INTERNATIONAL CENTRE FOR
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FOR TRIVALENT METAL HALIDES

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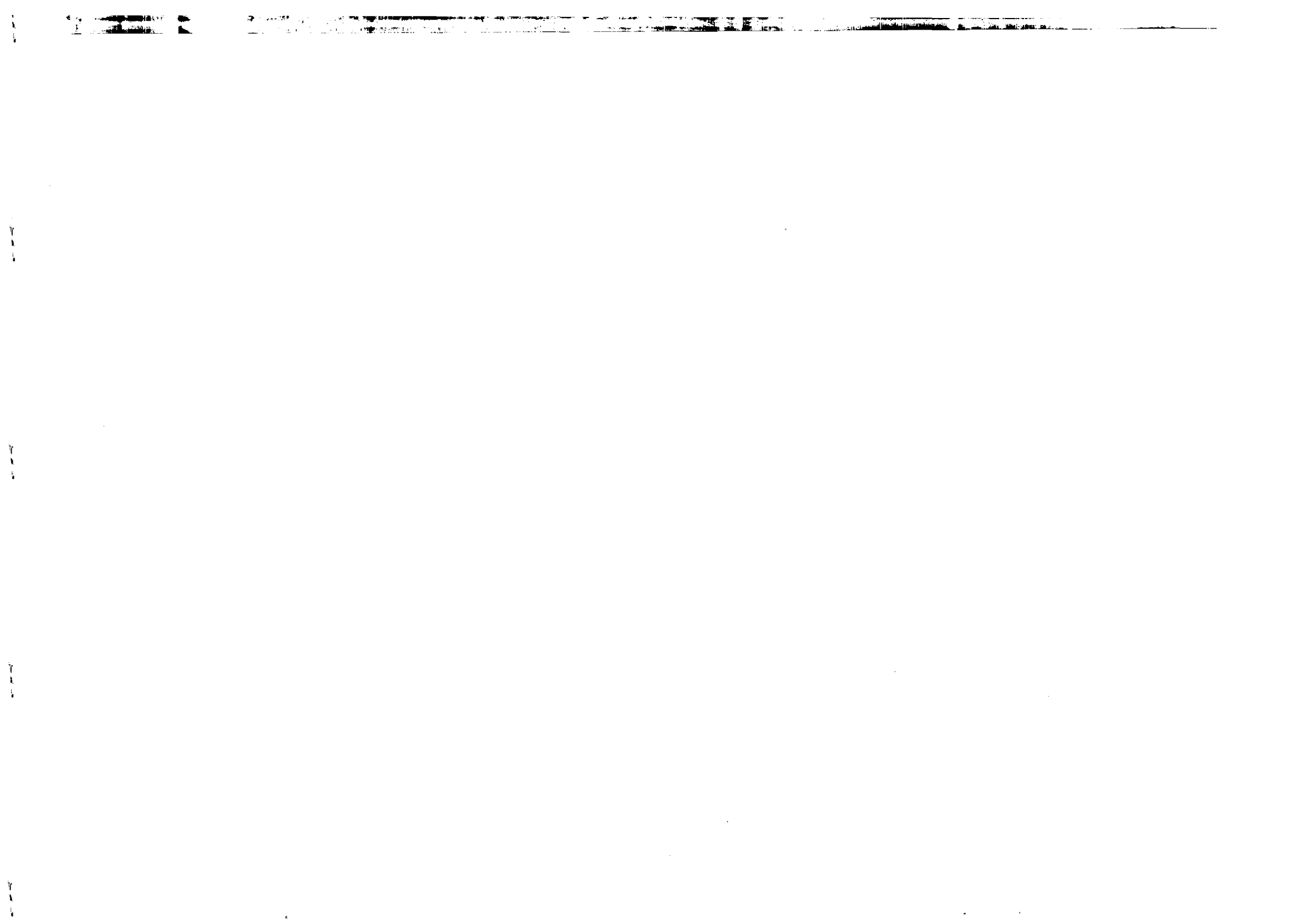
MIRAMARE-TRIESTE

