is an excited state (often the same as the donor state, as in Fig. 24d), the process is called ET upconversion. The term cooperative ET upconversion.

<i>n</i> -th nearest neighbour acceptor	Distance (pm) from Tm ³⁺ donor	Number of like neighbours	MD-MD transfer rate (s ⁻¹)	EQ-EQ transfer rate (s ⁻¹)
1	755.6	12	1.92×10^{4}	1.91×10 ⁵
2	1068.6	6	1200	4882
3	1308.8	24	1420	671
4	1511.2	12	230	187
5	1689.6	24	310	108
6	1805.9	8	60	11

Table 13 Structural data, MD-MD and EQ-EQ $^1G_4 {\rightarrow} ^3H_4$ resonant energy transfer rates between Tm^{3+} ions in Cs_2NaTmCl_6 at 300 K^a

^a Effective field effects have not been included. Data from [360, 364]

sion (or cooperative sensitization) is generally reserved for the 3-body process (not shown) where two donor ions, D^* , such as Yb^{3+} simultaneously excite an acceptor ion, A, such as Tb^{3+} [356].

Generally, the ET processes are studied by following the quenching of the donor emission D*, and its replacement by acceptor emission, A*. For elpasolite systems, resonant ET is uncommon in comparison with nonresonant transfer. One example is the quenching of ${}^{1}G_{4}$ emission in Cs₂NaTmCl₆, subsequently discussed. The cross-relaxation in Cs₂NaSm_xEu_yGd_{1-x-y}Cl₆: Sm³⁺ (${}^{4}G_{5/2}$) Γ_7 [18086] \rightarrow (${}^{6}H_{7/2}$) Γ_8 [1208] and Eu³⁺ (${}^{7}F_1$) Γ_4 [360] \rightarrow (${}^{5}D_0$) Γ_1 [17208] shows some mismatch although it has been treated as resonant [315].

The theory of resonant nonradiative ED-ED ET was formulated by Förster, and extended by Dexter to include other interaction mechanisms. From the Fermi Golden Rule, the ET rate, W_{DA} , between an excited donor (D^{*}) and an acceptor (A) in nondegenerate states is proportional to the square of the interaction matrix element, *J*, [358]:

$$W_{DA} = \frac{4\pi^2}{h} J^2 G_{overlap} \tag{64}$$

where the overlap integral $G_{overlap}$ is defined as

$$G_{overlap} = \int g_D(E)g_A(E)dE \tag{65}$$

and $g_D(E)$ and $g_A(E)$ are the normalized lineshape functions of the radiative emission of D^{*} and the radiative absorption of A. For electrostatic multipolar interactions, the interaction matrix element is given by

$$J = \langle \mathbf{D}, \mathbf{A}^* | \mathbf{H}_{ET} | \mathbf{D}^*, \mathbf{A} \rangle \tag{66}$$

in which H_{ET} is the ET interaction Hamiltonian between the k_1 -pole of D^{*} and the k_2 -pole of A [358]:

$$\mathbf{H}_{ET} = e^2 \sum_{\substack{k_1 k_2 \\ q_1 q_2}} C_{q_1 q_2}^{k_1 k_2} \mathbf{D}_{q_1}^{(k_1)} \mathbf{D}_{q_2}^{(k_2)}$$
(67)

and the angular factor is expressed as

$$C_{q_{1}q_{2}}^{k_{1}k_{2}}(\theta,\phi) = \frac{(-1)^{k_{1}}}{R^{k_{1}+k_{2}-1}} \left[\frac{(2k_{1}+2k_{2}+1)!}{(2k_{1})!(2k_{2})!} \right]^{1/2} \\ \times \begin{pmatrix} k_{1} & k_{2} & k_{1}+k_{2} \\ q_{1} & q_{2} & -(q_{1}+q_{2}) \end{pmatrix} C_{q_{1}+q_{2}}^{(k_{1}+k_{2})}(\theta,\phi)^{*}$$
(68)

which is another expression of the T factor in Eq. (34).

The overlap integral reflects the requirement of energy conservation in the ET process. Its value is uncertain because the homogeneous linewidth of solid-state spectra can be up to three orders of magnitude smaller than the inhomogeneous linewidth [359]. A value of 8×10^{21} J⁻¹ has been adopted for the calculation of MD-MD ET in Cs₂NaTmCl₆ [360].

Due to such uncertainties, and the lack of knowledge about the electronic matrix element, *J*, many previous analyses of ET phenomena have attempted to ascertain the mechanism from the inter-ion distance dependence of the transfer rate, which is R^{-10} , R^{-8} and R^{-6} for EQ-EQ, EQ-ED and ED-ED (or MD-MD) ET, respectively. In the Inokuti-Hirayama approach, the donor luminescence intensity as a function of time is given by [361]

$$[I(t)/I(0)] = \exp\left[-t/\tau_0 - \Gamma(1 - 3/s)(c/c_0)(t/\tau_0)^{3/s}\right]$$
(69)

where c_0 is the critical transfer concentration and c is the acceptor concentration; τ_0 is the lifetime in the absence of quenching by the acceptor; and Γ represents the gamma function. Here, s is the fitting parameter to identify the type of multipole interaction, being equal to 6, 8 and 10 for ED-ED, ED-EQ and EQ-EQ ET, respectively. The model neglects the migration between donor ions, and does not take into account the angular dependence of donor-acceptor transfer. It has been employed to analyse the quenching of the ${}^{1}G_{4}$ blue emission in neat Cs₂NaTmCl₆ [346]. Several of the cross-relaxation pathways are resonant to within experimental error, and one of these, Fig. 24c, is

$$D^{*}f'({}^{1}G_{4})\Gamma_{5g}[20,851] + Ai({}^{3}H_{6})\Gamma_{1g}[0] \rightarrow Df({}^{3}H_{5})a\Gamma_{4g}[8241] + A^{*}i'({}^{3}H_{4})\Gamma_{3g}[12,607]$$
(70)

The efficiency of luminescence quenching, η :

$$\eta = W_{DA} / (W_{RAD} + W_{DA}) = 1 - \tau / \tau_0 \tag{71}$$

where τ and τ_0 are the lifetimes with, and in the absence of ET, is >90% in a Cs₂NaGdCl₆:Tm³⁺ sample with 10 mol% doping. The results indicate that

s=6, although the curve fitting is rather insensitive to the value of s. The refinements to the theory which include migration [362] and the presence of acceptor sites as discrete shells [363] would require further parameters.

An alternative approach without any fitting is to assume a certain type of interaction, and then calculate *J* in Eq. (66), and hence W_{DA} in Eq. (64). This has been done for the MD-MD interaction in Eq. (70), since the donor and acceptor transitions are ED forbidden but MD allowed. The interaction energy is calculated between the magnetic dipoles μ_{D^*} and μ_A , for the appropriate orientations and numbers of ions in each acceptor shell [360]. The results are listed in Table 13, column 4. It is evident that the dominant D*-A ET interaction occurs for the 12 Tm³⁺ nearest neighbours, with a nonradiative ET rate of the order 10^4 – 10^5 s⁻¹, so that the efficiency of quenching the 1G_4 emission is almost 100% for neat Cs₂NaTmCl₆, as observed experimentally.

