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Raman spectra of ionic liquids: A simulation study of LaCl₃ and its mixtures with alkali chlorides

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Theoretical Raman spectra of the elpasolite-structured crystal Cs₂NaLaCl₆ and of molten mixtures of LaCl₃ with NaCl and CsCl have been obtained from computer simulations in order to examine how the Raman spectra reflect the coordination structure around the La³⁺ ions. This system is a model for many other trivalent metal halides and for examining how the network structure of the pure melts is broken down by the addition of alkali halides with different structure-breaking powers. The results suggest a way of reconciling the conclusions of Raman studies about the structures of the melts with those of neutron and x-ray-diffraction studies, which have already been examined with the same simulation methods. The Raman spectra, both polarized and depolarized, are calculated from a model for the dependence of the polarizability of the system on the ionic coordinates which was inspired by electronic structure calculations of the polarizabilities of ions in a condensed phase environment. Some results on the lifetimes of the coordination complexes responsible for the appearance of the discrete Raman bands are discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1792574]

I. INTRODUCTION

In a recent paper¹ (hereafter “paper 1”), we showed how it was possible to simulate the Raman spectra of moderately complex molten salts. We combined a model for the dependence of the fluctuating polarizability of the melt on ionic positions which had been suggested by electronic structure calculations²,³ with a polarizable interaction potential⁴ refined on the basis of structural studies. For pure LaCl₃ and for ScCl₃ and its mixtures with CsCl, regarded as representative of broad class of trivalent metal halides⁵,⁶ (La³⁺ being a large and Sc³⁺ a small cation) we obtained semi-quantitative agreement with experimental spectra.⁷,⁸ This development opens up the prospect of quantitative interpretation of such Raman spectra, which have, for many years, offered the most widely studied window onto the microscopic structure of these melts. The simulations offer a way of bridging an interpretative gap between the structure seen spectroscopically, where attention focuses on the coordination complexes responsible for the discrete Raman bands, as in a molecular system, and in diffraction experiments, where the data are discussed in terms of radial correlations in an ionic mixture.⁶ A further prospect is to relate the insights gained from spectroscopy to the transport properties of the melts. Apart from the intrinsic interest in completing these links, melts of the general composition MCl₃, where M is a lanthanide or actinide element, are of interest in a number of electrochemical technologies.⁹

A controversial finding of paper 1 was that the isotropic Raman spectrum of pure molten LaCl₃, which had traditionally been interpreted as showing an octahedral coordination complex of Cl⁻ ions around La³⁺,¹⁰ could be reproduced from a simulation in which the predominant coordination number was between 7 and 8. The simulation agreed, in this regard, with findings from neutron¹¹ and recent x-ray¹² diffraction experiments and, indeed, the structure factors calculated in the simulations agree extremely well with the experimental ones,⁴,¹² as does the x-ray absorption fine structure (XAFS) pattern.¹³

To resolve this dichotomy and to validate the simulations, in this paper we will follow the experimental scheme which leads to the assignment of the Raman bands. This involves tracing the evolution of the band structure from the elpasolite-structured crystal, Cs₂NaLaCl₆, in which the La³⁺ ions are unambiguously octahedrally coordinated to Cl⁻,¹⁴ through its melting, to form a melt of composition AₓLaCl₆, where A is an alkali cation, and then through a series of mixtures (AₓLaCl₃₋ₓ) to the limits of a dilute solution of LaCl₃ in ACl and to the pure LaCl₃. The experimental data,⁷,¹⁵,¹⁶ show a remarkable continuity of the Raman band positions through this process. In particular, the prominent band in the isotropic spectrum, due to the symmetric stretching of the octahedral complex in the crystal, maintains its position across melting (where it becomes known as the P₁ band) and across the composition range of these solutions. This similarity of the Raman spectra underpins the structural assignment across all compositions. The P₁ band broadens as the LaCl₃ concentration increases, and it acquires a weak feature on the high frequency side, known as the P₂ band. This pattern of behavior is found for all the lanthanide chlorides,⁷,¹⁵ though the P₂ feature becomes more prominent and its position concentration dependent for the smaller cation members of the series.
In this work, we have calculated Raman spectra across this range of systems and simultaneously studied the structure and dynamics of the coordination complexes of the melts. Using the methods introduced by Pavlatou et al.,\textsuperscript{17} we will link the Raman bands to normal modes of vibration of the coordination complexes. We will contrast the spectra and properties of solutions with both NaCl and CsCl, where the latter is regarded as a better network structure breaker.

Comprehensively, little progress has been made in relating the depolarized Raman spectra of the melts to the microstructure.\textsuperscript{7,15} The depolarized bands are much broader and less well defined than the isotropic ones. In paper 1 we did not calculate the depolarized spectra. One of the key questions to be answered is which of the four mechanisms which contribute to the polarizability fluctuations is most significant for the depolarized spectrum. We will show that the depolarized spectra from the simulations evolve with concentration in a very similar way to the experimental ones, and we are able to suggest some reasons for these changes.

II. MODEL FOR THE POLARIZABILITY AND SPECTRUM

A. Expressions for the Raman spectrum

The theory of the calculation of the Raman spectrum was discussed at length in paper 1, and here we simply re-capitulate the key points.

