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THE EMISSION SPECTRA FOR THE $Cs_2NaScCl_6$:$MoCl_6^{3-}$ SYSTEM IN THE $Fm3m$ SPACE GROUP

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On the basis of the data reported by Flint and Paulusz, we have undertaken a theoretical investigation of the intensity mechanism for the various emissions: $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$, $\Gamma_8(^2E_g)$, $\Gamma_8(^2T_{1g})$, $\Gamma_6(^2T_{1g})$ for the $Cs_2NaScCl_6$:$MoCl_6^{3-}$ system in the $Fm3m$-space group. The experimental data available refer to the visible and near infrared luminescence spectra of $MoCl_6^{3-}$ complex ion in different hosts, such as Cs_2NaMCl_6 (M = Sc, Y, In), measured between 15,000 cm^{-1} and 3,000 cm^{-1} at liquid helium temperatures. At least, five luminescence transitions have been identified and assigned and each of them show extensive vibronic structure. A careful analysis of this experimental data shows that for the various observed electronic transitions, the vibrational frequencies change only slightly, and therefore there is no indication that the system undergoes both a significant and relevant Jahn–Teller distortion (along an active coordinate). There is however clear evidence that for the chloro-elpasolites, there is a strong resonance interaction between $\nu_3(\tau_{1u}$: stretching) of the MoX_6^{3-}, complex ion and that of the host when M = In, Y. Thus for M = Sc, the slighter higher host ν_3, wave number is likely to minimize the effect of this coupling. This evidence will allow us for the $Cs_2NaScCl_6$:$MoCl_6^{3-}$ system to neglect, in the first-order approximation, the coupling among the internal and the external vibrations and to proceed using a both a molecular and the independent system models.

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1. Introduction

The lattice Cs_2NaMX_6 belongs to the space group $Fm3m(O_h^5)$ [1–3], in which the M^{3+} ions occupy sites of perfect octahedral symmetry. The vibrational symmetry species for this lattice are as follows: $Na^{1+}(\tau_{1u})$, $Cs^{1+}(\tau_{2g}+\tau_{1u})$,

$MX_6^{3-}(\alpha_{1g}+\varepsilon_g+2\tau_{1u}+\tau_{2g}+\tau_{2u})$. As we can see, in addition to the 15 degrees of freedom of the MX_6^{3-} complex ion, distributed into the irreducible representation of the O_h-point molecular group (as given below), there are four lattice modes of symmetries: $2\tau_{1u}$ (*IR active*), τ_{2g} (*Raman active*) and τ_{1g} (*inactive*). Lentz [4], in a magnificent paper, discussed the lattice vibrations for both the $A_3B'X_6$ and $A_2BB'X_6$, in the space group $Fm3m$ and using a modified version of a valence type of force field, concluded that ten force constants should be known to estimate all the fundamental vibrations in the $\boldsymbol{k}=\mathbf{0}$ approximation.

In the notation put forward by Lentz, the symmetry coordinates corresponding to the unit cell are labelled as follows:

$$\left\{\begin{array}{c} S_1=S_1(\mathrm{X}):\alpha_{1g},\ S_2=S_2(\mathrm{X}):\varepsilon_g,\ S_3=S_3(\mathrm{X}):\tau_{1g},\ S_4=S_4(\mathrm{X}):\tau_{2g},\\ S_5=S_5(\mathrm{Cs}):\tau_{2g},\ S_6=S_6(\mathrm{M,X,Na}):\tau_{1u},\ S_7=S_7(\mathrm{M,X,Cs,Na}):\tau_{1u},\\ S_8=S_8(\mathrm{M,Na}):\tau_{1u},\ S_9=S_9(\mathrm{M,X,Na,Cs}):\tau_{1u},\ S_{10}=S_{10}(\mathrm{X}):\tau_{2u}. \end{array}\right\}$$

When this notation is adopted, it is clear that the symmetry blocks are as follows: $\alpha_{1g}(1\times1),\varepsilon_g(1\times1),\tau_{1g}(1\times1),\tau_{1u}(4\times4),\tau_{2g}(2\times2)$ and $\tau_{1u}(1\times1)$, and hence the odd parity symmetry coordinates (S) are related to the normal coordinates (Q), by means of the transformations:

(A) the τ_{1u} symmetry block

$$\begin{pmatrix} S_{6t}\\ S_{7t}\\ S_{8t}\\ S_{9t}\end{pmatrix}=\begin{pmatrix} L_{66} & L_{67} & L_{68} & L_{69}\\ L_{76} & L_{77} & L_{78} & L_{79}\\ L_{86} & L_{87} & L_{88} & L_{89}\\ L_{96} & L_{97} & L_{98} & L_{99}\end{pmatrix}\begin{pmatrix} Q_{6t}\\ Q_{7t}\\ Q_{8t}\\ Q_{9t}\end{pmatrix}.$$

(B) the τ_{2u} symmetry block

$$(S_{10t})=(L_{10,10})(Q_{10t})$$

for $t=a,b,c$.

It is interesting to make a few comments with regard to the transformations given above. For the τ_{1u}-symmetry block there is an obvious coupling among the internal and the lattice vibrations, being the extension of this mixing determined by the details of the interacting vibrational force field. It is also to be noticed that we have not included in this preliminary analysis the long range Coulombic interactions.

A proper treatment of this problem is to actually solve the dynamical equation of motion [5–7]

$$D(\boldsymbol{k})E(\boldsymbol{k})=E(\boldsymbol{k})\Omega^2(\boldsymbol{k}).$$

In this notation, $\Omega^2(\boldsymbol{k})$ is a diagonal matrix whose eigenvalues are $w^2_{p\boldsymbol{k}}$, and $E(\boldsymbol{k})$ represents the matrix of the eigenvectors $e_\alpha(\mu i|p\boldsymbol{k})$. The lattice sums are evaluated using the Ewald method [8, 9]. A full discussion of the lattice dynamics as applied for M_2XY_6 type systems in the $Fm3m$-space group may be found in Refs. [5, 6, 10] and the advantages and disadvantages of the model calculations putforward are discussed in detail. Though, it is worth mentioning that the experimental data available to undertake full lattice dynamic calculations is either incomplete or scarce. Only, very rarely we will have a large enough and accurate data base to fully test the theoretical models against the experimental data for these systems. We have initiated a program to undertake these kind of calculations for the elpasolite type systems and works on the pure $\mathrm{Cs_2NaErCl_6}$, $\mathrm{Cs_2NaEuCl_6}$, and $\mathrm{Cs_2NaMoCl_6}$ crystals are in progress [11]. It is well known that the set of symmetry coordinates does not represent the normal modes of motions for the crystal, then it is necessary to solve the dynamical equations of motion so that to have a semiquantitative idea about the mixing of the various symmetry coordinates belonging to the same symmetry species, so that to give support to assignments of peaks in the spectra for these crystals. At first glance, the pure symmetry coordinates representing internal motions of the cluster $\mathrm{MoCl_6^{3-}}$ are: $S_1(\alpha_{1\mathrm{g}} : \nu_1), S_2(\varepsilon_{\mathrm{g}} : \nu_2), S_4(\tau_{2\mathrm{g}} : \nu_5)$ and $S_{10}(\tau_{2\mathrm{u}} : \nu_6)$. The standard ν_3 and ν_4 are mixed up with the counter ion motions, and therefore at this stage it does not seem convenient to adopt the convention $S_6(\tau_{1\mathrm{u}} : \nu_3)$ and $S_7(\tau_{1\mathrm{u}} : \nu_4)$, unless we have solid evidence of either a small or negligible coupling among the internal $\mathrm{MoCl_6^{3-}}$ vibrations and those of the counter ions [10–15].

In this research paper, we will introduce a molecular model for the $\mathrm{MoCl_6^{3-}}$ complex ion, and will assume that the coupling among the internal and the external vibration is weak enough, though we recognize the importance of carrying out a full lattice dynamic calculation for this system. The results to be obtained will crucially depend on the assumption adopted in the model calculation, though they will serve as a basis for both a more comprehensive and sophisticated understanding of these complex phenomena in the solid state spectroscopy.