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ABSTRACT

Octahedral–type coordination by halogens in the liquid state has been reported for a number of trivalent metal ions from diffraction and Raman scattering experiments on their molten trihalides and from Raman scattering spectroscopy of liquid mixtures of trihalides with alkali halides. We analyze the available data on bond lengths and Raman frequencies by treating an isolated $(MX_6)^{3-}$ species within a model which adopts charged–soft–sphere interionic potentials supplemented by an account of ionic polarization. The trivalent metal ions that we consider are $M = La, Ce, Pr, Nd, Sm, Gd, Dy$ and Y for $X = Cl$ and $M = Al$ for $X = F$. The main result of the analysis is the prediction of trends in the soft–sphere repulsive parameters for the trivalent metal ions, leading to estimates of all the vibrational frequencies and the binding energy of such octahedral species.

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1. - Introduction

There has very recently been a rapidly growing interest in studying and understanding the liquid structure and the melting mechanisms of trivalent metal halides, following extensive work on monovalent and divalent metal halides which has already been the subject of a number of reviews [1-3]. A neutron diffraction study of molten YCl_3 [4], combined with the results of earlier Raman scattering experiments on yttrium-alkali chloride mixtures [5], has demonstrated that the Y ion in the melt is in a state of rather stable octahedral-type coordination by chlorine first neighbours and that this type of local structure develops via chlorine sharing into intermediate range order in the YCl_3 melt. These data on the liquid structure of YCl_3, when contrasted with the results of earlier diffraction studies of molten $AlCl_3$ [6] and $SbCl_3$ [7] and combined with data on macroscopic melting parameters and transport coefficients, have led to a classification of the melting mechanisms of many trichlorides into three main types in correlation with the character of the chemical bond [8]. One of these melting mechanisms leads from essentially ionic crystal structures into essentially ionic liquid structures having the characters of short and intermediate range order that we have recalled above for molten YCl_3, and was predicted to apply to lanthanide metal chlorides in addition to YCl_3. This prediction has been confirmed by independent X-ray diffraction and Raman scattering studies of several rare-earth trichlorides [9]. An earlier Raman scattering study of lanthanum-alkali chloride mixtures [10] had already given evidence for octahedral-type coordination of the La ion in these melts.

For the class of essentially ionic trichloride melts that we have mentioned above, namely the lanthanide metal chlorides and YCl_3, a calculation of liquid structure in a simple ionic model can already provide useful insights into partial structure factors and partial pair distribution functions. It has been shown for molten YCl_3 [11] that a charged-soft-sphere (CSS) model for interionic pair potentials predicts (a) the correct topology and stability of the local liquid structure and (b) the presence of an intermediate range order, which is mainly reflected in the Y-Y correlations. Of course, in its basic physical contents a CSS model is not

crucially different from a charged-hard-sphere model, but has some substantial advantages. In particular, it allows an unambiguous evaluation of preferred bond lengths in the melt in addition to distances of closest approach. A CSS model is at any rate an essential first step towards more sophisticated representations of the potential energy function. The main aim of the present work is to determine the trends of the CSS interactions in lanthanide metal and yttrium chlorides. We also treat by similar methods the Al-F interactions in molten cryolite (Na_3AlF_6), in view of its importance in the electrowinning of Al metal and of the fact that an octahedral coordination of Al by fluorines has been studied by Raman spectroscopy on the melt [12,13] and by infrared and Raman spectroscopy on the crystal [14].

The form of the CSS pair potentials that we have adopted describes each ion by its nominal valence Z_i and by an effective repulsive radius R_i and an effective repulsive hardness ρ_i. This form was proposed in early work of Busing [15], who included also van der Waals interactions. A careful determination of the interaction parameters in the Busing potential for the dihalides of alkaline earth metals, excluding Be, was carried out from crystalline data by Yuen, Murfitt and Collin [16]. It was subsequently shown that these model interactions, with due account of ionic polarization in a deformation dipole model, could be successfully used to predict properties of isolated alkaline earth dihalide molecules [17] and of tetrahedral molecular ions formed by some of these divalent metals with halogens in the liquid state [18]. These properties are the molecular shape, the metal-halogen bond length and the vibrational frequencies. On this basis, the bond length and the vibrational frequencies of tetrahedral molecular ions formed by Be and Al with chlorine have been brought into the estimation of interaction parameters for Be and Al halides [18]. We follow basically the same approach in the present work to assess the trends of the CSS model parameters from available data on bond length and vibrational frequencies of $(MX_6)^{3-}$ octahedral units, where M = La, Ce, Pr, Nd, Sm, Gd, Dy and Y for X = Cl and M = Al for X = F. A by-product of our work is an assessment of the trends in the vibrational frequencies of these molecular ions in the many cases where they are not experimentally known. In addition, we give estimates of the binding energy of the molecular ions against dissociation into free ions, which are needed for liquid state calculations on mixtures of trivalent metal halides and alkali halides [19]. We anticipate regular trends for all these calculated properties in the chlorides as the trivalent metal is changed from La to Y in the order indicated above.