Other resonant (as well as nonresonant) quenching mechanisms are however, possible, for this system. For example, considering the fact that both nonradiative transitions are EQ allowed, the site-site coupling strength is given by

$$J = \langle {}^{3}\mathrm{H}_{4}, {}^{3}\mathrm{H}_{5}|\mathrm{H}_{DA}| {}^{3}\mathrm{H}_{6}, {}^{1}\mathrm{G}_{4} \rangle \tag{72}$$

where H_{DA} is the EQ-EQ interaction operator, and the values of W_{DA} thus calculated [364] for EQ-EQ interaction are listed in Table 13, column 5. The ET rate now exceeds that due to MD-MD interaction, for the nearest acceptor shells, and the first nearest-neighbour EQ-EQ ET dominates. It has been pointed out that the EQ-EQ ET rate differs from the MD-MD ET rate not only in its stronger dependence (by a factor R^{-4}) upon donor-acceptor distance, but also regarding its geometrical anisotropy [364, 365].

EQ-EQ energy migration is calculated to be fast ($\sim 10^7 \text{ s}^{-1}$) for the ${}^{1}\text{G}_4$ state of Tm³⁺ in Cs₂NaTmCl₆ [364], and of the order 10⁹ s⁻¹for the ${}^{2}\text{F}_{5/2}$ state of Yb³⁺ in Cs₂NaYbCl₆ [366]. For other cases, such as the ${}^{5}\text{D}_{0}$ state of Eu³⁺ in Cs₂NaEuCl₆, migration is not possible by ED-ED, MD-MD or EQ-EQ mechanisms. Besides exchange interactions, one further mechanism can be formulated by taking Förster-Dexter theory to higher order, where donor and acceptor ions undergo virtual transitions to opposite-parity intermediate states, as in Fig. 24e, where D and A are the same species [367]. Following this ED,ED-ED,ED mechanism, the migration rate to first shell neighbours for the ${}^{5}\text{D}_{0}$ state of the above Eu³⁺ system is calculated to be $\sim 500 \text{ s}^{-1}$. Experimental measurements of the luminescence decay from ${}^{5}\text{D}_{0}$ in neat Cs₂Na EuCl₆ have been made at long decay times [321]. In this regime, migration becomes important and the decay is exponential with a decay constant $k+k_M$, where k_M is the migration rate. The derived value of k_M was in the region 10^2 s^{-1} , in reasonable agreement with calculation.

13.2 Phonon-assisted Energy Transfer: Diagonal Process

The CF of Ln³⁺ varies from site to site due to the presence of defects, dislocations or lattice strains which inhomogeneously broaden and shift the energy levels. In this case, and also in other cases where there is an energy mismatch between the donor and acceptor excitations, energy conserving mechanisms are required. These can involve many-body processes [356] or the absorption or emission of phonons (crystal lattice vibrations). The conventional theory of phonon-assisted ET has been proposed [368] (and following the authors Holstein, Lyo and Orbach, it is hereafter abbreviated to HLO theory), and incorporates electron-phonon coupling as well as multipole interactions between the donor and acceptor ions. This diagonal process involves electronic matrix elements between only the donor and acceptor f-electron energy levels, such as in Fig. 24f. The matrix element for the site-site coupling Hamiltonian is given by Eq. (66). Since the multipole interaction in a centrosymmetric system is limited to EQ (and higher terms), the process may be represented by $(EQ \leftrightarrow EQ, V)$, where this includes (EQ - EQ, V)and (V,EQ-EQ) [369], so that theory is of second-order, but it refers to a parity allowed electronic process. As pointed out in [368], the "Förster" ET rate for a one-phonon process would be given by the square of the site-site coupling matrix element, multiplied by the convolution of the emission profile at one site with the absorption profile of the other (with both profiles including the vibronic sidebands). However the 'spectral overlap' treatment approaches the HLO treatment only when the ion-phonon interaction takes place at one site only. If phonon interactions take place at both sites in the ET process, the ET rate cannot be obtained from spectral overlap considerations [368].

We only consider the one-phonon-assisted process in the weak-coupling limit, where D and A are taken to be the same species. For an isotropic crystal, the donor-acceptor ET rate is given, for a large energy mismatch (~100 cm⁻¹) between the donor and acceptor excitations, ΔE (also equal to the phonon energy), under the Debye phonon model, by the expression [368]

$$W_{DA} = \frac{J^2 (f-g)^2 |\Delta E|}{\pi \hbar^4 \rho} \left(\sum_s \frac{\alpha_s}{u_s^5} \right) \left\{ \begin{array}{l} n(|\Delta E|) + 1\\ n(|\Delta E|) \end{array} \right\}$$
(73)

where *f* and *g* denote the (diagonal) electron-phonon coupling strengths for ground and excited states, respectively; ρ is the mass density; u_s is the velocity of sound (spread velocity) for the particular polarization index *s*; α_s is about 1, and concerns the average value of the strain tensor of solid angle Ω :

$$\alpha_{s}k^{2} = \frac{1}{4} \left\langle \left(e_{s,\alpha}k_{\beta} + e_{s,\beta}k_{\alpha} \right)^{2} \right\rangle_{\Omega}$$
(74)

where $e_{s,\alpha}$ is the α th component of the polarization vector for the *s* polarization (i.e. longitudinal or transverse); and *k* is the magnitude of the phonon wavevector. The quantities at the top $(n(|\Delta E|)+1)$, referring to phonon emission) and bottom $(n(|\Delta E|))$, referring to phonon absorption) of Eq. (73) are Bose factors, where

$$n(|\Delta E|) = [\exp(|\Delta E|/k_B T) - 1]^{-1}$$
(75)

When $|\Delta E| < k_B T$, the expression at Eq. (73) simplifies to

$$W_{DA} = \frac{J^2 (f-g)^2}{\pi \hbar^4 \rho} \left(\sum_s \frac{\alpha_s}{u_s^5} \right) k_B T$$
(76)

By contrast, when there is a small energy mismatch between the donor and acceptor excitations, the donor-acceptor ET rate is given by

$$W_{DA} = \frac{J^2 (f-g)^2 |\Delta E|^2 R^2}{6\pi \hbar^6 \rho} \left(\sum_s \frac{\alpha_s}{u_s^7} \right) k_B T$$
(77)

where *R* is the donor-acceptor intersite distance.

Several conclusions may be drawn from the results from Eqs. (76) and (77). First, Eq. (77) is considerably smaller than Eq. (76), so that for small energy mismatch, ET between similar ions is unlikely to occur by this mechanism. Second, the phonon modulation of the lattice serves to make the site energies equal, only when the electron-phonon coupling strengths (at each site) differ in the ground and excited electronic states, and when the phonon wavelength is less than the distance between the two sites. Thus the transfer rate of the one-phonon-assisted process (Eq. 76) is independent of the energy mismatch, and linearly dependent upon temperature. These considerations led HLO to formulate higher-order mechanisms for phonon-assisted ET involving two phonons [368]. However, in general the ET rates between lanthanide ions in elpasolite lattices appear to be far too small, when estimated from the diagonal mechanism, since the electronic matrix elements J_{QQ} are small, and the difference (f-g) between f^N excited-state and ground state electron-phonon coupling constants is small.