2. Theoretical background and model calculations

In this section, we shall provide the reader with a summary of the symmetry adopted vibronic coupling theory as employed for the elpasolite type system, within both the seven-atom system and the independent system models. Judd [16] and Ofelt [17] put forward a formalism to account for the observed spectral intensities in noncentrosymmetric $\mathrm{LnX_6^{3-}}$ complex ions. Both authors worked out master equations to deal with the crystal field contribution to the total transition dipole moment and the basic assumption was that an $f \rightarrow f$ transition acquires its intensity from either an $f \rightarrow d$ and/or an $f \rightarrow g$ or both, excitations through the odd parity components of the crystal field potential. In this formalism, the integral chains are in the first-order approximation of the forms

$$\langle f|\mu^{\alpha}|\psi_i(\mathrm{odd})\rangle\langle\psi_i(\mathrm{odd})|V^{CF}(\mathrm{odd})|f\rangle$$

and

$$\langle f|V^{CF}(\mathrm{odd})|\psi_i(\mathrm{odd})\rangle\langle\psi_i(\mathrm{odd})|\mu^{\alpha}|f\rangle,$$

where the intermediate odd parity central metal's wave functions have been labeled as $\psi_i(\mathrm{odd})$. Also, in the integral chains, there is a summation over all these odd parity states, and when closure is adopted, it is assumed that there is a complete and orthonormal set of wave functions, and all these infinite sets occur at the same energy, say $\overline{(\Delta E)}$. Thus, it is straightforward to show that under these constraints, the α-th vector component of the crystal field (static) transition dipole moment becomes

$$\mu^{\alpha}_{1\rightarrow 2} \cong \frac{2}{\overline{(\Delta E)}}\langle 1|\mu^{\alpha}V(\mathrm{odd})|2\rangle. \tag{2}$$

In the above identity, we have assumed that the condition

$$\sum_{i=1}^{\infty} |\psi_i(\mathrm{odd})\rangle\langle\psi_i(\mathrm{odd})| = 1$$

is fulfilled. It is important to fully understand the nature and the origin of the approximations involved when closure procedure is employed. To a first glance, it does seem that when this approximation is invoked, the nature of the intermediate odd parity central metal's wave function becomes irrelevant except of the choice of the effective energy gap $\overline{(\Delta E)}$. We certainly never employ a complete set of wave functions, at the most we use a truncated set of functions and in explicit direct calculations we evaluate the integral chains either for a subset of d-states ($l = 2$) or for a manifold of g states ($l = 3$).

It is currently, in the literature, to use some kind of average energy for $\overline{(\Delta E)}$, corresponding to a "virtual electronic transition", allowed by both spin and parity. For $d \rightarrow d$ excitation the value used is about 100,000 cm^{-1}, whereas for $f \rightarrow f$ we currently use values ranging from 50,000 cm^{-1} up to 80,000 cm^{-1} [18–24]. A series of pioneering works for both centrosymmetric and noncentrosymmetric complex ions of the lanthanide trivalent ions have been put forward by Richardson et al. [25–29] and a fair degree of success has been achieved. We have, instead, used a model calculation based upon a few number of parameters to be fitted from the experimental data [18–23]. Our strategy is largely based on the well known fact that for most of the systems of interest, the data base is either scarce or incomplete and therefore it is essential to model vibronic intensities with modified versions of current vibronic models. We have recently completed a work on the vibronic intensities for several selected absorption in the $\mathrm{Cs_2NaTmCl_6}$, for which a very careful and updated data base is available from infrared, Raman and luminescence spectra [19]. For this system, the calculation has been carried out using a modified version of the crystal field-ligand polarization formalism and as it will be shown the success achieved is more than satisfactory for a simple model, with a few sets of adjustable parameters.