2. - Binding and vibrational frequencies of octahedral $(MX_6)^{3-}$ species.

We give in this section a brief presentation of the main formulae that we shall use in the numerical calculations to be reported in the following sections.

We consider first the determination of the equilibrium M-X bond length and of the binding energy for an octahedral $(MX_6)^{3-}$ unit. As already indicated in section 1, the CSS pair interaction potential $\Phi_{ij}(r_{ij})$ between ions of types i and j at relative distance r_{ij} is written as

$$\phi_{ij}(r_{ij}) = Z_i Z_j \frac{e^2}{r_{ij}} + f\,(\rho_i + \rho_j)\,\exp[(R_i + R_j - r_{ij})/(\rho_i + \rho_j)] \quad . \tag{2.1}$$

In constructing the total potential energy of the octahedral unit we include, in addition to the contributions from the above pair interactions, the contributions from electronic polarization dipoles located on each halogen and outwardly directed along the bond. The total potential energy U(r, p) of the unit, relative to free ions and as a function of the M-X bond length r and of the magnitude p of the halogen dipole moment, is given by

$$U(r,p) = 6\phi_{MX}(r) + 12\phi_{XX}(\sqrt{2}r) + 3\phi_{XX}(2r) - 6p[E(r) - B(r)]$$
$$+ \left(3\sqrt{2} + \frac{1}{2}\right)\frac{3p^2}{(2r)^3} + 3\frac{p^2}{\alpha_X} \quad , \tag{2.2}$$

α_X being the halogen polarizability. Electronic polarization is treated in eq. (2.2) by a deformation dipole model [17]: E(r) is the magnitude of the electric field created by the ionic charges on a halogen,

$$E(r) = \left(3 - \sqrt{2} - \frac{1}{4}\right)\frac{e}{r^2} \quad , \tag{2.3}$$

and $B(r)$ accounts for the deformation dipole from short-range overlap between the M^{3+} ion and each X^- ion. It is given by

$$B(r) = \frac{|Y|}{\alpha_X K} \left|\frac{d\phi_{MX}^{rep}(r)}{dr}\right| \tag{2.4}$$

where Y and K are the effective halogen shell charge and shell-core force constant, while $\phi_{MX}^{rep}(r)$ is the overlap repulsive contribution to the M-X interactions in eq. (2.1).

The equilibrium value $p_o(r_o)$ of the dipole moment is immediately obtained by minimization of eq. (2.2). Neglecting thermal vibrations, numerical minimization of the function $U(r, p_o(r))$ then yields the equilibrium value r_o of the bond length and the molecular well depth $U_0 = - U(r_o, p_o(r_o))$. The change in energy under a small stretching of the bonds yields the frequency v_1 of the A_{1g} breathing mode of the octahedral unit, which is strongly Raman active and easily observable in Raman scattering experiments on M-alkali mixtures and in strongly structured MX_3 melts.

As is well known, an octahedral $(MX_6)^{3-}$ unit has six independent vibrational frequencies (see for example Ferraro and Ziomek [20]), corresponding to normal modes which are reproduced in fig. 1 for the convenience of the reader. The modes from v_2 to v_6 involve distortions of the equilibrium octahedral shape, which may be described in terms of small changes Δr_i in the M-X_i bond lengths for the six halogens and small changes $\Delta\alpha_{ij}$ in the X_i-M-X_j angles for the various pairs of halogens. The potential energy of the $(MX_6)^{3-}$ unit in an arbitrarily distorted configuration is easily written as a function of these geometrical distortion parameters within the ionic model that we have introduced in eqs. (2.1)-(2.4). This involves also an account of the electronic polarization dipole arising on the metal ion in the two F_{1u} modes.