The light scattering spectrum\textsuperscript{16,18,19} for the scattering geometry characterized by the scattering vector \( \mathbf{q} \) and where the polarizations of the incident and scattered radiation are the Cartesian directions \( b \) and \( a \) is proportional to the spectrum of the correlation function of the \( q \)th spatial Fourier component of polarizability density of the system, \( \Pi_{ab} \), i.e.,

\[
I_{ab}(q, \omega) \propto \Re \int_0^\infty dt e^{i\omega t} \langle \Pi_{ab}(\mathbf{q}, t) \Pi_{ab}(\mathbf{q}, 0)^* \rangle. \tag{2.1}
\]

For an ionic material, we\textsuperscript{2,3} distinguish four contributions to the polarizability:

\[
\Pi_{ab} = \Pi_{ab}^{SR} + \Pi_{ab}^\gamma + \Pi_{ab}^B + \Pi_{ab}^{\text{DID}}. \tag{2.2}
\]

The terms \( \Pi_{ab}^{SR} \) and \( \Pi_{ab}^\gamma \) represent the changes in the anion polarizability by hyperpolarization due to first-order dipole-induced dipole effects. \( \Pi_{ab}^B \) is the contribution due to short-range dipole-induced dipole effects. \( \Pi_{ab}^{\text{DID}} \) contains the contribution due to the changes in the polarizability \( \alpha_{ab}^i \) of an anion by the compression and deformation of the ion by its short-range interactions with its neighbors.\textsuperscript{3,21}

The contributions of the short-range mechanism to \( \Pi_{ab} \) are given by

\[
\Pi_{ab}^{SR}(q) = \sum_i \left( (\mathbf{K}'((\mathbf{R}^i)))_{ab}^{-1} - \alpha_{ab}^i \right) \delta_{ab} e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{2.3}
\]

where \( \mathbf{K}' \) is a tensor (representing the instantaneous value of the force constant matrix of ion \( i \) in a Drude model of polarizability) which depends upon the positions of the neighboring ions.

\[
K_{\alpha\beta}^i = (\alpha_i^{\text{D}})^{-1} \delta_{\alpha\beta} + \sum_{j=1}^N \left[ f(r_{ij}) \delta_{\alpha\beta} + 3r_{ij} \delta_{\alpha\beta}^2 \right] g(r_{ij}),
\]

with \( f \) and \( g \) short-ranged functions of the interionic separation. This form was proposed on the basis of electronic structure calculations of ionic polarizabilities.\textsuperscript{3,21} The remaining contributions to \( \Pi \) are

\[
\Pi_{ab}^{DID}(q) = \sum_i \sum_{j \neq i} \alpha_{i,\text{crys}}^j \alpha_{j,\text{crys}}^i T_{ab}^{ij} e^{i\mathbf{q}\cdot\mathbf{r}},
\]

\[
\Pi_{ab}^B(q) = \sum_i B_{\text{crys}}^{i,\text{crys}} F_{ab}^i(r) e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{2.5}
\]

\[
\Pi_{ab}^\gamma(q) = \sum_i \gamma_{\text{crys}}^{i,\text{crys}} F_{ab}^i(r) e^{i\mathbf{q}\cdot\mathbf{r}}.
\]

The time-dependent fluctuations in \( \Pi_{ab} \) responsible for the spectrum arise from the time dependence of the relative positions of the ions, as reflected in these expressions; the interionic Coulomb field and field gradients \( F_a \) and \( F_b \) at ion \( i \) depend on its position with respect to all other ions in the sample.

The light scattering spectrum of an ionic system is thus quite complicated as four mechanisms, with different dependencies on the interionic separations, can be expected to contribute. As discussed in the Introduction, the primary interest is in the isotropic spectrum, which reflects fluctuations in the trace of the polarizability density,

\[
\Pi_I = \Pi_{xx} + \Pi_{yy} + \Pi_{zz}.
\]

This dominates the polarized spectra. It can be shown that only the short-range (\( \Pi_{SR}^{\text{SR}} \)) and gamma mechanisms (\( \Pi_{\gamma} \)) contribute to the trace of \( \Pi \), due to the traceless nature of the \( T \) tensor and the Coulomb field gradient. The depolarized spectrum of the melt may be calculated from any one of the five independent anisotropic components of \( \Pi \), such as \( \Pi_{xy} \), and will, in general, be affected by all four mechanisms. As we discussed in paper 1, it is possible to calculate reasonably noise-free depolarized spectra for the melts by averaging over the spectrum of \( \Pi_{ab}(q = 0) \) for these five independent components. For the isotropic spectrum no such averaging is possible and we have again exploited the projection method, introduced in paper 1, to get spectra of the quality reported below.

B. Polarizability models

Explicit polarizability models of several alkali halides have been constructed from \textit{ab initio} electronic structure calculations. These have been shown to lead to predictions for the spectral shapes and intensities of the light scattering spectra\textsuperscript{3,5} which, in the best characterized cases, are found to be quantitatively accurate. Unfortunately, we have as yet no \textit{ab initio} information with which to parametrize a model for the \( MCl_3 \) systems directly. However, given that the principal polarizable species is the \( Cl^- \) ion, a reasonable model might be obtained from that for the alkali chlorides. Good estimates for the crystal polarizabilities of the Na\textsuperscript{+} (\( \approx 1 \) a.u.), La\textsuperscript{3+} (\( \approx 8 \) a.u.)
and Cs+(= 15 a.u.) (Ref. 22) and Cl− (= 20 a.u.) (Ref. 23) are known and reasonable estimates for the Cl− hyperpolarizabilities [B = −342 a.u., γ=2270 a.u. (Ref. 24)] can be taken from work on alkali halides. We will neglect the B and γ hyperpolarizabilities of the cations and further neglect the short-range effect on the cation polarizabilities. The \( \sum \) of the La\(^{3+}\) and Cs\(^+\) (Ref. 4) for the alkali halides, but the ionic radii \( \alpha \) are taken to be the same as the radii used in the construction of pair potentials for the ions, and \( \alpha^0 \) for Cl−, is 26.5 a.u. Finally, we check that the short-range model gives a reasonable value for the in-crystal polarizability by setting up the \( \text{MCl}_3 \) system in the (high symmetry) \( \text{ReO}_3 \) structure,\(^{35}\) but with the experimental value of the cation-anion separation in the observed crystal structure, and checking that the Cl− polarizability is close to the experimental value, deduced from the refractive index.