The fundamentals are such that the total potential is written using the tensorial form worked out by Carlson and Rushbrooke [30] as

$$V = \sum_{L} \sum_{k_1 q_1, k_2 q_2} T^{(k_1+k_2)}_{-(q_1+q_2)}(R_L, \theta_L, \phi_L) D^{k_1}_{q_1}(\theta_M, \phi_M) D^{k_2}_{q_2}(\theta_L, \phi_L) \tag{3}$$

and in terms of potential, we may write an explicit first-order vibronic correction terms, as given below

$$\widehat{H}^{(1)} = V^{(1)}_{CF} + V^{(1)}_{LP}, \tag{4}$$

where it is straightforward to show that the following identities hold:

$$V^{(1)}_{CF} = -\sum_{L} Z_L e \sum_{\nu_t} \sum_{\Gamma\gamma i} \sum_{\tau} \left(\frac{\partial G^{CF,L}_{\Gamma\gamma}(i,\tau)}{\partial Q_{\nu_t}} \right)_0 M^{\Gamma}_{\gamma}(i,\tau) Q_{\nu_t} \tag{4.1}$$

and also

$$V^{(1)}_{LP} = \sum_{L} \sum_{\nu_t} \sum_{\Gamma\gamma} \sum_{i,\tau} \sum_{\alpha} \left(\frac{\partial G^{LP,L}_{\Gamma\gamma,\alpha}(i,\tau)}{\partial Q_{\nu_t}} \right)_0 M^{\Gamma}_{\gamma}(i,\tau) \mu^{\alpha}(L) Q_{\nu_t}. \tag{4.2}$$

Thus, for the vibronic crystal field contribution to the total transition dipole moment, we may write the master equation

$$\mu_{\nu_t}^{CF,\alpha}[|a\rangle \to |b\rangle] = \sum_m U_{\nu_m}^{CF,\alpha} L_{mt} \langle 0|Q_{\nu_t}|1\rangle$$

$$\text{(for the } \nu_t\text{-th normal mode of vibration)}, \tag{5.1}$$

where the electronic factor $U_m^{CF,\alpha}$ may be defined as [31–33]

$$U_{\nu_t}^{CF,\alpha} = \sum_{\overline{\Gamma}} \sum_{k,\tau} C_k^{CF} (-1)^{\Gamma_1 + \gamma_1^+} V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \overline{\Gamma} \\ \gamma_1^+ & \gamma_2 & \overline{\gamma} \end{pmatrix} A_{\nu_t}^{\overline{\Gamma}\overline{\gamma}}(k-1,\tau)$$

$$\times \langle (LSJ)\Gamma_1 \parallel O^{\Gamma}(k,\tau) \parallel (L'SJ')\Gamma_2 \rangle \tag{5.2}$$

and also

$$C_k^{CF} = \frac{2e^2 \langle r^k \rangle}{(\Delta E)(R_0^{k+1})}(e). \tag{5.3}$$

TABLE I

Vibronic coupling coefficients.

CF*: $A^{\Gamma\gamma}_{\Gamma\overline{\gamma}}(j)$				
	Γ	ν_3	ν_4	ν_6
$j = 1$	T_1	$2\sqrt{2}$	$\sqrt{2}$	0
	T_2	0	0	0
$j = 3$	T_1	$4\sqrt{2}$	$-\frac{3\sqrt{2}}{2}$	0
	T_2	0	0	$\frac{\sqrt{30}}{2}$
LP: $B^{\Gamma\gamma,T_1 0}_{\Gamma\overline{\gamma}}(k)$				
$k = 2$	$B^{E\theta,0}_{T_1 0}$	$12\sqrt{2}$	$-\frac{9\sqrt{2}}{2}$	0
	$B^{E\varepsilon,0}_{T_2 0}$	0	0	$\frac{5\sqrt{6}}{2}$
	$B^{T_2 1,0}_{T_1 -1} = -B^{T_2 -1,0}_{T_1 +1}$	$4\sqrt{6}$	$-\frac{3\sqrt{6}}{2}$	0
	$B^{T_2 1,0}_{T_2 +1} = -B^{T_2 -1,0}_{T_2 -1}$	0	0	$-\frac{5\sqrt{6}}{2}$
$k = 4$	$B^{A_1 a_1,0}_{T_1 0}$	$5\sqrt{42}$	$\frac{5\sqrt{42}}{2}$	0
	$B^{E\theta,0}_{T_1 0}$	$-5\sqrt{30}$	$-\frac{\sqrt{30}}{4}$	0
	$B^{E\varepsilon,0}_{T_2 0}$	0	0	$-\frac{21\sqrt{10}}{4}$
	$B^{T_1 1,0}_{T_1 +1} = -B^{T_1 -1,0}_{T_1 -1}$	$-3\sqrt{70}$	$-\frac{3\sqrt{70}}{2}$	0
	$B^{T_1 1,0}_{T_2 -1} = -B^{T_1 -1,0}_{T_2 +1}$	0	0	$-\frac{3\sqrt{70}}{2}$
	$B^{T_2 1,0}_{T_1 -1} = -B^{T_2 -1,0}_{T_1 +1}$	$3\sqrt{10}$	$-3\sqrt{10}$	0
	$B^{T_2 1,0}_{T_2 +1} = -B^{T_2 -1,0}_{T_2 -1}$	0	0	0