Such a calculation of the change ΔU in the potential energy function, up to quadratic terms in the distortions from the equilibrium configuration, is equivalent to an evaluation of

force constants in a specific realization of the general valence force field (GVFF) method [20,21]. The present model retains six non-vanishing force constants, which are f_d (stretching of a bond), f_{dd} (stretching of two orthogonal bonds), $f_{dd'}$ (stretching of two colinear bonds), f_α (change in bond angle), $f_{\alpha\alpha}$ (change in two adjacent coplanar bond angles) and $f_{d\alpha}$ (change of bond angle and stretching of adjacent bond). These force constants are conveniently evaluated from the change ΔU of the potential energy function associated with the following six distorted configurations of the $(MX_6)^{3-}$ unit:

(i) $\Delta r_i = \Delta r$ and all $\Delta\alpha_{ij} = 0$, leading to

$$\Delta U = 3 (f_d + 4f_{dd} + f_{dd'}) (\Delta r)^2 \quad ; \tag{2.5}$$

(ii) $\Delta r_1 = \Delta r_4 = - 2\Delta r_2 = - 2\Delta r_3 = - 2\Delta r_5 = - 2\Delta r_6 = \Delta r$ and all $\Delta\alpha_{ij} = 0$, leading to

$$\Delta U = \frac{3}{2} (f_d - 2f_{dd} + f_{dd'}) (\Delta r)^2 \quad ; \tag{2.6}$$

(iii) $\Delta r_1 = - \Delta r_4 = \Delta r$, with all other $\Delta r_i = 0$ and all $\Delta\alpha_{ij} = 0$, leading to

$$\Delta U = (f_d - f_{dd'}) (\Delta r)^2 \quad ; \tag{2.7}$$

(iv) $\Delta\alpha_{24} = \Delta\alpha_{34} = \Delta\alpha_{54} = \Delta\alpha_{64} = - \Delta\alpha_{12} = - \Delta\alpha_{13} = - \Delta\alpha_{15} = - \Delta\alpha_{16} = \Delta\alpha$, all other $\Delta\alpha_{ij} = 0$ and all $\Delta r_i = 0$, leading to

$$\Delta U = 4 r_o^2 f_\alpha (\Delta\alpha)^2 \quad ; \tag{2.8}$$

(v) $\Delta r_1 = - \Delta r_4 = \Delta r$ and $\Delta\alpha_{24} = \Delta\alpha_{34} = \Delta\alpha_{54} = \Delta\alpha_{64} = - \Delta\alpha_{21} = - \Delta\alpha_{31} = - \Delta\alpha_{51} = - \Delta\alpha_{61} = \Delta\alpha$, with all other $\Delta r_i = 0$ and $\Delta\alpha_{ij} = 0$, leading to

$$\Delta U = (f_d - f_{dd'}) (\Delta r)^2 - 8r_o f_{d\alpha} \Delta\alpha \Delta r + 4r_o^2 f_\alpha (\Delta\alpha)^2 \quad ; \tag{2.9}$$

(vi) $\Delta\alpha_{23} = \Delta\alpha_{56} = - \Delta\alpha_{35} = - \Delta\alpha_{26} = \Delta\alpha$, all other $\Delta\alpha_{ij} = 0$ and all $\Delta r_i = 0$, leading to

$$\Delta U = 2r_o^2 (f_\alpha - 2f_{\alpha\alpha}) (\Delta\alpha)^2 \quad . \tag{2.10}$$

The mode frequencies are immediately evaluated from the force constants and the ionic masses, using the expressions given for instance by Ferraro and Ziomek [20]. For the frequency of the F_{2u} mode we take $v_6 = v_5/\sqrt{2}$ as implied by the GFVV.