### C. Details of the simulations

The simulations were carried out with polarizable ion interaction potentials, as described elsewhere.\(^{4,26}\) The particular parameters used in the calculations have been refined somewhat from those used in the previous work. As we wish to compare results for solutions of varying composition, we decided that the only way to do this was to simulate all the systems at the same (zero) pressure. Before beginning then, we made small adjustments to the interaction potentials so that the pure melts (LaCl3, NaCl, and CsCl) had the correct molar volume\(^ {27}\) at 1300 K and zero pressure and that solid \( \text{Cs}_2 \text{NaLaCl}_6 \) adopted the correct crystal structure with the correct volume.\(^ {14}\) The new potential parameters are given in Table I. Only the Cl− and Cs+ ions are treated as polarizable: the polarizability of Na+ is comparatively much smaller than for these two ions; for La\(^{3+}\) we have shown that inclusion of the polarizability has a very small effect on the structure. The values for the ionic polarizabilities and short-range damping parameters\(^ {26}\) discussed elsewhere\(^ {2,28}\) are given in Table II. For pure LaCl3 the potential reproduces the neutron,\(^ {11}\) x-ray, and XAFS structural information on liquid LaCl3 with high accuracy.\(^ {12}\) The potentials also give good transport coefficients for all three melts, as will be described elsewhere. Values for the short-range polarizability parameters [Eq. (2.8)] used in the Raman scattering calculation are given in Table III.

Notice that, in the representation of the interionic interactions, the facts that the Na\(^+\) and La\(^{3+}\) cations are polarizable and that the polarizabilities of the anions fluctuate are

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>( \alpha )</th>
<th>( B_{ij} )</th>
<th>( \alpha_{ij} )</th>
<th>( C'_{ij} )</th>
<th>( C''_{ij} )</th>
<th>( b' )</th>
<th>( b'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl−−Cl−</td>
<td>3.04</td>
<td>100.0</td>
<td>1.53</td>
<td>319.9</td>
<td>6400</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>La(^{3+})−Cl−</td>
<td>…</td>
<td>450.0</td>
<td>1.80</td>
<td>137.6</td>
<td>1582</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Na(^+)−Cl−</td>
<td>…</td>
<td>45.6</td>
<td>1.67</td>
<td>17.08</td>
<td>248.8</td>
<td>1.74</td>
<td>1.16</td>
</tr>
<tr>
<td>Cs(^+)−Cl−</td>
<td>…</td>
<td>942.1</td>
<td>1.8586</td>
<td>195.0</td>
<td>5190</td>
<td>1.49</td>
<td>0.99</td>
</tr>
<tr>
<td>La(^{3+})−La(^{3+})</td>
<td>3.05</td>
<td>15.0</td>
<td>3.00</td>
<td>66.67</td>
<td>200.0</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Na(^+)−Na(^+)</td>
<td>2.211</td>
<td>15.6</td>
<td>1.67</td>
<td>1.588</td>
<td>12.93</td>
<td>2.06</td>
<td>1.38</td>
</tr>
<tr>
<td>Cs(^+)−Cs(^+)</td>
<td>3.078</td>
<td>700.6</td>
<td>1.8586</td>
<td>125.9</td>
<td>4708</td>
<td>1.48</td>
<td>0.99</td>
</tr>
<tr>
<td>La(^{3+})−Na(^+)</td>
<td>…</td>
<td>15.0</td>
<td>3.00</td>
<td>9.398</td>
<td>52.36</td>
<td>1.73</td>
<td>1.16</td>
</tr>
<tr>
<td>Na(^+)−Cs(^+)</td>
<td>…</td>
<td>15.0</td>
<td>3.00</td>
<td>91.11</td>
<td>1612</td>
<td>1.49</td>
<td>0.99</td>
</tr>
<tr>
<td>Na(^+)−Na(^+)</td>
<td>…</td>
<td>87.35</td>
<td>1.759</td>
<td>12.31</td>
<td>249.6</td>
<td>249.6</td>
<td>1.15</td>
</tr>
</tbody>
</table>

\( f(r_{ij}) = a_{ij} \exp[-c_{ij}(r_{ij}−\sigma_{ij})] \),

\( g(r_{ij}) = b_{ij} \exp[-d_{ij}(r_{ij}−\sigma_{ij})] \),

\(^ {205.170.15.173} \text{On: Tue, 09 Dec 2014 06:53:26} \text{iP: }
TABLE II. Dipole polarization parameters. All the parameters are given in a.u.

<table>
<thead>
<tr>
<th>Ion pair i-j</th>
<th>a_{ij}</th>
<th>b_{ij}</th>
<th>c_{ij}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl^{-}-La^{3+}</td>
<td>20.0</td>
<td>1.258</td>
<td>1.0</td>
</tr>
<tr>
<td>Cl^{-}-Na^{+}</td>
<td>1.54</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Cl^{-}-Cs^{+}</td>
<td>1.235</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Cs^{+}-Cl^{-}</td>
<td>15.28</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cs^{+}-La^{3+}</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Cs^{+}-Na^{+}</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

ignored. In this sense, the interaction potential is not consistent with the polarizability model used for the Raman scattering calculations. Cation polarization tends to be less important than anion polarization, as the cations are normally found in more symmetrical, more highly coordinated environments than anions, and we have checked that its inclusion has no discernible effect on the structures in the simulated fluids. The anion polarizability used in the potentials is the mean condensed phase potential, i.e., it already includes substantial deviations from the gas-phase value due to the ionic interactions. The light scattering calculation shows that the mean amplitude of the fluctuation of the polarizability of any ion about this mean value is less than 10% of the mean, so that the polarizability fluctuations should make a relatively small change to the ionic forces.

We followed the same protocol for all simulations. All the runs contained between 500 and 600 ions, depending on stoichiometry. We carried out a 100 000 step equilibration run (36 ps) in an NPT ensemble, using the integration algorithm suggested by Martyna and co-workers. We then performed a 500 000 NVT run, at the cell volume to which the system had equilibrated at zero external pressure, during which time correlation function, etc. were calculated. Ewald sums were used for all Coulomb and multipolar interactions.