*The above listed values are independent of the components of both the T_1 and T_2 irreducible representations.

TABLE II

Overall oscillator strengths and relative vibronic intensity distributions [1].

(1.1) The $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g})$ transition

(1.1.1) Dipole strengths for the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^4A_{2g}) + \nu_k(k = 3, 4, 6)$transitions

	D^{CF}	D^{LP}	$D^{(CF,LP)}$	D^{Total}	Notes
ν_3	1.55×10^{-3}	7.64×10^{-6}	-2.18×10^{-4}	1.34×10^{-3}	The values are given in units of $C_4 = \frac{2e^2\langle r^4\rangle}{(\Delta E)R_0^5}$
ν_4	8.15×10^{-4}	1.25×10^{-4}	-6.40×10^{-4}	0.30×10^{-3}	
ν_6	9.97×10^{-4}	4.10×10^{-7}	$+4.04 \times 10^{-5}$	1.04×10^{-3}	

(1.1.2) Total oscillator strengths and relative vibronic distribution

$f(\nu_3) = 1.05 \times 10^{-6}, f(\nu_4) = 2.32 \times 10^{-7}, f(\nu_6) = 8.03 \times 10^{-7}, f_{\text{Total}} = 2.09 \times 10^{-6}$

$f(\nu_3) : f(\nu_4) : f(\nu_6) = 4.53 : 1.00 : 3.46$ [exp : 5.50 : 1.00 : 5.00]

(1.2) The $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2T_{1g})$ transition

(1.2.1) Dipole strengths for the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2T_{1g}) + \nu_k(k = 3, 4, 6)$ transitions

	D^{CF}	D^{LP}	$D^{(CF,LP)}$	D^{Total}	Notes
ν_3	17.9791	4.36012	+17.70774	40.04696	The values are given in units of $C_4 = \frac{2e^2\langle r^4\rangle}{(\Delta E)R_0^5}$
ν_4	16.7892	4.85330	–18.05360	3.5889	
ν_6	2.0192	0.21068	–1.30445	0.92543	

(1.2.2) Total oscillator strengths and relative vibronic distribution

$f(\nu_3) = 1.13 \times 10^{-5}, f(\nu_4) = 9.846 \times 10^{-7}, f(\nu_6) = 2.522 \times 10^{-7}, f_{\text{Total}} = 1.25 \times 10^{-5}$

$f(\nu_3) : f(\nu_4) : f(\nu_6) = 44.79 : 3.90 : 1.00$ [exp : 20.00 : 1.00 : 5.00]

(1.3) The $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2E_g)$ transition

(1.3.1) Dipole strengths for the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2E_g) + \nu_k(k = 3, 4, 6)$ transitions

	D^{CF}	D^{LP}	$D^{(CF,LP)}$	D^{Total}	Notes
ν_3	8.4718	1.2816	+6.5902	16.3436	The values are given in units of $C_4 = \frac{2e^2\langle r^4\rangle}{(\Delta E)R_0^5}$
ν_4	0.0482	1.7594	–0.5821	1.2255	
ν_6	3.3550	0.3180	–2.0654	1.6076	