13.3 Phonon-assisted Energy Transfer: Nondiagonal Process

A second type of mechanism, (EQ \leftrightarrow EDV) for phonon-assisted ET involves nondiagonal electronic matrix elements, since one phonon is involved in an EDV transition at one site to compensate the energy mismatch, whilst also introducing odd-parity electronic operators making a transition from a 4f^N state to a $4f^{N-1}5d^1$ state. An EQ transition occurs at the other site. One case is illustrated in Fig. 24g, where the EQ transition at the donor is coupled by multipolar interactions with the EDV transition at the acceptor ion. The Debye phonon model approximation was used as in HLO theory, although it is a good approximation only when the phonon involved is an (odd-parity) acoustic mode with small wavevector **k**. Then, when the intersite energy mismatch is large, and $|\Delta E| < k_B T$, the ET rate is given by [369]

$$W_{DA} \simeq \frac{J^2 (\Delta E)^2}{\pi \hbar^4 \rho} \sum_s \frac{\alpha_s}{u_s^5} (k_B T)$$
(78)

where from Eq. (66):

$$J = \langle [\mathbf{D}], \mathbf{A}^* | \mathbf{H}_{DQ} | [\mathbf{D}^*], \mathbf{A} \rangle$$
(79)

and H_{DQ} is the dipole-quadrupole interaction operator. The square brackets represent the first-order approximative perturbation wavefunctions of the donor by taking the localized electron-phonon coupling Hamiltonian as the perturbation operator. Under the same conditions, $|\Delta E| < k_B T$, the ET rate for the case when the intersite energy mismatch is small, is found to be twice that in Eq. (78). It is important that the interference factor $|e^{\pm i \mathbf{k} \cdot \mathbf{R}} - 1|^2 \approx$ $|1-1|^2 = 0$ present in the diagonal HLO treatment is changed to be $|e^{\pm i \mathbf{k} \cdot \mathbf{R}} + 1|^2 \approx |1+1|^2 = 4$ now, so that a small energy mismatch in nonresonant ET (including energy migration) can be made up by one nondiagonal phonon-assisted ET process, provided that the phonon density of states is sufficient. The ET rate for this process increases quadratically with increasing intersite energy mismatch, and linearly with temperature.

The phonon involved has recently been described by a running lattice wave model and the same significant difference between the coherence effects of the diagonal and nondiagonal ET cases was found to occur [369]. However, some further insights are gained. In particular, optical phonons with k=0 and appreciable energy (250 cm⁻¹, for example) can make important contributions to one-phonon-assisted nondiagonal ET processes. The site selection rule (Eq. 29) for the EDV process operates, as well as certain 3j symbol triangle selection rules for angular momentum. For example, under the Judd-closure approximation, for an EDV donor transition, the triangle relation $(J_{f_i} \lambda, J_i)$ with $\lambda = 2,4,6$ must be satisfied; and for an EQ acceptor transition, $(J_{f_i}, 2, J_i)$. The extension of the nondiagonal phonon-assisted ET model though the formulae are more complex, simple vibronic selection rules operate. Contrary to HLO theory, according to the running lattice wave model of the phonon involved [369], an optical phonon with nonzero k and high symmetry (therefore, high density of states), can make an important contribution to *both* the nondiagonal and diagonal ET processes.

The HLO model has generally been tested by observing the temperaturedependence of the transfer rate, but no detailed calculations of ET rates, by including the evaluation of electronic factors, have been made for Ln^{3+} systems. In principle, such calculations are tractable for the nondiagonal case but have not yet been forthcoming. The general approach of the data analysis for nonresonant ET processes in lanthanide elpasolite systems has been to utilize a R^{-6} dependence of the transfer rate (i.e. for EDV \leftrightarrow EDV processes) and to allow for transfer to successive shells of acceptor neighbours (without detailed consideration of the electronic matrix elements or the phonons involved, Sect. 13.4.1), or to employ a spectral overlap model (Sect. 13.4.2). Some of these studies are now reviewed.

13.4 Experimental Studies of Energy Transfer

13.4.1 Concentration Quenching in Neat Elpasolite Systems

The emission from certain multiplets of diluted lanthanide elpasolite systems is quenched by ion-ion cross relaxations in the neat materials (Fig. 24c, where D and A are the same species). Some examples of these concentration quenchings are the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$ emission of Nd³⁺ in Cs₂NaNdCl₆ [308] and M₂KNdF₆ (M=Rb, Cs) [309]; the ${}^{5}D_{1} \rightarrow {}^{7}F_{0}$ emission of Eu³⁺ in Cs₂NaEuCl₆ [322] and Cs₂NaYF₆:Eu³⁺ [25]; the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ emission of Sm³⁺ in Cs₂NaSmCl₆ [314]; the ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ emission of Er³⁺ in Cs₂NaErCl₆ [305]. All of the cross-relaxation processes responsible for these quenchings are nonresonant and presumably correspond to (EDV \leftrightarrow EDV) processes, since the ET rate is inversely proportional to the sixth power of the interion separation, *R*. The nearest neighbour dependence of the transfer rate has been systematically calculated using a shell model [305, 306] and a crystal model [370, 371], and the application to Pr³⁺ is summarized here.

In the absence of migration between donors or acceptors, and of acceptor-donor back-transfer, the decay of the emission of the Ln³⁺ donor ion participating in a two-ion cross-relaxation process with identical acceptors, Fig. 24c is described by [305]

$$\frac{I(t)}{I(0)} = \exp\left(-k - \sum_{n}^{shells} r_n k_n\right) t$$
(80)

at weak excitation intensities, where k_n is the transfer rate to the *n*th-shell acceptor, with occupancy factor r_n ; k is the (radiative plus nonradiative) decay constant for an isolated donor ion. Considering only ED-ED interactions in a face-centred cubic lattice, this equation may be formulated as

$$\frac{I(t)}{I(0)} = \exp\left(-kt\right) \prod_{n}^{\text{allshells}} \exp\left(-r_n \left(\frac{R_1}{R_n}\right)^6 k_{ET}t\right)$$
(81)

where k_{ET} is the ET rate to a single ion at the position of nearest neighbour acceptor at distance R_1 . This equation applies to a single donor ion, which thus has an exponential decay. However, for diluted crystals, randomly-distributed donors will have different shell occupancy factors for acceptor ions, so that the sum of the exponential decay processes will become non-exponential. This is taken into account by including the statistical probability, $O_{r_n}^{N_n}(x)$, of a specific shell n in which surrounding r_n sites are occupied by a lanthanide ion from N_n possible positions (and the remaining sites occupied by the ion Y³⁺ in M₂ALn_xY_{1-x}Cl₆, which is not involved in ET processes). The probability of a particular distribution with r_1 Ln³⁺ ions in shell 1, r_2 in shell 2, etc., is then the product of these statistical probabilities over the nshells, so that Eq. (81) may be written as

$$\frac{I(t)}{I(0)} = \exp\left(-kt\right) \prod_{n}^{\text{allshells}} \sum_{r_n}^{N_n} O_{r_n}^{N_n}(x) \times \exp\left(-r_n \left(\frac{R_1}{R_n}\right)^6 k_{ET}t\right)$$
(82)

As pointed out in Section 13.1, even at x=1, some 98% of the ET to the acceptors is included up to the 3rd shell. At x<0.02, only the singly-occupied shell is probable, whereas at x=0.15 there is an equal probability of single and double occupancy of the shell. The model assumes a uniform dielectric, even though some nearby ions block the ET pathway to more distant ones. Deviations from exponential decay are apparent when k_{ET} -k, but at large values of k_{ET} the n=1 factor dominates to give a double-exponential decay, with the fast process giving k_{ET} directly. For x=1, the decay is exponential with a decay constant equal to $k(1)=k+14.4k_{ET}$. Figure 25a shows the computed decay curves for various ratios of k_{ET} and k.