In the calculations that we report in the next two sections we have adopted for the halogen ions values of the repulsive parameters, the electronic polarizability and the shell

parameters that are taken from earlier work on tetrahedral molecular ions ([18]). These values are collected in Table 1. We remark in this connection that the assumption of transferability for the CSS parameters is implicit in the adoption of the Busing form in eq. (2.1), and that the polarizability contributions are much less important in the present octahedral configuration than in the tetrahedral one, so that inaccuracies in the relevant parameters correspondingly have less severe consequences. The values of the electronic polarizability for the trivalent metal ions have been obtained from the work of Tessman, Kahn and Shockley ([22]), using an interpolation between those given for La^{3+}, Ce^{3+} and Y^{3+}. These values enter only the calculation of the frequencies for the F_{1u} modes and affect them to a very minor extent. The remaining model parameters are the CSS radius and hardness for the metal ions, which will be determined from the analysis given in the next two sections.

3. - Lanthanide metal and yttrium chlorides.

A major role in our evaluation of CSS parameters for lanthanide ions and for Y^{3+} in their chlorides is played by the M-Cl bond length r_0. This is known in the pure trichlorides of these metal ions both from crystal structure data ([23]) and from liquid state diffraction data ([4,9]). From indicators of the nature of the chemical bond such as Pettifor's chemical scale of the elements ([24]), we expect regular trends in physical properties as one proceeds through the series of trivalent metals from La to Y through Ce, Pr, Nd, Sm, Gd and Dy. Such a trend is shown by the crystalline state values of the M-Cl bond length, that we have consequently taken as our first choice for incorporation in our analysis. The reported liquid state values for the preferred M-Cl bond length instead show some fluctuations around a similar trend at the level of a few hundredths of an Å, which may be indicative of minor inaccuracies in their determination from total diffraction patterns. Aside from such fluctuations, the M-Cl bond length appears to be shortened in the liquid by about 0.1 Å in trihalides crystallizing in the UCl_3 structure ($LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$ and

$GdCl_3$) and to be expanded by a few hundredths of an Å in $DyCl_3$ and YCl_3, crystallizing in the $AlCl_3$ structure. In the above structural assignment we have referred to the high temperature crystal structure for $GdCl_3$ and $DyCl_3$. These differences in the preferred bond length between the crystalline and the liquid state imply corresponding adjustments of the CSS radii for the metal ions relative to their values as determined from the crystalline bond length. We have accordingly repeated our calculations with a second choice for the M-Cl bond lengths, which is based on their liquid state values after smoothing out the fluctuations around a regular trend. The two alternative sets of values for the M-Cl bond length and the ensuing results for CSS parameters, vibrational frequencies and binding energy are shown in Tables 2 and 3.

The available experimental information on vibrational frequencies for the $(MCl_6)^{3-}$ units of present interest is instead very sparse. It mostly refers to the frequency v_1 of the A_{1g} mode, from Raman scattering experiments on liquid mixtures for $(YCl_6)^{3-}$ ([5]) and $(LaCl_6)^{3-}$ ([10]) and on pure trihalide melts for $(PrCl_6)^{3-}$, $(GdCl_6)^{3-}$ and $(DyCl_6)^{3-}$ ([9]). The frequencies v_2 of the E_g mode and v_5 of the F_{2g} mode are also approximately known for $(YCl_6)^{3-}$ ([5]) and $(LaCl_6)^{3-}$ ([10]) from Raman data on mixed crystals and on liquid mixtures, respectively. These values are shown in parentheses in both Table 2 and Table 3. Our determination of CSS parameters has aimed at reproducing the trends that may be expected from these scanty data, with particular attention to the frequencies of the A_{1g} and E_g modes.

From both Table 2 and Table 3 it is seen that the general trends from La to Y are a decrease in the radius and the hardness of the metal ions and an increase in the vibrational frequencies and the binding energy. These trends are consistent with the trends shown by the bond length. From the quantitative viewpoint, the frequency v_1 appears to be underestimated in Table 2 relative to its value for $(MCl_6)^{3-}$ units in the liquid state for all the metal ions from La to Gd. This is related to the contraction of the bond length in the liquid state for UCl_3-type crystals. This defect is seen to be largely mended by our results in Table 3, which therefore provide our preferred estimate of CSS parameters of metal ions for liquid-state calculations.