(1.3.2) Total oscillator strengths and relative vibronic distribution

$f(\nu_3) = 4.76 \times 10^{-6}, f(\nu_4) = 3.50 \times 10^{-7}, f(\nu_6) = 4.51 \times 10^{-7}, f_{\text{Total}} = 5.54 \times 10^{-6}$

$f(\nu_3) : f(\nu_4) : f(\nu_6) = 13.54 : 1.00 : 1.30$ [exp : 0.30 : 1.00 : 16.50]

(1.4) The $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_8(^2T_{1g})$ transition

(1.4.1) Dipole strengths for the $\Gamma_8(^2T_{2g}) \rightarrow \Gamma_6(^2T_{1g}) + \nu_k(k = 3, 4, 6)$ transitions

	D^{CF}	D^{LP}	$D^{(CF,LP)}$	D^{Total}	Notes
ν_3	6.4786	0.2927	+2.7542	9.5255	The values are given in units of $C_4 = \frac{2e^2\langle r^4\rangle}{(\Delta E)R_0^5}$
ν_4	9.8222	0.0380	–1.2220	8.6382	
ν_6	0.5750	0.9848	–1.5043	0.0551	

(1.4.2) Total oscillator strengths and relative vibronic distribution

$f(\nu_3) = 2.60 \times 10^{-6}, f(\nu_4) = 2.30 \times 10^{-6}, f(\nu_6) = 1.45 \times 10^{-8}, f_{\text{Total}} = 4.92 \times 10^{-5}$

$f(\nu_3) : f(\nu_4) : f(\nu_6) = 197.31 : 158.62 : 1.00$ [exp : 2.90 : 1.00 : 2.20]

As for the ligand polarization contribution to the total transition dipole moment, we write the identity given below

$$\mu_{\nu_t}^{LP,\alpha}[|a\rangle \rightarrow |b\rangle] = \sum_m U_{\nu_m}^{LP,\alpha} L_{mt} \langle 0|Q_{\nu_t}|1\rangle$$

(for the ν_t-th normal mode of vibration) (5.4)

and the ligand polarization electronic factor becomes

$$U_{\nu_t}^{LP,\alpha} = \sum_{\Gamma} \sum_{k} C_k^{LP} (-1)^{\Gamma_1+\gamma_1^+} V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1^+ & \gamma_2 & \gamma \end{pmatrix}$$

$$\times \langle (LSJ)\Gamma_1 \parallel M_{\nu_t}^{\Gamma}(k) \parallel (L'SJ')\Gamma_2 \rangle B_{\nu_t}^{\Gamma\gamma,\alpha}(k). \quad (5.5)$$

The reader may obtain all the relevant tabulations of the above reduced matrix elements, upon request from R.A. (The vibronic crystal field and ligand polarization coupling magnitudes are listed in Table I, whereas in Table II we display our final overall and relative vibronic intensities for four selected emissions in this system.)

3. Results and conclusions

To advance in the understanding of the observed spectral intensities in these elpasolite type systems, we have initiated a program to rationalize the coupling among vibrational modes of the symmetry in the crystal. In the classic paper by Lentz [4], this author pointed out that by means of group theoretical considerations, both the Mo^{3+} and Na^{1+} ions are bonded octahedrally to six Cl^{-1} ions, while the Cs^{1+} ions have the coordination number 12 to the Cl^{-1} ions and lie in the tetrahedral holes of Ln^{3+} lattices. The Cs^{1+} ions occupy tetrahedral holes with respect to both the Mo^{3+} and Na^{1+} ions. Also the static selection rules indicate that, within the framework of the $\boldsymbol{k} = \boldsymbol{0}$ approximation, these compounds should have four Raman active $\alpha_{1\mathrm{g}}$, ε_{g}, and $2\tau_{2\mathrm{g}}$, and four infrared active $4\tau_{1\mathrm{u}}$ vibrations. Both, the $\tau_{1\mathrm{g}}$ (rotatory mode) and the $\tau_{2\mathrm{u}}$ vibrational modes are both inactive in the Raman and infrared spectra. It is accepted that with a high covalent bond character between Ln^{3+} and Cl^{-} ions, stretching ν(Mo–Cl) and bending δ(Cl–Mo–Cl) vibrational modes for the $MoCl_6^{3-}$ groups may be separated in discussion from the remaining lattice vibrations. Next, a set of internal coordinates is introduced, and they represent the various possible interactions among bonded and nonbonded atoms in the crystals. For the sake of the argumentation, we further give the set of internal coordinates which are convenient to describe the lattice dynamics for this system. These are the following: (a) $\{\Delta r_i : r = r(\text{Na–Cl})\}$, (b) $\{\Delta R_i : R = R(\text{Mo–Cl})\}$, (c) $\{\Delta D_i : D = D(\text{Cs–Cl})\}$, (d) $\{\Delta q_i : q = q(\text{Cl–Cl})$, nonbonded$\}$, (e) $\{\Delta\alpha_{ijk} : \alpha = \alpha(\text{Cl–Mo–Cl}\}$ and (f) $\{\Delta\beta ijk : \beta = \beta(\text{Cl–Na–Cl}\}$.