In the case of $Cs_2NaPr_xY_{1-x}Cl_6$, the cross-relaxation for quenching ${}^{3}P_0$ emission, Fig. 24c, is nonresonant and is a EDV-EDV process, of which there are several pathways, such as

$$({}^{3}P_{0})\Gamma_{1}[20,602](D^{*}) \rightarrow ({}^{1}G_{4})\Gamma_{5}[10,325] + \nu_{4}[99](D)$$
 (83a)

$$({}^{3}\text{H}_{4})\Gamma_{1}[0](\text{A}) \rightarrow ({}^{1}\text{G}_{4})\Gamma_{4}[9894] + \nu_{3}\text{ZB}[285](\text{A}^{*})$$
(83)

where the square brackets denote energies (cm^{-1}) , referring to $Cs_2NaYCl_6:Pr^{3+}$. Note that both processes are spin-forbidden so that the ET process does not completely quench the ${}^{3}P_{0}$ emission even for x=1. The emission decay curves, Fig. 25a, show the effect of the shortening of the life-time and the non-exponential behaviour as x increases. The two fitted curves (x=0.25 and 0.5) in Fig. 25b utilise $k=3610 \text{ s}^{-1}$ (from the pure expo-



Fig. 25a, **b** Luminescence decay curves **a** computed for different ratios of k_{ET} and k (Eq. 82 with x=0.25 and $k=500 \text{ s}^{-1}$) [314]; **b** 468 nm excited 80 K luminescence decay curves for Cs₂NaY_{1-x}Pr_xCl₆ for different x, with the computed curves for x=0.25, 0.5 employing $k=3610 \text{ s}^{-1}$ and k_{ET} ~1350 s⁻¹ (Adapted from [305, 314])

nential decay of a very dilute crystal) and k_{ET} =1350 s⁻¹ (from the exponential decay of a crystal with *x*=1, with constant k_{ET}) [305].

The shell model has been applied to the quenching of the ${}^{4}G_{5/2}$ emission of Sm³⁺ in Cs₂NaY_{1-x}Sm_xCl₆, with less satisfactory results. Again, the crossrelaxation processes are certainly nonresonant, but the EQ \leftrightarrow EDV process cannot be excluded. Some factors which might account for the deviation of fitted decay profiles from experiment have been discussed [310, 314], including the presence of migration and the size inequality of Ln³⁺ and Y³⁺, which would affect the shell occupancies. Better agreement of simulated decay curves with experimental decay curves was found when the donor-acceptor ET was truncated to occur just over the first few shells [311], so that the nature of the multipole-multipole interaction then becomes unclear. One factor which is not taken into account is the fact that the quenching can occur by many different EDV-EDV and/or EQ \leftrightarrow EDV pathways, each with a different cross-relaxation rate, and that the relative importance will change with temperature if the initial states are thermally populated.

A more general microscopic model, the crystal model [370], has been formulated for dipole-dipole ET in which an 'angular class' of ions (made up, from the translational symmetry properties of the lattice, of the set of acceptor ions having the same angular orientation with respect to the donor ion) is employed instead of a shell. The model does not include migration between donor ions, or back transfer. The phonon part is not considered, since the model is based upon the distance-dependence of the transfer rate to the angular classes of acceptor ions. The master equation for (EDV \leftrightarrow EDV) processes is [370]

$$\frac{I(t)}{I(0)} = \exp\left[\left(-k - x\zeta(6)L(l)k_{ET}\right)t\right]$$
(84)

where $\zeta(6)$ is the Reimann zeta function for the order 6 of dipole-dipole interaction, and L(l) is a lattice parameter for the *l*-th angular class. Note that $\ln[(I(t)/I(0)]]$ shows a linear dependence with acceptor concentration, *x*. The crystal model was further extended [371] to take into account the deviations of fitted curves, using the behaviour (Eq. 84), from experimental data at intermediate values of *x*. These deviations were not attributed to migration effects, but to the statistical fluctuations of the populations of angular classes. Thus a correction term, $\Delta_{stat}(x,t)$, was introduced which depends upon the average of the statistical fluctuations in the population of acceptors and which leads to closer agreement with experiment at early time stages.

Finally, it is noted that the absence of emission from a particular energy level, in a crystal with a high concentration of optical centres, may arise from several other reasons. First, level bypassing may occur in the more concentrated crystals when the excitation is into an upper level which can undergo a cross-relaxation process to a rather lower level. This is the case for the quenching of ${}^{5}F_{4} \rightarrow {}^{5}I_{8}$ green emission of Ho³⁺ in neat Cs₂NaHoCl₆,

when excitation is into the next-highest multiplet term, ${}^{5}F_{3}$. The (nonresonant) cross-relaxation process ${}^{5}F_{3} \rightarrow {}^{5}F_{5}$ at the donor, and ${}^{5}I_{8} \rightarrow {}^{5}I_{7}$ at the acceptor produces intense red ${}^{5}F_{5} \rightarrow {}^{5}I_{8}$ emission [333]. Second, the elpasolite systems Cs₂NaLnX₆ (X=Cl, Br) are particularly hygroscopic so that defect-sites readily occur with the Ln³⁺ ion adjacent to oxychloride or hydroxide ions. Thus, the ${}^{5}D_{0}$ state of Eu³⁺ in Cs₂NaEuCl₆ exhibits a non-exponential, faster decay for samples where such defects are present [319]. It is interesting, however, that the decay characteristics are more sensitive to the presence of these defects than are the emission spectra themselves.

13.4.2 Cross-relaxation Involving Different Donor and Acceptor Species

The shell model has been utilized in the interpretation of the ET cross-relaxation processes in systems of the type $Cs_2NaLn_xLn'_{1-x}Cl_6$ and $Cs_2NaLn_xLn'_yB_{1-x-y}Cl_6$, where Ln=Sm, Ln'=Eu, B=Gd or Y [312, 313, 316-318], with varying degrees of success. A two-centre crystal model has been developed for these types of system and the predicted emission decay behaviour resembles the double exponential type [372].

Other M₂ALnLn'Cl₆ systems where $f^{N}-f^{N}$ ET processes have been observed between Ln and Ln' are Ho and Er [186]; and Yb and Ho or Nd [149, 333, 348]. The f¹d¹ Pr³⁺-d¹ Ce³⁺ ET is evident when exciting into Pr³⁺ absorption bands and observing the Ce³⁺ d¹ \rightarrow f¹ emission [206, 260]. By fitting the decay of the 295 K Ce³⁺ emission to an expression of the form

$$I = A\left[\exp\left(-t/\tau_{Ce}\right) - \exp\left(-t/\tau_{Pr}\right)\right]$$
(85)

where I(0)=0 and A is a constant, the d \rightarrow f emission lifetimes were found to be 30 ns and 20 ns for Ce³⁺ and Pr³⁺, respectively [260]. The decay of the Pr³⁺ f¹d¹ \rightarrow f² emission has also been measured in neat Cs₂NaPrCl₆ (13 ns) and dilute Cs₂NaY_{0.99}Pr_{0.01}Cl₆ (18 ns) at 8 K, where the concentration quenching was attributed to a nonresonant cross-relaxation from the lowest f¹d¹ level [206].