The other frequencies are affected only to a relatively minor extent by the choice of bond length. By comparison with the measured vibrational frequencies of the $(AlF_6)^{3-}$ unit (see section 4 below) and of many other octahedral hexachloride molecules [21], it appears that the trend of the calculated frequencies in Tables 2 and 3 in going from v_1 to v_6 for each $(MCl_6)^{3-}$ unit is essentially correct, except that the value of v_3 is somewhat underestimated. In fact, the quality of our results is not drastically worse than that achieved in GVFF fits of the various force constants to all the measured values of the vibrational frequencies in hexahalide molecules [21].

As a final comment, we note that the CSS parameters that we propose in this work for the Y^{3+} ion are somewhat different from those already used in liquid structure calculations on molten YCl_3 [11]. The present values are somewhat more accurate, in view of our approximate account of all the available evidence.

4. - Aluminium fluoride.

In the crystal structure of AlF_3 the fluorines form a considerably distorted hexagonal close packing, inside which the metal ions occupy octahedral sites [23]. The local structure around a metal ion is variously reported as consisting of three fluorine neighbours at 1.70 Å and three further fluorine neighbours at 1.89 Å [23] or of an almost regular octahedron of fluorines with an Al-F bond length of 1.79 Å [25]. The value of the preferred Al-F bond length in an $(AlF_6)^{3-}$ unit in the liquid state seems to be unknown.

We have first attempted a determination of CSS parameters for Al^{3+} by assuming a value for the Al-F bond length near the middle of the crystalline range indicated above and by optimizing our results for the frequencies v_1 and v_2, which are both experimentally known from Raman data on liquid mixtures [12]. This approach, which parallels that followed in obtaining the results in Table 2 for chlorides, yields the results that are reported in the first row of Table 4 for the choice $r_0 = 1.81$ Å. Clearly, these results are to be rejected in view of

the very poor fit that can be obtained for the frequency v_2. In fact, the E_g mode tends to go unstable on decreasing the Al-F bond length below 1.81 Å.

A slight upward adjustment of the Al-F bond length to $r_0 = 1.85$ Å suffices to allow a satisfactory account of the frequency v_2 of the E_g mode, without inducing major changes in the calculated values of the other vibrational frequencies. Our best results for the $(AlF_6)^{3-}$ octahedral unit are given in the second row of Table 4. Comparison with measured values of its vibrational frequencies from Raman spectroscopy on liquid AlF_3-NaF mixtures [12] and from Raman and infrared spectroscopy on stoichiometric mixed crystals [14], which are reported in the third and fourth row of Table 4, shows that the magnitudes of the calculated frequencies are approximately correct and that the observed trend is reproduced. Our results for v_2 and v_6 may also be compared with those obtained by Baran and Lavat [26], who fitted the forced constants in the GVFF to the four vibrational frequencies measured in the solid by Reisfeld [14] and calculated from them $v_2 = 400$ cm^{-1} and $v_6 = 228$ cm^{-1}. Our results suggest that the Al-F bond length in the $(AlF_6)^{3-}$ unit may be somewhat expanded in the liquid state.

Using our calculated CSS parameters for Al^{3+}, we have examined the stability of octahedral $(AlCl_6)^{3-}$, $(AlBr_6)^{3-}$ and $(AlI_6)^{3-}$ units, in order to assess the origin of the different behaviour of fluorine relative to the other halogens in the formation of such a unit with Al. We have found that the above octahedral units are all unstable against vibration in the E_g mode, which clearly is the precursor for dissociation of $(AlX_6)^{3-}$ into $(AlX_4)^-$ and two X^- ions (see fig. 1). This results is consistent with thermodynamic data such as the phase diagram of $AlCl_3$-NaCl mixtures, showing insolubility of NaCl into molten $AlCl_3$ beyond the stoichiometric 1:1 composition.

5. - Concluding remarks.

We have determined in this work the parameters for a charged-soft-sphere model of several trivalent metal halides, with the help of data on bond lengths and vibrational

frequencies. Our best results are given in Table 3 and in the second row of Table 4.