When a 27-atom model is used, then the atom numbering is as indicated in Fig. 1:

(A) Na^{1+} : $(8, 17, 18, 19, 20, 21)$
(B) Cl^{-1} : $(1, 2, 3, 4, 5, 6, 1', 2', 3', 4', 5', 6')$

(C) Mo^{3+} : (7: reference atom)
(D) Cs^{1+} : (9, 10, 11, 12, 13, 14, 15, 16).

This model may still be simplified further, when the redundancies are excluded. The simplest model contains 10 atoms, as used by Lentz [4], who also informed about a set of linear combinations of Cartesian nuclear displacement coordinates for the ten-atom system, though the projection along the three polarization directions has not been done properly. It is also to be noticed that the Cartesian nuclear displacement coordinates do not form a complete and orthonormal set of coordinates and therefore, the S_{op} coordinates are not the symmetry coordinates. Nevertheless, a more complete work on the lattice dynamics for these elpasolite type systems is in progress in our group. It is interesting to observe the number of interactions which are neglected when a seven-atom system is adopted.

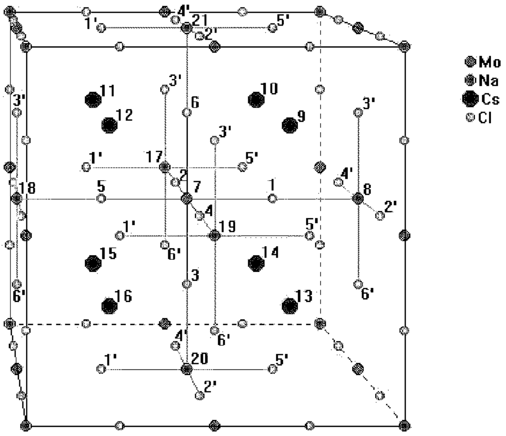

Fig. 1. Twenty seven-atom model.

There is however a necessity of more theoretical work on this research area, leading to the modeling of the interacting vibrational force field, the long-range Coulombic sum lattices and the phonon dispersion curves along all relevant polarization directions. The problem of the understanding of the dispersion phenomena is a question still open to discussion, and the answer to all the outline issues does not necessarily lie on full parameterization schemes, which ultimately obscure both the physics and the chemistry of the very problem we want to solve.

The results obtained, using our seven-atom system model, are as good as could be expected for this simple calculation model. It is also to be added that, in spite of the apparent simplicity of our model calculations, our strategy and modeling seem to be most appropriate and suitable to gain understanding on these complex radiative processes. The deviation from the experimental results, for some of the selected emissions may be explained on the basis of the model and many necessary simplifications used throughout the course of the current work. There are several ways to improve the calculation, though at this point we feel that a more complete data base of fairly accurate data is needed to account for the observed overall and relative vibronic intensities due to several emissions. The calculation is somehow very successful, since it is transparent (just a few parameters are adjusted from experimental data) and flexible. We strongly believe that this type of explicit algebraic calculation may be used as the basis for future more elaborated models.

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