III. RAMAN SPECTRA FOR Cs$_2$NaLaCl$_6$

Cs$_2$NaLaCl$_6$ forms a cubic (elpasolite) crystal structure at low temperature in which each La$^{3+}$ ion is octahedrally coordinated by six Cl$^{-}$ ions. This structure can be derived from a perovskite structure (e.g., KMgF$_3$) by replacing the divalent cations by alternating monovalent and trivalent ones and doubling the unit cell. Consequently, its framework consists of LaCl$_6$ octahedra that are interconnected via NaCl$_6$ octahedra; so there is no sharing of Cl$^{-}$ ions by La$^{3+}$ ions. The Cs$^{+}$ ions sit in a cubic cage surrounded by 12 Cl$^{-}$ first neighbors.

In Fig. 1 we display the calculated isotropic Raman spectra for the Cs$_2$NaLaCl$_6$ crystal at 298 and 853 K (just below the experimental melting point), for the melt of Cs$_2$NaLaCl$_6$ at 1300 K and for a melt of Na$_2$LaCl$_6$, to show that the differences brought about by changing the “solvent” from a 2CsCl/NaCl mixture to pure NaCl are not large. The data have been plotted in this way to facilitate comparison with a figure showing corresponding experimental spectra in Ref. 31. In the second panel from the top, this corresponds to the “$P_1$” band of the liquid state spectrum.

![Isotropic Raman spectra calculated for the SR (full line) and $\gamma$ (dashed line) polarizability mechanisms for Cs$_2$NaLaCl$_6$ in its crystalline (elpasolite) forms, bottom two panels, and above melting, second from top. In the top panel, the liquid spectrum for Na$_2$LaCl$_6$ is shown for comparison. The vertical dashed lines show the position of the strong band in the experimental spectra, taken from Ref. 31. The inclusion of crystal and liquid data in the same figure allows one to see the relationship between the band positions in the two phases. We have shown separately the subspectra calculated from the short-range and $\gamma$-hyperpolarizability mechanisms. The DID and B-tensor mechanisms make no contribution to the isotropic spectrum. We have plotted the two spectra separately, in order to see if the different mechanisms reflect different aspects of the ion dynamics. Except for a slight difference in the position of the main band and a peak at ~50 cm$^{-1}$ in the $\gamma$ spectrum of the solid, this does not seem to be the case. We would expect both mechanisms to contribute to the fluctuating polarizability in reality, so that the total spectrum should contain an...](image)
Admixture of both the SR and \( \gamma \) spectra and any features which arise from cross correlations between the two terms. However, as we remarked above, since we are unsure about the relative magnitudes of the two terms, we have not attempted to calculate the total spectrum, instead showing the subspectra to suggest the origins of spectral features.

The depolarized spectra (shown in Fig. 2) are considerably more complicated. Not only are there now four mechanisms, leading to four subspectra, but, in the cubic crystal, the five anisotropic components of the polarizability tensor group into two sets: the \( xy \), \( xz \), and \( yz \) elements transform as \( T_{2g} \) in the cubic point group, and \( 2zz-\cdot xx-yy \) and \( xx-yy \) transform as \( E_g \), so that two distinct sets of depolarized spectra arise. In the liquid, all five elements become equivalent. In the solid, it can be seen that the different mechanisms give rise to very similar spectra in each polarization, but the spectra for the two polarizations for a given mechanism are very different (reflecting the involvement of different modes of vibration). The exception to this generalization is that there is a strong band in the \( \gamma \) spectrum in the \( xy \) polariza-

tion at \( \sim 50 \text{ cm}^{-1} \), which is not present for the other mechanisms.

The appearances of the calculated spectra are very similar to the experimental ones shown in Ref. 31. In particular, we see the preservation of the strong feature at \( \sim 300 \text{ cm}^{-1} \) in the isotropic spectrum upon melting, which parallels the emergence of the \( P_1 \) band in the experimental data, as alluded to in the Introduction. The depolarized spectra in the crystal exhibit (in total) three prominent bands, but these become strongly broadened and indistinct on melting. The positions of the features in the experimental spectra have been indicated by the vertical dashed lines. We see that the calculated bands are systematically at high frequencies compared to the experimental ones, which indicates a deficiency in the potential (allowing the La\(^{3+} \) ion to be polarizable might remedy this).

**A. Assignment of the Raman features to normal modes**

Pavlatou and co-workers\(^ {17} \) described a way to associate the lines seen in the Raman spectrum with (approximate) normal modes of vibration of coordination complexes within the melt. For example, the density of states associated with symmetric breathing of the LaCl\(^{3-} \) complexes can be obtained by calculating the instantaneous velocity of the symmetric breathing \( (A_1g) \) mode for each complex (labeled by the identity, \( i \) of the La\(^{3+} \) ion at its center). This is given by

\[
V_{i1g}^a = \sum_{ia=1-6} v_{i1}^a,
\]

where the sum runs over the six Cl\(^- \) ions coordinated to La\(^{3+} \) ion \( i \), and \( v_{i1}^a \) is the radial component of the velocity of Cl\(^- \) ion \( i \),

\[
v_{i1}^a = \mathbf{v}_{i1} \cdot \hat{\mathbf{r}}_{i1},
\]

where \( \hat{\mathbf{r}}_{i1} \) is the unit vector along the La\(^{3+} \)-Cl\(^- \) “bond” \( \mathbf{r}_{i1} \). The density of states (DOS) is now calculated by forming the correlation function of this velocity and Fourier transforming it,

\[
C_{V_{i1g}}(\omega) = \text{Re} \int_0^\infty dt e^{i\omega t} \langle V_{i1g}^a(t) \cdot V_{i1g}^a(0) \rangle.
\]

It is similarly straightforward to obtain the DOS for the other \( T_{1u}, E_g, \) and \( T_{2g} \) symmetry coordinates. For most cases, the DOS shows a single band, which can therefore be associated with the vibrational frequency of a mode of that symmetry in the complex. In the \( T_{2g} \) case we see two bands, the higher frequency corresponds to a bending vibration of the LaCl\(^{3-} \) unit, whereas the lower frequency band is a “lattice mode”\(^ {7,31} \) of the same symmetry.