The major interest in this section focuses upon the Tb^{3+} to Eu^{3+} ET in the systems $Cs_2NaTb_{1-x}Eu_xCl_6$, $Cs_2NaEu_xTb_{0.005}Y_{0.995-x}$ and $Cs_2NaEu_{0.05}Tb_yY_{0.95-y}$ because the explanation for this ET process is elusive up to the present. This $Tb^{3+} \rightarrow Eu^{3+}$ ET has been investigated in the system $Tb_{0.66}Eu_{0.33}P_5O_{14}$ [373], and a summary of previous work is given therein. It was found that the ${}^5D_1 \rightarrow {}^7F_1$ emission lines of Eu^{3+} were observed on excitation of the 5D_4 manifold of Tb^{3+} , and the 5D_1 lifetime was found to be equal to the 5D_4 lifetime under these conditions [373]. Two possible transfer processes were considered at low temperature:

$$Tb^{3+}({}^{5}D_{4}) + Eu^{3+}({}^{7}F_{0}) + phonon(s) \rightarrow Tb^{3+}({}^{7}F_{4}) + Eu^{3+}({}^{5}D_{0})$$
(86a)

$$Tb^{3+}(^{5}D_{4}) + Eu^{3+}(^{7}F_{0}) \to Tb^{3+}(^{7}F_{6}) + Eu^{3+}(^{5}D_{1}) + phonon(s)$$
 (86b)

where the phonon energies are \sim 20–300 cm⁻¹ in Eq. (86a), and \sim 1000 cm⁻¹ in Eq. (86b), and Eq. (86b) was concluded to be the most important process.

The energy level diagrams for the Tb^{3+} and Eu^{3+} systems in elpasolite lattices are shown in Fig. 26a. In the first experimental study of $Tb^{3+}-Eu^{3+}$ transfer in elpasolite hosts, the quenching of the ${}^{5}D_{4}$ emission produced luminescence from the ${}^{5}D_{0}$ level of Eu^{3+} . No emission was detected from ${}^{5}D_{1}$, although this luminescence could be observed upon direct excitation of ${}^{5}D_{1}$ in $Cs_{2}NaTb_{1-x}Eu_{x}Cl_{6}$, so that Eq. (86b) was excluded from the ET, and the most likely processes were formulated as Eqs. (86a) and (86c):

$$Tb^{3+}(^{5}D_{4}) + Eu^{3+}(^{7}F_{1}) \to Tb^{3+}(^{7}F_{4}) + Eu^{3+}(^{5}D_{0}) + phonon(s)$$
 (86c)

Equation (86c) would infer a strong temperature dependence, by a factor >100, between the 77 K and 295 K ET rates.

The emission intensity from ⁵D₄ in the system Cs₂NaTb_{1-x}Eu_xCl₆ was fitted to an equation of the type of Eq. (80), where the summation was just represented by k_{ET} [324–326]. The graph of the resulting parameter, k_{ET} with concentration of Eu^{3+} , x, at 293 K is shown in Fig. 26b, and its linearity was taken to indicate that (i) the same process operates over the entire concentration range at 293 K, and (ii) the ET involves only one Eu³⁺ ion. The behaviour was found to be different at 80 K (Fig. 26b), where k_{ET} varies linearly with x only for x=0.01-0.15, but is smaller, and independent of x when x=0.85-0.99 [325]. The luminescence decay curves for Cs₂NaEu_xT $b_{0.005}Y_{0.995-x}$ at 77 K and 295 K showed slight deviation from exponential behaviour [374], and the ET rate is again greater at room temperature, and varies roughly linearly with Eu³⁺ concentration (Fig. 26b). In this system the migration between donors is negligible, so that the transfer occurs from the excited Tb³⁺ ion to nearest neighbour Eu³⁺ ion. For the system $Cs_2NaEu_{0.05}Tb_{\nu}Y_{0.95-\nu}Cl_6$, where the Tb³⁺ concentration was varied [374], only the decay curves for $y \ge 0.5$ were single exponential at 295 K. The plot of the $Tb^{3+} \rightarrow Eu^{3+}$ ET rate against Tb^{3+} concentration, y, for this system is shown in Fig. 26c. The regions where k_{ET} is independent of y (e.g. up to $y\sim0.05$ at 77 K) correspond to negligible donor migration. The transfer rate decreases above $\gamma \sim 0.5$.

The intensity of the Eu³⁺ ${}^{5}D_{0}$ emission in Cs₂NaTb_{1-x} Eu_xCl₆, following pulsed excitation into Tb³⁺ ${}^{5}D_{4}$, was well-fitted to an expression analogous to Eq. (85), where the first lifetime corresponds to that of ${}^{5}D_{0}$ for the corresponding concentration of Eu³⁺ diluted into Cs₂NaYCl₆, and the second lifetime to the Tb³⁺ ${}^{5}D_{4}$ lifetime. This shows the direct feeding of ${}^{5}D_{0}$ from ${}^{7}F_{4}$, in the presence of fast migration between Tb³⁺ donors.

Attempts have been made to calculate the cross-relaxation rate from Tb³⁺ to Eu³⁺ by using the spectral overlap model, which employs the donor emission spectrum and its overlap with the acceptor absorption spectrum. It is





noted that this model treats these EDV transitions as if they are electronic transitions. Both of the Tb³⁺ emission and the Eu³⁺ absorption spectra are EDV in character, with the exception of a few MD lines. The electronic transition element, J, in the Fermi Golden rule (Eq. 64) was calculated from the components of the transition moments, M_{if} and M_{fi} , which in turn were related with the transition oscillator strengths (Eq. 15). Explicitly, the interaction energy, J, between the dipole at the donor site, M_D , and that at the acceptor site, M_A , is given by the expression

$$J = \frac{1}{4\pi\varepsilon_0 R^3} M_D \cdot C \cdot M_A \tag{87}$$

where M_B comprises the Cartesian vector components of the transition moment of B=A or D; and C is the dipolar coupling tensor [375]. The interaction energies were summed over the nearest neighbour shells. The lineshape function (Eq. 65) was calculated from the widths and energies of the spectral features, assuming Lorentzian shapes. From the spectral profiles, the Tb³⁺-Eu³⁺ spectral overlap must occur between hot bands in the $({}^{7}F_{0})\Gamma_{1g} \rightarrow ({}^{5}D_{0})\Gamma_{1g}$ absorption spectrum (with oscillator strengths 10^{-11} to 10^{-12}), and vibronic structure in the ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ emission spectrum (with oscillator strengths $<10^{-9}$). By an examination of the individual spectral overlaps, the $Tb^{3+} \rightarrow Eu^{3+}$ ET rate was calculated to be of the order $10^{-4} s^{-1}$ [376], which is far from the measured value at 80 K in Cs₂NaTb_{0.1}Eu_{0.1}Cl₆ of 228 s⁻¹. A more detailed calculation along similar lines has also been made of the transfer rate in Cs₂NaY_{0.995-x}Tb_{0.005}Eu_xCl₆, and the discrepancy with experiment was also found to be of the order 10^{-4} to 10^{-5} [374]. Near agreement between experimental and calculated (by the spectral overlap approach) ET rates could only be achieved by treating the $Tb^{3+5}D_4 \rightarrow {}^7F_4$ and $Eu^{3+7}F_0$, ${}^7F_1 \rightarrow {}^5D_0$ multiplet to multiplet transition manifolds as continuous and perfectly overlapping spectral distributions [374]. This pseudo-agreement is then a similar result just as for $Tb^{3+} \rightarrow Eu^{3+}$ ET in low-symmetry systems, where spectral features are broad (e.g. in mixed tris-(acetylacetonato) Tb³⁺-Eu³⁺ dimers, where in solution at 295 K, k_{ET} (calc)~(3–8)×10⁴ s⁻¹ and k^{ET} (obs)~5×10⁴ s⁻¹) [377]. However, as pointed out by Moran et al., there is little justification to ignore the detailed, well-characterized structural and spectral information available from the elpasolite systems when making this type of calculation.