As has already been shown in the case of YCl_3 [11], we expect that these results will be useful in liquid structure calculations to elucidate the nature and the trends in the short-range order shown by trihalides in the liquid state. The model that we have constructed should be expected to embody a well defined and rather stable octahedral-type coordination of the trivalent metal ions by halogens, leading into intermediate range order. The use of our best CSS parameters should ensure that the local structure and stiffness in the liquid are approximately correct at a quantitative level.

We stress again that the detailed topology of the intermediate-range order in the liquid will arise from angle-dependent forces that are missing in the present model. This topology is bound to reflect the actual relative weights of the various types of halogen sharing that are in principle possible among pairs of metal ions. Depending on whether corner or edge or face sharing between octahedral units is preferred, the intermediate range order will show predominant 3D or 2D or 1D character. We expect that a pair potentials model will tend to favour corner-sharing and hence 3D character, relative to the other possibilities. An important experimentally accessible quantity to distinguish among these possibilities clearly is the preferred first-neighbour distance between metal ions. In this respect it is interesting to note that the estimated value of this distance in the present model, which is of order 5 Å [11], agrees with the values reported by Mochinaga et al. [9] from X-ray diffraction on the molten trihalides of lanthanide metals.

<div align="center">ACKNOWLEDGMENTS</div>

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TABLE I. - *Model parameters for halogen ions*

	R_X (Å)	ρ_X (Å)	α_X (Å^3)	IYI/K (Å^3/e)	f (e^2/Å^2)
F$^-$	1.32	0.215	0.88	0.48	0.05
Cl$^-$	1.71	0.238	3.00	0.83	0.05

TABLE II. - *Bond length, CSS parameters, vibrational frequencies and binding energy of* $(MCl_6)^{3-}$ *units* (*).

	r_0 (Å)	R_M (Å)	ρ_M (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	ν_5 (cm^{-1})	ν_6 (cm^{-1})	U_0 (kcal/mol)
$(LaCl_6)^{3-}$	2.95	1.56	0.125	202	190	145	127	116	82	826
				(242)	(≈193)			(≈106)		
$(CeCl_6)^{3-}$	2.92	1.54	0.123	205	183	149	135	118	83	834
$(PrCl_6)^{3-}$	2.90	1.52	0.121	207	177	149	130	120	85	840
				(≈230)						
$(NdCl_6)^{3-}$	2.88	1.49	0.110	212	185	152	134	123	87	849
$(SmCl_6)^{3-}$	2.86	1.45	0.101	217	187	154	137	126	89	860
$(GdCl_6)^{3-}$	2.83	1.42	0.092	222	192	156	139	128	91	869
				(≈250)						
$(DyCl_6)^{3-}$	2.63	1.14	0.023	267	199	188	171	157	111	954
				(≈260)						
$(YCl_6)^{3-}$	2.63	1.14	0.022	267	200	221	191	157	111	954
				(261)	(≈205)			(≈135)		

(*) The values of the bond length have been fitted to data on the crystalline state (see text). Values of vibrational frequencies in parentheses are from experiment: for $(LaCl_6)^{3-}$ and $(YCl_6)^{3-}$, from data on liquid mixtures for ν_1 and ν_5 and on mixed crystals for ν_2 [5,10]; for $(PrCl_6)^{3-}$, $(GdCl_6)^{3-}$ and $(DyCl_6)^{3-}$, from data on pure trihalide melts [9].

TABLE III. - *Bond length, CSS parameters, vibrational frequencies and binding energy of* $(MCl_6)^{3-}$ *units* (*).

	r_0 (Å)	R_M (Å)	ρ_M (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	ν_5 (cm^{-1})	ν_6 (cm^{-1})	U_0 (kcal/mol)
$(LaCl_6)^{3-}$	2.85	1.44	0.096	219	193	157	134	127	90	863
				(242)	(≈193)			(≈106)		
$(CeCl_6)^{3-}$	2.83	1.41	0.089	223	195	162	146	129	91	871
$(PrCl_6)^{3-}$	2.81	1.38	0.081	227	199	164	145	131	93	879
				(≈230)						
$(NdCl_6)^{3-}$	2.79	1.36	0.076	231	196	165	146	134	95	887
$(SmCl_6)^{3-}$	2.75	1.30	0.062	240	198	170	152	139	98	904
$(GdCl_6)^{3-}$	2.72	1.26	0.051	247	201	174	156	143	101	917
				(≈250)						
$(DyCl_6)^{3-}$	2.69	1.22	0.040	254	203	178	160	148	105	929
				(≈260)						
$(YCl_6)^{3-}$	2.68	1.20	0.036	256	205	212	186	149	105	934
				(261)	(≈205)			(≈135)		

(*) The values of the bond length have been fitted to data on pure trihalide melts (see text). Values of vibrational frequencies in parentheses are from experiment (see the footnote to Table 2).