In Fig. 3 we compare the densities of states calculated in this way with some of the Raman subspectra described above. In the left-hand panel we show the comparison for the \( P_{1g}, E_g, \) and \( T_{2g} \) symmetry coordinates. In the right-hand panel, that for the Cs\(_2\)NaLaCl\(_6\) melt. In both panels, the DOS is shown in the bottom half, and selected Raman subspectra are shown above. We have not shown all the subspectra in order to avoid too much congestion since, as we remarked above, many of the subspectra exhibit very similar spectral features. In the liquid-

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**FIG. 2.** (Color) Anisotropic, or depolarized, Raman spectra calculated for the same systems as in Fig. 1. “Subspectra” for four mechanisms are shown: SR (black), \( \gamma \) (red), B tensor (green), and DTD (blue). In the cubic crystal, two polarizations may be distinguished, denoted by \( x^2-y^2 \) (dashed lines) and \( xy \) (full lines), whereas in the molten phases these become equivalent. The positions of bands in the experimental spectra (Ref. 31) are shown by vertical dashed lines: in the second panel from the top, this corresponds to the position of the “\( D_1 \)” band of the liquid-state spectrum polarizability mechanisms for pure LaCl\(_3\).
state DOS (lower right hand), we show the DOS of the symmetric breathing of seven-coordinate centers as well as the normal modes of the six-coordinate ones. Note that this band appears at only a slightly lower frequency than the symmetric stretch of the six-coordinate unit.

In the crystal case, the assignments of the Raman bands obtained by comparing their positions with the DOS are clear-cut, and agree with those deduced from the polarization analysis of the experimental spectra. In particular, the comparison suggests that the lattice mode becomes spectrally active through the \( \gamma \) mechanism. The strong band in the isotropic spectrum is due to the symmetric stretching of the octahedral coordination complexes. Raman scattering by the \( T_{1u} \) mode is forbidden, and none is seen. The quality of the comparison of the DOS and Raman features in the crystal gives confidence in extending the analysis to the melt.

In the melt the DOS bands are much broader. The strong isotropic band may still be associated with symmetric stretching vibrations. However, since the stretches of the six- and seven-coordinate complexes are seen to be so similar (bottom right-hand panel), it is not possible to assign the dominant coordination number by these considerations alone. Although the depolarized spectrum shows weak bands at frequencies corresponding to the DOS peaks of the \( E_g \) and \( T_{2g} \) vibrations of the octahedral complexes, the correspondence of the band shapes is not sufficiently good to assert that the vibrations of these complexes account for the whole spectrum.

**IV. CONCENTRATION DEPENDENCE OF THE SOLUTION SPECTRA**

In pure molten \( \text{LaCl}_3 \) the La-centered coordination structures must be linked with, at each instant, a \( \text{Cl}^- \) ion belonging to the coordination shells of two or more \( \text{La}^{3+} \) ions. If the sixfold coordination of the elpasolite crystal were to be maintained in the pure melt, stoichiometry dictates that the \( \text{Cl}^- \) ions would have a coordination number of 2. When an alkali chloride is added to such a melt, the network is broken down by the incorporation of the added \( \text{Cl}^- \) ions into the coordination shells of the \( \text{La}^{3+} \) ions. The extent to which this happens depends on the facility with which the alkali cations “release” their \( \text{Cl}^- \) ions; \( \text{Cs}^+ \) is expected to do this to a greater extent than \( \text{Na}^+ \) and from this perspective is a better structure breaker. If the \( \text{La}^{3+} \) coordination number were six at all mixture compositions, then, in a mixture with a good structure breaker (ACl), a melt with less than 25% molar \( \text{LaCl}_3 \) would consist of independent \( \text{LaCl}_6^{3-} \) units with no sharing of \( \text{Cl}^- \) ions between \( \text{La}^{3+} \) ions. For more concentrated mixtures, or for less good structure breakers, there would always be some linking of coordination structures. A further possibility is that the coordination number of \( \text{La}^{3+} \) changes with the mixture composition, which further complicates this scenario. The way in which the addition of an alkali halide breaks down the network will affect the transport coefficients of the melt and the activity coefficients of the ions in it; the process will therefore have an important impact on the (electro)chemistry of the melt. Any substantial change in the local structure coordination structure would be expected to result in corresponding changes in the Raman spectrum.

In Figs. 4 and 5 we show simulated Raman spectra of \( \text{LaCl}_3 \) mixed with \( \text{CsCl} \) and \( \text{NaCl} \) at various concentrations. The solution spectra are shown in the so-called \( R(\omega) \) representation, which has been used to present the experimental data with which we shall compare. Here the spectra are multiplied by a function of \( \omega \) to enhance the high frequency features, and give a spectral shape which is more directly comparable to a density of states,

\[
R(\omega) = I(\omega) \alpha B(\omega,T),
\]  

**FIG. 3.** (Color) Comparison of some of the calculated subspectra (top panels) for the \( \text{Cs}_2\text{NaLaCl}_6 \) crystal at 853 K (left-hand side) and for molten \( \text{Cs}_2\text{NaLaCl}_6 \) (right-hand side), with the densities of states of symmetry coordinates of the octahedral \( \text{LaCl}_6^{3-} \) complexes (bottom panels). The close similarity between the Raman and DOS bands in the crystal allows us to associate the Raman bands with these vibrational motions. In the liquid state, while the isotropic band is clearly linked to stretching, the frequency does not distinguish between sixfold and sevenfold coordinated La species. The depolarized bands only loosely reflect the characteristic frequencies of the coordination complex vibrations.
where \( B(\omega, T) \) is the Bose-population factor. As before, we have shown the sub-spectra for the different mechanisms separately. We expect the total spectrum to resemble some combination of them.