A more recent spectral study of $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ ET in the system Cs₂ KTb_{0.9}Eu_{0.1}Cl₆ showed that ET occurs from Tb³⁺ ⁷F₄ to Eu³⁺ ⁵D₀ (and not to ⁵D₁) at 300 K, but that this was totally quenched at 11 K [378], so that the initial Eu³⁺ acceptor state is not ⁷F₀. Finally, it is noted that the spectral overlap model has been used successfully to account for the Tb³⁺ \rightarrow Eu³⁺ ET in Na₃[Tb_{0.01}Eu_{0.99}(ODA)₃]·2NaClO₄·6H₂0 (ODA=oxydiacetate), where k_{ET} 100 s⁻¹ at 295 K [379].

13.4.3 Upconversion

Various processes can lead to upconversion (i.e. emission of photons of higher energy than the pump energy) for M_2ALnX_6 systems, but with the exclusion of second harmonic generation. Considering one-colour excitation only in the following, (simultaneous) TP absorption, Fig. 24h, is a single-ion process which can populate an electronic state (or a vibronic state involving an even parity vibration, subject to the relevant selection rules) which occurs only during the laser pulse. Second, (sequential) ESA is another single ion process occurring during the laser pulse, which may populate a terminal electronic state (f, Fig. 24i) or vibronic state (dotted line above f, Fig. 24i) from an initially populated excited state f (Fig. 24i). This process frequently competes with ET upconversion, Fig. 24d, which is at least a two-ion process.

Some of the upconversions reported for neat lanthanide elpasolite systems are: from red (${}^{5}F_{5}$) to ultraviolet/blue (${}^{5}G_{5}$, ${}^{5}F_{3}$) in Cs₂NaHoCl₆ [334]; red to blue [338] and green to ultraviolet [35, 277, 336, 380] in Cs₂NaErCl₆; from blue (${}^{1}D_{2}$) to ultraviolet (${}^{3}P_{2}$) in Cs₂NaTmCl₆ [344]; and for doped systems, from infrared to green (${}^{4}S_{3/2}$) in Cs₂NaEr_{0.2}Yb_{0.4}Y_{0.4}Cl₆ [337, 381]; blue (${}^{5}D_{4}$) to ultraviolet in Rb₂KInF₆:Tb³⁺ [329]; and blue to ultraviolet in Cs₂NaY_{1-x}Pr_xCl₆ [260]. Generally, the upconversion mechanism has not been conclusively identified, but some ways of attempting this are now reviewed.

Ignoring ESA, and the population of f from higher levels in Fig. 24d, then in the case of continuous excitation, assuming the steady state [382], the time dependent populations of levels f and f' in Fig. 24d are given by

$$\frac{dn_f}{dt} = Pn_i - \frac{n_f}{\tau_f} - 2Un_f^2 \tag{88a}$$

$$\frac{dn_{f'}}{dt} = Un_f^2 - \frac{n_{f'}}{\tau_{f'}}$$
(88b)

where *P* is the ground state absorption rate constant; *U* is the ion pair upconversion rate coefficient; n_j the population of level *j*; and τ_j are the singleion lifetimes, so that

$$2Un_f^2 + \frac{n_f}{\tau_f} = Pn_i \tag{89}$$

which infers that for a given pump power, an increase in τ_f will lead to an increase in n_f , and to stronger emission from level f. By contrast, the emission from f following ESA (Fig. 24i), from a short pulse is independent of τ_f , and decays exponentially with lifetime $\tau_{f'}$.

Other distinguishing features between ESA and ET upconversion have been discussed in detail elsewhere [382], and in summary are (i) the presence of a risetime under pulsed excitation (which may disappear under square wave excitation) in the emission from f for the latter, but not the former; (ii) under certain experimental conditions, the intensity of an *n*-photon excitation process will scale as the *n*-th power of the excitation power [383]; (iii) the ET upconversion excitation spectrum closely resembles the (ground state) absorption spectrum, with the line profile of the former being approximately the square of that of the latter. In the case of ESA, additional features may be present, corresponding to the multiple absorption peaks in the upconversion process; (iv) the luminescence following ET upconversion will show a quadratic concentration dependence, whereas no such marked variation will result following ESA.

The most numerous, and most studied upconversions are those of Er^{3+} in $Cs_2NaLnCl_6$ (Ln=Y, Er, Yb). Referring to the energy levels of this system in Fig. 9d, the following upconversions have been observed. First, red to blue upconversion was reported at 15 K, with excitation into ${}^{4}F_{9/2}$ [277]. The blue emission exhibited a quadratic intensity dependence upon the laser power. The intensity was Er^{3+} -concentration dependent, with samples of Cs_2NaYCl_6 doped with <1 mol% Er^{3+} not giving detectable emission. Using a 10-ns pulse with frequency 1 Hz (to eliminate a possible population build-up in long-lived excited states), the upconverted emission from ${}^{2}G_{9/2}$ exhibited a rise-time >10 ms, so that it derives from a cross-relaxation process [277]. Several schemes can be formulated, whether phonon-assisted, or as follows for resonant EQ-EQ ET:

$${}^{4}I_{9/2}a\Gamma_{8}[12,358](D^{*}) + {}^{4}I_{9/2}a\Gamma_{8}[12,358](A^{*}) \rightarrow {}^{2}G_{9/2}a\Gamma_{8}[24,425](A^{**}) + {}^{4}I_{15/2}c\Gamma_{8}[287](D)$$
(90a)

or
$$\rightarrow^2 G_{9/2}\Gamma_6[24,459](A^{**}) + {}^4 I_{15/2}\Gamma_6[259](D)$$
 (90b)

Equation (90) can be modelled by a 4-level system, involving ${}^{2}G_{9/2}(f')$, ${}^{4}F_{9/2}$, ${}^{4}I_{9/2}(f)$ and ${}^{4}I_{15/2}$ [380], similar to Eqs. (88)a,b, except that level f is fed by branching from ${}^{4}F_{9/2}$, instead of being pumped directly from the ground state. Whereas the solution Eq. (89) refers to the steady state, the solution for the decay of ${}^{2}G_{9/2}$ luminescence following pulsed excitation is rather more complex. Although the experimental decay curve can be well-modelled, the upconversion rate constant U is not well-determined [380].