TABLE IV. - *Bond length, CSS parameters, vibrational frequencies and binding energy of the* $(AlF_6)^{3-}$ *unit* (*).

r_0 (Å)	R_M (Å)	ρ_M (Å)	ν_1 (cm⁻¹)	ν_2 (cm⁻¹)	ν_3 (cm⁻¹)	ν_4 (cm⁻¹)	ν_5 (cm⁻¹)	ν_6 (cm⁻¹)	U_0 (kcal/mol)
1.81	0.804	0.0001	540	235	613	411	356	252	1329
1.85	0.844	0.0001	531	390	588	453	340	240	1305
			(555)	(390)			(345)		
			(541)		(568)	(387)	(322)		

(*) See the text for the approaches leading to the theoretical values in the first two rows. The third and fourth row give the measured frequencies from Raman spectroscopy on liquid mixtures ([12]) and from Raman and infrared spectroscopy on mixed crystals ([14]), respectively.
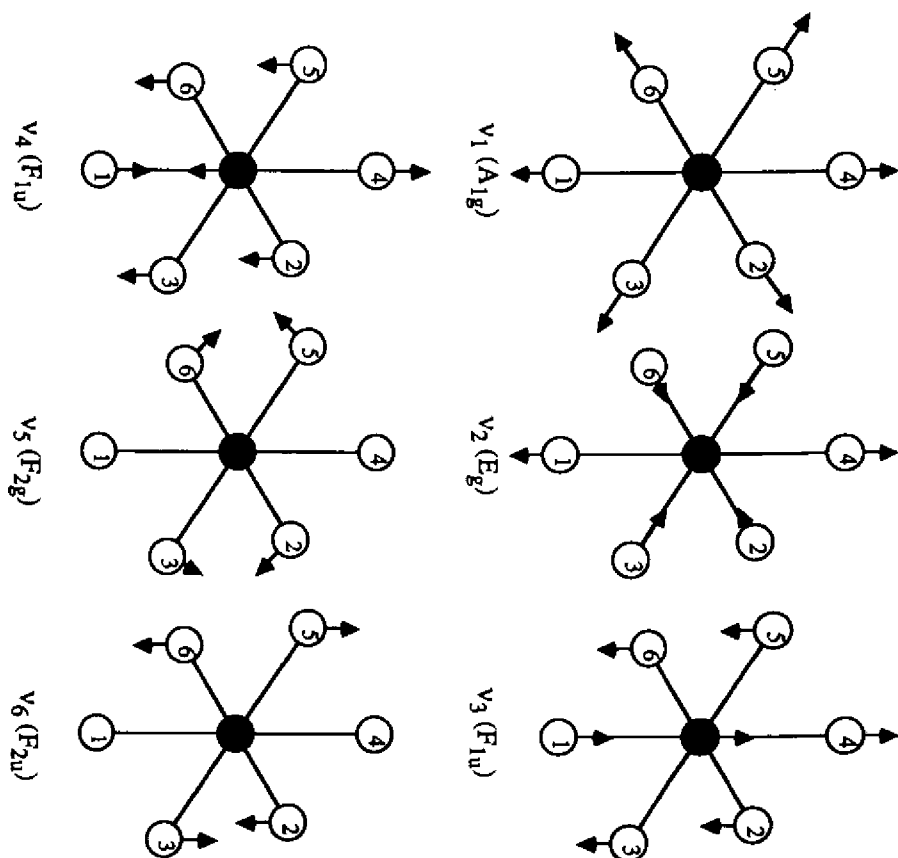
Fig. 1. - Normal modes of vibration of octahedral MX_6 molecules. The A_{1g}, E_g and F_{2g} modes are Raman active and the F_{1u} modes are infrared active.