### A. Isotropic solution spectra

Note that the composition of 25% corresponds to that of the \( \text{LaCl}_3 \) crystal, discussed above. In such a solution, and
the more dilute 5% solution, we see, in Figs. 4(a) and 5(a) that both the SR and \( \gamma \) subspectra exhibit a prominent band at the same frequency as the band assigned to the symmetric stretching motion of the octahedral units in the crystal, which suggests that similar vibrational motions remain present in the melt. As the concentration increases above 25\% the band in the SR spectrum shifts slightly to lower frequency, whereas the \( \gamma \) band increases in frequency. Both bands broaden considerably (as would be expected from cross linking of the coordination polyhedra), so that the band in the \( \gamma \) spectrum becomes indistinct in pure LaCl\(_3\). The intensity of the \( \gamma \) band decreases with increasing concentration; this may reflect the increased asymmetry around a La\(^{3+}\)-coordinated Cl\(^-\) ion at low concentration resulting in an increase in the average electric field. At high concentrations such an ion is likely to be symmetrically bridging between La\(^{3+}\) ions, whereas in dilute solution it will have an La\(^{3+}\) ion on one side and only low-charged Cs\(^+\) ions on the other. The spectra for the NaCl and CsCl mixtures resemble each other closely at higher LaCl\(_3\) concentrations but for the 25\% mixture and below, the bands in the CsCl solutions are significantly sharper. This suggests that the independent coordinate complexes are better defined in this mixture and is indicative of the better structure-breaking quality of CsCl.

The evolution of the isotropic spectral shapes with solution composition follow the experimentally observed ones remarkably well. \( R(\omega) \) spectra for NdCl\(_3\) (the Nd\(^{3+}\) ion has a ionic radius similar to La\(^{3+}\) and shows very similar Raman spectra) in KCl over a range of compositions are shown in Ref. 7 and spectra for LaCl\(_3\) and a 25\% solution in KCl appear in Ref. 15. The positions of the experimental \( P_1 \) and \( P_2 \) bands for the pure melt are shown by vertical dashed lines in the figure. The \( P_2 \) band is a weak bulge on the high frequency side of the \( P_1 \) band in these large cation systems. Despite the fact that the calculated bands are at slightly too high a frequency, it seems reasonable to associate the main band in the SR spectrum with the \( P_1 \) band and that in the \( \gamma \) spectrum with the weak \( P_2 \) feature. In fact, total spectra, resembling the experimental ones quite closely, could be obtained by simply adding the SR and \( \gamma \) subspectra with equal amplitudes. As shown in Fig. 3 for the 25\% solution, and also in paper 1 more generally, the SR band appears at the frequency of the symmetric breathing of the coordination polyhedra. A tentative explanation for the displacement of the \( \gamma \) band to higher frequencies as the melt becomes more networklike was suggested in paper 1.

**B. Depolarized solution spectra**

The depolarized subspectra for the LaCl\(_3\)/ACl mixtures are shown in Figs. 4(b) and 5(b). The story is complicated by existence of four mechanisms which couple the ionic motions to the radiation field. Furthermore, the spectral features are much broader than in the isotropic spectra, so that detailed comparisons with the experimental data become more difficult. The DID spectrum, in particular, is almost featureless. In the 25\% solution, by reference to the density-of-states comparison in Fig. 3, we might associate the broad peak in the SR and \( B \)-tensor mechanisms at \( \sim 200 \text{ cm}^{-1} \) with motions similar to the \( E_g \) type vibrations of an octahedral complex, and the main peak of the \( \gamma \) spectrum at about 120 cm\(^{-1}\) with a \( T_{2g} \)-like bending motion. As in the isotropic spectrum, the \( \gamma \) spectrum becomes more intense and more distinct at lower concentrations. The bands are again significantly sharper in the dilute CsCl solutions and the \( E_g \)-like bands in the SR and \( B \)-tensor bands remain more noticeable.

A high frequency feature remains prominent in the \( \gamma \) spectrum, unlike the NaCl case. It appears to have a concentration-dependent shift and to move closer to the expected position of the \( E_g \) band in the very dilute solution.

Experimental spectra (for NdCl\(_3\) and LaCl\(_3\)) appear in Refs. 7, 15. Like the calculated spectra they are relatively featureless, compared to the isotropic spectra, and have defied detailed analysis. Remarkably, combining the calculated subspectra with equal amplitudes again produces total spectra which resemble the concentration-dependent experimental spectra extremely well. The experimental \( R(\omega) \) spectra at low concentration show a whalelike shape with a maximum at about 110 cm\(^{-1}\) tailing away to high frequency; this peak is known as the \( D_1 \) band. At these low concentrations, there is a hump on the high frequency side at about 200 cm\(^{-1}\), known as \( D_2 \). As the concentration increases, \( D_2 \) grows in intensity relative to \( D_1 \), so that in the pure melt only a broadband centered at the \( D_2 \) position remains. The position of this \( D_2 \) band is shown in the top panel of Figs. 4(b) and 5(b). The change in the depolarized spectral shape could therefore be explained by the increase in intensity of the \( \gamma \) spectra, relative to the SR or \( B \)-tensor spectra, as the concentration is lowered, as seen in both Figs. 4(b) and 5(b).

**V. Structure and Dynamics of the Coordination Shells**

In Fig. 6 the radial distribution functions (rdf) for the different ions around a La\(^{3+}\) center in the 25\% LaCl\(_3\) in CsCl (left panel) and NaCl (right panel) are shown (note that the La-La and La-A functions have been multiplied by 2 for clarity). In both cases, the first coordination shell of Cl\(^-\) ions...
is very well defined by the first peak in the La-Cl rdf; this is narrower in the CsCl case, and the minimum between the first and second peaks is deeper, which suggests that the Cl⁻ ions are more tightly bound and less likely to exchange with the bulk. The La-Cl separation is about 0.28 nm in both cases.