Upconversion to ${}^{4}G_{11/2}$ has been reported under red excitation, and attributed to the ET process involving ${}^{4}F_{9/2}$ and ${}^{4}I_{9/2}$ initial excited states [384]. Upconversion to ${}^{2}G_{9/2}$ has also been reported at 10 K under continuous wave green (514.5 nm) or blue (488 nm) excitation [335]. Again the presence of a risetime in the ${}^{2}G_{9/2}$ emission suggests that an ET process occurs, but in this case the ${}^{4}S_{3/2}$ term is involved, for example:

$${}^{4}S_{3/2}a\Gamma_{8}[18,265](D^{*}) + {}^{4}I_{13/2}\Gamma_{6}[6492](A^{*})$$

$$\rightarrow {}^{4}I_{15/2}a\Gamma_{8}[0](D) + {}^{2}G_{9/2}b\Gamma_{8}[24,519] + \nu_{3}[238](A^{**})$$
(91)

although the contribution of ESA from ${}^{4}I_{13/2}$ has not been investigated.

Concerning the green to ultraviolet upconversion of Er^{3+} in elpasolites, a TP excitation process has been proposed for the population of the Er^{3+} ²H(2)_{9/2} a Γ_8 state at 36,224±12 cm⁻¹ in Cs₂NaErCl₆ at 15 K under pulsed laser excitation at 18,270 cm⁻¹ [277], because the emission did not exhibit a rise-time and it could not be observed under continuous excitation. There is no pure electronic state at 2×18,270=36,540 cm⁻¹, but a vibronic state could be populated, corresponding to the excitation of one quantum of v_1 in the a Γ_8 state. More recently, this upconversion to ²H(2)_{9/2} has been achieved at 10 K using pulsed laser excitation at approximately 19,130 cm⁻¹ (or several higher energies) so that in this case the upconversion mechanism is either ESA or cross-relaxation involving ⁴S_{3/2} [35].

Finally, the infrared or red to green upconversion of Er^{3+} has also received attention. Luminescence from ${}^{4}\text{S}_{3/2}$ showed a risetime of ~6 ms, and exhibited a quadratic dependence upon incident laser power, upon excitation into the ${}^{4}\text{F}_{9/2}$ term of Cs₂NaErCl₆ [277]. Continuous wave infrared (~1 μ m) excitation into ${}^{4}\text{I}_{11/2}$ is upconverted to green emission for Cs₂NaEr-Cl₆ [385] and Cs₂NaEr_{0.2}Yb_{0.4}Y_{0.4}Cl₆ [337, 381]. The power-emission intensity dependence in the case of Cs₂NaErCl₆ is quadratic, and the emission intensity does not vary much between 100–300 K. The process has been assigned to a mechanism involving two ions initially in the ${}^{4}\text{I}_{11/2}$ state [385].

The reverse of upconversion is downconversion, where each quantum of (vacuum) ultraviolet radiation is converted to several quanta of infrared or visible radiation (quantum cutting) [386]. For example, the highest energy emission for the excitation of Cs₂LiTmCl₆:Nd³⁺ by 476.9 nm radiation is below ca. 11,300 cm⁻¹, since the cross-relaxation of ¹G₄ Tm³⁺ level leads to the excitation of Tm³⁺ ³H₅ and Nd³⁺ ⁴F_{3/2} [344].

13.4.4

Energy Transfer in Transition Metal-Lanthanide Systems

Some studies have been undertaken to investigate upconversion phenomena in elpasolite lattices doped with both rare earth and d-block ions. These have generally employed the d-block element as a sensitizer, having (i) a large (often spin-allowed) absorption cross-section in the near infrared-visible region, which overlaps the f^N emission; (ii) a wide gap to the next lower energy level, to minimize nonradiative losses and the probability of backtransfer from the lanthanide ion; and (iii) the capability of chemical tuning of the energy levels, to match the activator requirements, by ligand replacement. Cresswell et al. [345] chose Re⁴⁺ (5d³) as sensitizer because it has electronic states at 13,850 and 15,300 cm⁻¹ (but no others up to 29,000 cm⁻¹) which have intraconfigurational d-d transitions with lifetimes ~60 μ s at 295 K. Thus when Cs₂NaYCl₆ was co-doped with Tm³⁺ and Re⁴⁺, ET from the latter to the former occurred under 647 nm excitation, since the Re⁴⁺ emission at 727 nm was quenched and the Re⁴⁺ ${}^{2}T_{2g}$ absorption bands appeared in the excitation spectrum of the Tm³⁺ infrared emission. A similar behaviour was found for the Cs₂ZrCl₆ host [387]. The ET was envisaged to occur to the ${}^{3}H_{4}$ or ${}^{3}H_{5}$ Tm³⁺ states, which then led to upconversion to the ${}^{1}D_{2}$ and ${}^{1}G_{4}$ states. Yb³⁺ \rightarrow Re⁴⁺ ET is very efficient in Cs₂NaYbCl₆:Re⁴⁺, leading to upconverted emission from the Re⁴⁺ ${}^{2}T_{2g}$ state [388]. Upconverted luminescence was also observed from both Tm³⁺ and Mo³⁺ in Cs₂NaY_{0.9}Tm_{0.05}. Mo_{0.05}Cl₆ upon excitation in the ${}^{3}H_{4}$ Tm³⁺ state [387]. ET from Yb³⁺ to Mo³⁺ in Cs₂NaYbCl₆:Mo³⁺ is very efficient [369]. Taking advantage of the long lifetimes of Er³⁺ intermediate states, and of the near-transparency of Os⁴⁺ (5d⁴) between 12,000 and 20,000 cm⁻¹, Cs₂NaYCl₆ was co-doped with Os⁴⁺ and Er³⁺ to give green Er³⁺ emission upon excitation into Os⁴⁺ levels near 11,000 cm⁻¹ [343]. IR to visible upconversion was found to be inefficient in Cs₂NaScCl₆:Pr³⁺:V³⁺ [389].

13.4.5 Photon Avalanche

Photon avalanche is a phenomenon where strong emission is obtained at shorter wavelengths than the excitation wavelength, even with very weak ground-state absorption at the pump wavelength [390-394]. The term refers to the orders-of-magnitude jump in emission intensity when the pump laser intensity crosses just above the critical threshold. A general energy level scheme for the avalanche process is shown in Fig. 24j. Very weak pump absorption from the ground state populates the f^{N} (vibronic) level l', which relaxes nonradiatively to the metastable level l. The strong ESA $l \rightarrow f$ is followed by nonradiative decay to the emitting level f. Avalanche can then occur if the cross-relaxation probability $f \rightarrow l$ at the donor, and $i \rightarrow l$ at the acceptor, is higher than the relaxation rate from f to levels below l. Thus the ESA from level l is enhanced because one cross-relaxation decay of level fproduces two ions, each in level l, which can then undergo ESA to level f. The mechanisms for the initial population of level *l*, besides thermal population, include absorption into a weak phonon sideband with subsequent nonradiative relaxation, and absorption of Raman scattered radiation. By analogy to Eq. (88), assuming that the phonon relaxations $f \rightarrow f$ and $l' \rightarrow l$ are fast compared with other processes, then the following equations describe the excitation process in Fig. 24j [392]:

$$\frac{dn_i}{dt} = -P(l')n_i + W_l n_l + bW_f n_f - Un_i n_f$$

$$\frac{dn_l}{dt} = P(l')n_i - P(f')n_i - W_l n_i + (1 - b)W_l n_i + 2Un_i n_i$$
(92a)

$$\frac{dn_l}{dt} = P(l')n_i - P(f')n_l - W_l n_l + (1-b)W_f n_f + 2Un_i n_f$$
(92b)