By doubling this distance, we can estimate the largest separation between two La³⁺ ions which are bridged by a Cl⁻ ion common to both coordination shells, i.e., the length of a linear La-Cl-La “bond.” Examination of the La-La rdf shows that there are a significant number of neighboring La³⁺ ions within this separation, indicating that, even in the 25% solution, there is still a significant degree of cross linking between La³⁺ centers. The degree of cross linking is greater in the NaCl solution. In both cases, the first peak of the La-La rdf appears at smaller separations than 0.56 nm: this indicates that the La-Cl-La bond is bent, on average, and may well imply that much of the cross linking involves two Cl⁻ ions bridging between a given pair of La³⁺ ions (corresponding to “edge sharing” of the coordination polyhedra). The first peak in the La-La rdf is split in the CsCl solution case, with the outermost maximum close to 0.56 nm. This indicates an admixture of the linear and bent La-Cl-La bonds, whereas in the NaCl solution the bent-bond or edge-sharing motif seems to predominate.

The first peak in the La-Cs and La-Na distributions is prominent in both cases and overlaps the position of the first peak in La-La. This suggests a competition between the alkali ions and the La³⁺ ions for the next-neighbor position, with the Cs⁺ better at “solvating” the inner coordination shell and breaking up the cross linking between different La³⁺ ions. Note from the position of the first peaks in the La-Cs and La-Na rdfs, compared to 0.56 nm, that these solvating alkali ions must be nesting between the Cl⁻ ions which make up the first shell around La³⁺.

### Table IV. Distribution of coordination numbers in LaCl₁₋ NaCl.

<table>
<thead>
<tr>
<th>LaCl₁ - NaCl mole fraction</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.4%</td>
<td>53.3%</td>
<td>40.1%</td>
<td>5.1%</td>
<td>0.1%</td>
<td></td>
<td>6.48</td>
</tr>
<tr>
<td>0.25</td>
<td>0.8%</td>
<td>30.7%</td>
<td>49.1%</td>
<td>18.1%</td>
<td>1.3%</td>
<td></td>
<td>6.87</td>
</tr>
<tr>
<td>0.5</td>
<td>0.4%</td>
<td>15.9%</td>
<td>45.7%</td>
<td>32.3%</td>
<td>5.4%</td>
<td>0.2%</td>
<td>7.29</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3%</td>
<td>9.3%</td>
<td>38.5%</td>
<td>40.8%</td>
<td>10.6%</td>
<td>0.6%</td>
<td>7.54</td>
</tr>
<tr>
<td>1</td>
<td>0.3%</td>
<td>8.4%</td>
<td>36.8%</td>
<td>41.6%</td>
<td>12.2%</td>
<td>0.8%</td>
<td>7.61</td>
</tr>
</tbody>
</table>

### Table V. Distribution of coordination numbers in LaCl₁₋ CsCl.

<table>
<thead>
<tr>
<th>LaCl₁ - CsCl mole fraction</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>2.7%</td>
<td>93.8%</td>
<td>3.6%</td>
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<td></td>
<td></td>
<td>6.01</td>
</tr>
<tr>
<td>0.25</td>
<td>3.3%</td>
<td>81.4%</td>
<td>14.4%</td>
<td>1.0%</td>
<td></td>
<td></td>
<td>6.13</td>
</tr>
<tr>
<td>0.5</td>
<td>1.2%</td>
<td>29.5%</td>
<td>50.0%</td>
<td>19.6%</td>
<td>1.7%</td>
<td></td>
<td>6.91</td>
</tr>
<tr>
<td>0.75</td>
<td>0.4%</td>
<td>11.3%</td>
<td>41.7%</td>
<td>38.1%</td>
<td>8.2%</td>
<td>0.4%</td>
<td>7.43</td>
</tr>
<tr>
<td>1</td>
<td>0.3%</td>
<td>8.4%</td>
<td>36.8%</td>
<td>41.6%</td>
<td>12.2%</td>
<td>0.8%</td>
<td>7.61</td>
</tr>
</tbody>
</table>

### A. Coordination numbers

In Tables IV and V we have collected values for the distribution of coordination numbers of Cl⁻ around La³⁺ in the NaCl and CsCl solutions at each composition. These values are obtained by counting, for each configuration during the MD run, the proportion of La³⁺ ions which have 5, 6, etc., neighboring Cl⁻ ions within a separation given by the position of the first minimum in the La-Cl rdfs, i.e., 0.4 nm. This position is almost independent of composition and, given the depth of the minimum, the concept of a coordination shell is very well defined.

The last columns of the tables give the average La-Cl coordination numbers, and we will discuss these values first. In both solutions, the average coordination number is seen to be composition dependent. It increases from a value close to six for the most dilute solutions, to a value of 7.61 for pure LaCl₁. The latter value is close to what we have reported previously⁴ and to the values deduced directly from analysis of neutron¹¹ and recent x-ray data.¹² It differs from the octahedral coordination deduced from Raman measurements and from earlier x-ray work.¹⁰ As we have seen, our calculated Raman spectra follow the composition dependence of the experimental spectra very well, and this is the basis on which the experimental Raman structural assignment is made. Furthermore, we now see that, despite the predominance of seven- and eight-coordination units in the mixtures for LaCl₁ concentrations above 25%, no new features appear in the calculated Raman spectra—at least insofar as we can resolve them, given the breadth of the depolarized bands. It would appear that in these higher coordinate units, the stretching and bending motions appear sufficiently close to those in the six-coordinate units that no substantial changes are seen in the Raman spectrum, merely a broadening of the lines.
closer to the value of 9 obtained for the experimentally observed crystal structure (the UCl$_3$ structure$^{25}$) than the presumed octahedral coordination (which is observed for the smaller lanthanide ions, such as Dy$^{3+}$ and Y$^{3+}$). In many aspects of molten salt chemistry of the more heavily charged cations, it has been presumed that the coordination number is a characteristic of the ion, which is not composition dependent. A well-known exception is AlF$_3$ (Ref. 32) in its mixtures with NaF, i.e., cryolitic melts: here the coordination number decreases with increasing concentration of AlF$_3$ in NaF, which is a trend opposite to that noted here.

The distribution of coordination numbers, appearing in the remainder of the table, gives some indication of what is occurring in these melts. The CsCl data, in particular, indicates a sharp change as the LaCl$_3$ concentration increases beyond 25%. For the more dilute solutions, the probability distribution is sharply peaked at 6. When the concentration increases beyond 25%, where even six-coordinate La$^{3+}$ ions would have to engage in some cross linking, the distribution shifts so that seven- and eight-coordinate La$^{3+}$ ions become the norm. The NaCl solutions also seem to be approaching the six-coordinate limit for very low concentrations, but they are approaching the limit much more slowly than in the CsCl case. For 50% and above, the coordination number distributions for both the CsCl and NaCl solutions are very similar.

If we deduce from this that the “ideal” coordination number, adopted by an isolated coordination complex in the limit of very dilute solution, for the La$^{3+}$ ion with Cl$^-$ is 6, we can postulate that the increase in coordination number in more concentrated solutions is related to the degree of cross linking. Furthermore, the different behavior of the distributions for the NaCl and CsCl solutions arises because CsCl is the better structure breaker and leads to a lower degree of cross linking at the same composition. Support for this interpretation comes from an examination of the average La-La coordination number as a function of composition (i.e., the number of La$^{3+}$ ions inside a shell defined by the position of the first minimum of the La-La rdf). These data are plotted in Fig. 7 versus the number density of the La$^{3+}$ ions in the mixtures; the points correspond to the familiar 5%, 25%, etc. compositions, and the points for the NaCl and CsCl solutions are displaced from each other because of the different molar volumes of NaCl and CsCl. The dotted line corresponds to the “ideal” solution limit, where the probability of finding a solute in a given volume (here that of the La coordination shell) is simply proportional to its density. We can see that both solutions follow this ideal line relatively closely for 50% compositions and above, and that in the CsCl solution the amount of cross linking becomes smaller than this ideal value as soon as the composition reaches 25% and complete dissociation is allowed. That is, the Cs$^+$ ions “solvates” the LaCl$_6^{2-}$ coordination shell sufficiently well to promote the breakup of the network, whereas the Na$^+$ ion only does this as well as another La-containing complex.

From the differences between the CsCl and NaCl mixtures of the composition dependencies of the La-Cl and La-La coordination numbers, we can postulate that the increase in the La-Cl coordination number beyond 6 is promoted by the cross linking between coordination shells.

![Figure 7](Image)

**FIG. 7.** The La-La coordination numbers for mixtures of LaCl$_3$ with NaCl (circles) and CsCl (crosses) plotted versus the number density of La$^{3+}$ ions in the solution. If the solutions behaved “ideally,” the coordination numbers would be expected to follow the dotted line. Note the substantial negative departure from this prediction for the two lowest concentration points for the CsCl mixture (corresponding to the 5% and 25% compositions)—indicating a more pronounced tendency for coordination complexes to separate in this mixture.

### B. Lifetimes of the coordination complexes

This structural view of the competition between solvation and cross linking is supported by dynamical information on the lifetimes of the coordination shells. A useful measure of the lifetime of a coordination complex$^{33}$ is obtained by calculating the “cage correlation function.”$^{34}$ The cage correlation function measures the rate at which the identities of the ions in the coordination shell of a given cation change. If the cage correlation function used here (see Ref. 33 for a detailed description) were to relax exponentially, $e^{-t/\tau}$, the decay time $\tau$ would give the time it would take for $(1/e)$th of the coordination complexes to change the identity of one of their ligands, by exchange with the bulk.

Figure 8 shows the cage correlation functions for the coordination complexes around the La$^{3+}$ ions in the CsCl (lower panel) and NaCl (upper) mixtures of different composition. The correlation functions have been plotted logarithmically, in accord with the expectation that the decay will be exponential at long times. The same scales are used for both panels, to facilitate comparison. It can be seen that the coordination shell relaxation is almost independent of composition in the NaCl solutions, which can be interpreted as meaning that a La$^{3+}$ ion will exchange its Cl$^-$ ligands with a Na$^+$ ion and another La$^{3+}$ ion with equal facility. For the CsCl solutions, on the other hand, we see a very strong lengthening of the relaxation time of the coordination shell when the LaCl$_3$ concentration is 25% or less, i.e., when, according to the structural studies above, most of the La$^{3+}$ ions are coordinated to six Cl$^-$ ions in non-cross-linked molecular ion units. These long relaxation times indicate a considerable degree of stability for the isolated LaCl$_6^{2-}$ units which are able to form in the CsCl solutions. In the more concentrated
solutions, where cross linking occurs, the relaxation rates are similar to those in the NaCl solutions.

VI. CONCLUSIONS

We have described calculations of the Raman spectra of Cs$_2$NaLaCl$_6$ and of LaCl$_3$ and its mixtures with NaCl and CsCl. These calculations are much more extensive than those described in paper 1 and have allowed a systematic exploration of the spectra across this range of systems. Furthermore, the depolarized spectra have been studied here. Although there is a systematic overestimation of the vibrational frequencies, the pattern of the spectra and their evolution with composition in the mixtures conform remarkably well to those seen experimentally. In particular, we have been able to show how the shape of the depolarized spectrum in the mixtures changes through the dominance of different mechanisms for the fluctuating polarizability at different concentrations. In the crystal, we are able to make a clear link between the spectral bands and a measure of the vibrational densities of states of the LaCl$_6$ coordination centers (in agreement with the experimental interpretation). In the molten mixtures, bands are seen at similar frequencies, despite the fact that 6-coordination is no longer predominant, except in dilute solutions. The coordination number of the La$^{3+}$ ions increases from a dilute solution of 6 to between 7 and 8 for the pure melt. This increase appears to occur when the coordination centers begin to cross link. CsCl appears to be a much better structure breaker than NaCl, so that the coordination units consist of long-lived, isolated LaCl$_6^{3-}$ units for LaCl$_3$ concentrations below 25%.

ACKNOWLEDGMENTS

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