Fig. 27 a Power dependence of the 480 nm blue upconverted emission intensity of $Cs_2NaGdCl_6:Tm^{3+}$ (6, 10 and 15 mol%). b Temporal dependence of this emission (*continuous line, left-hand ordinate*) and of the transmitted laser beam (dotted line, right-hand ordinate) for the 10 mol% sample under high excitation power, 14.5 P_{thres} . (Adapted from [347])

$$\frac{dn_f}{dt} = P(f')n_l - W_f n_f - Un_i n_f \tag{92c}$$

with $n_i+n_f+n_l=1$, and where W_x is the single ion relaxation rate of level x; and b is the branching ratio of the decay of level f. P(l') is the pump rate to feed l', P(f') feeds f'; and U is the cross-relaxation rate constant. Although these beam energies are equal, the pump rate also depends upon the absorption cross section, which is very small for P(l'), but large for P(f'). Then, if $U>bW_f$, photon avalanche appears above the following threshold value of P(f') [392]:

$$P_{thres} = \frac{W_l (U + W_f)}{U - bW_f} \tag{93}$$

Whereas many examples of the photon avalanche phenomenon exist in the literature, only one study has been made for elpasolite systems [347], for Cs₂NaGdCl₆:Tm³⁺, where the blue upconverted emission is due to the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transition. However, the situation is rather more complex than in Fig. 24j because several other processes can occur, which also lead to emission from ¹D₂. Three features related to the ¹G₄ emission are highlighted here. First, Fig. 27a shows that a quadratic emission intensity-excitation power dependence is obtained at low excitation intensities for samples of Cs₂NaGdCl₆:Tm³⁺ doped with between 6–15 mol% Tm³⁺. However, a dramatic increase of the emission intensity appears above the excitation threshold value, ca. 9 kW cm⁻². In Fig. 27a, the slope increases to 6 for the 10 mol% Tm³⁺-doped sample. Second, the time-dependence of the upconverted emission exhibits different behaviour at different excitation powers. A notable difference from other systems is that, at the threshold excitation power, P_{thres} , the blue emission has an almost linear rise-time which is followed by a further slower rise over several seconds. Third, at high excitation powers, the establishment of the stationary state is quicker, and the ${}^{3}F_{4} \rightarrow {}^{1}G_{4}$ ESA decreases the transmitted laser light by several percent, Fig. 27b.

14 Conclusions

This review has summarised and commented upon the literature up to the end of 2002. The electronic spectra of elpasolite systems are complex and mainly vibronic in character. Whereas the major features can be interpreted in terms of localized moiety-mode vibrations, our understanding of the fine structure requires a more detailed investigation of the lattice dynamics of these systems in the future. One- and two-photon studies of certain lanthanide elpasolite systems have recently enabled extensive energy level datasets to be obtained, and the parametrization of these has revealed the need for the incorporation of other interacting configurations into the calculation. The study of f-d transitions of Ln^{3+} in M_2ALnX_6 systems is in its infancy, but promises to yield more clearly-resolved spectra than for the lower-symmetry hosts studied thus far. This is partly because of the higher degeneracy of CF levels in the elpasolite hosts, leading to fewer possible transitions, as well as to the more restrictive selection rules pertaining to these transitions. Resonant energy transfer in elpasolite systems is well-understood, but the understanding and calculation of nonresonant processes is far from satisfactory.

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1 Appendix

The O_h point group character table and the O (and O^* double group) multiplication table are given in Tables A1 and A2.

0 _h (m3m)		Е	8C3	6C ₂	6C ₄	3C ₂	i	6S ₄	8S ₆	$3\sigma_{\rm h}$	$6\sigma_{\rm d}$		
Γ_{1g}	A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
Γ_{2g}	A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
Γ _{3g}	Eg	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
Γ_{4g}	T_{1g}	3	0	-1	1	$^{-1}$	3	1	0	-1	-1	(R_x, R_y, R_z)	
Γ _{3g}	T _{2g}	3	0	1	-1	-1	3	-1	0	$^{-1}$	1	2	xz, yz, xy
Γ_{1u}	A_{1u}	1	1	1	1	1	$^{-1}$	$^{-1}$	-1	$^{-1}$	$^{-1}$		
Γ_{2u}	A_{2u}	1	1	-1	-1	1	-1	1	-1	$^{-1}$	1		
Γ_{3u}	Eu	2	-1	0	0	2	-2	0	1	-2	0		
Γ_{4u}	T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
Γ_{5u}	$T_{2u} \\$	3	0	1	-1	-1	-3	1	0	1	-1		

Table A1 Character table for O_h molecular point group

Table A2 Multiplication table for *O* and *O*^{*} molecular point group ($O_h = O \times C_i$)

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0	A_1	A_2	E	T_1	T ₂	$E'(\Gamma_6)$	$E''(\Gamma_7)$	U' (Γ ₈)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$A_1(\Gamma_1)$	A1	A ₂	E	T ₁	T ₂	E'	E″	U'
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$A_2(\Gamma_2)$ E(Γ_3)	A ₂ E	A ₁ E	E A ₁ +A ₂ +E	T_{1}^{1}	$T_1 T_1 + T_2$	E U'	E U'	U E'+E"+U'
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_1(\Gamma_4)$	T_1	T_2	$T_1 + T_2$	$A_1 + E + T_1 + T_2$	$A_2 + E + T_1 + T_2$	E'+U'	E''+U'	E' + E'' + 2U'
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_2(\Gamma_5)$	T ₂ E'	T ₁ E″	$T_1 + T_2$	$A_2 + E + T_1 + T_2$	$A_1 + E + T_1 + T_2$ E'' + U'	E"+U'	E'+U'	E'+E"+2U'
$U' (\Gamma_8) U' \qquad U' \qquad E' + E'' + U' \qquad E' + E'' + 2U' \qquad E' + E + 2U' \qquad E + T_1 + T_2 \qquad E + T_1 + T_2 \qquad A_1 + A_2 + E + 2T_1 + 2T_2 \qquad A_2 + E + 2T_1 + 2T_2 \qquad A_1 + A_2 + E + 2T_1 + 2T_2 \qquad A_2 + E + 2T_1 + 2T_2 \qquad A_2 + E + 2T_1 + 2T_2 \qquad A_3 + A_4 + E + 2T_1 + 2T_2 \qquad A_4 + A_5 + E + 2T_1 + 2T_2 \qquad A_4 + A_5 + E + 2T_1 + 2T_2 \qquad A_4 + A_5 + E + 2T_1 + 2T_2 \qquad A_4 + A_5 + E + 2T_1 + 2T_2 \qquad A_4 + A_5 + E + 2T_1 + 2T_2 \qquad A_5 + 2T_1 $	$E'(\Gamma_6)$ $E''(\Gamma_7)$	Е Е″	E E'	U'	E + U' E'' + U'	E' + U'	$A_1 + T_1$ $A_2 + T_2$	$A_2 + T_2$ $A_1 + T_1$	$E+T_1+T_2$ $E+T_1+T_2$
	U' (Γ ₈)	U'	U'	E'+E''+U'	E'+E''+2U'	E'+E+2U'	$E{+}T_1{+}T_2$	$E{+}T_1{+}T_2$	$A_1 + A_2 + E + 2T_1 + 2T_2$

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