Technical Note

LATTICE DYNAMICAL CALCULATIONS OF DEFICIENT NaCl SUPERSTRUCTURE-TYPE Li$_2$CoCl$_4$ AND Li$_2$MnBr$_4$

HEM CHANDRA GUPTA*, JÖRG ZWINSCHER† and HEINZ DIETER LUTZ†
*Department of Physics, Indian Institute of Technology, New Delhi, India
†Universität Siegen, Anorganische Chemie 1, D-57068 Siegen, Germany

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Abstract—Lattice dynamical calculations on SnMn$_2$S$_4$-type (ordered deficient NaCl superstructure) Li$_2$CoCl$_4$ and Li$_2$MnBr$_4$ were performed using a short-range force constant model. The results obtained reveal that the assignments of the Raman active phonon modes (and those of the structure related Suzuki-type Li$_6$M$_5^II$X$_4$) reported in the literature have to be changed. The 11 hitherto unknown infrared active modes have been calculated to range 233–339 and 70–98 cm$^{-1}$, and 227–266 and 50–71 cm$^{-1}$ for Li$_2$CoCl$_4$ and Li$_2$MnBr$_4$, respectively.

Keywords: D. lattice dynamics.

INTRODUCTION

Ternary lithium halides Li$_2$M$^II$X$_4$ ($M^II$ = Mn, Mg, Fe, Co, $X$ = Br, Cl) are among the best lithium ion conductors [1–4]. The ionic conductivity of these compounds is associated with their existence in various polymorphic phases like spinel, inverse spinel, olivine, Suzuki, SnMn$_2$S$_4$-type, etc. The various phases are characterised by different Raman and infrared phonons at the zone centre and their study is quite important to the understanding of various physical properties of these compounds. In this paper, we confine ourselves to the investigation of the phonons of the SnMn$_2$S$_4$-type phase of these ternary lithium halides, namely, Li$_2$MnBr$_4$ [5], Li$_2$CoCl$_4$ [6].

The structure of SnMn$_2$S$_4$ is orthorhombic with Cmmm space group ($Z = 2$) crystallising in an ordered NaCl defect type [5, 6]. Group theoretical treatment of the zone centre phonons of these compounds yield [5]

$$\Gamma = 2A_g + 1A_u + 2B_{1g} + 3B_{1u} + 1B_{2g} + 4B_{2u} + 1B_{3g} + 4B_{3u}$$

with six Raman active modes of the species $A_g$, $B_{1g}$, $B_{2g}$, $B_{3g}$ and 11 infrared active modes of the species $B_{1u}$, $B_{2u}$, $B_{3u}$. The symmetry coordinates for this structure are described by Lutz et al. [5], where they have also reported the Raman spectrum of two of these compounds Li$_2$MnBr$_4$ and Li$_2$CoCl$_4$. The assignment of the observed bands was performed in analogy to that in the case of structure related Suzuki-type Li$_6$M$_5^II$X$_4$ compounds [7].

In the present work, the aim is to apply a short-range force constant model in order to confirm the assignment of these reported Raman frequencies [5]. Then, in the future, on the basis of the suggested interpretation of Raman results presented here, it would enable the attribution of the Raman and the infrared phonons in other isostructural compounds.

THEORY

A short-range force constant model (SRM) has been developed involving six valence and repulsive force constants $K_1(M^II − X(1))$, $K_2(M^II − X(2))$, $K_3(Li − X(1))$, $K_4(Li − X(2))$, $F_1(X(1))$ and $F_2(X(1))$ as shown in Fig. 1. For simplification and the reduction of the repulsive force constants, the $x$ and $y$ structural parameters have been taken as 0.25 (instead of really 0.23312(8) and 0.24002(7), and 0.24338(8) and 0.2415(4) for Li$_2$CoCl$_4$ [6] and Li$_2$MnBr$_4$ [5], respectively). Using these force constants, initially, the dynamical matrix elements were written and then the dynamical matrix was solved for the first time analytically at the zone centre. The expressions for the Raman active phonon frequencies...
are as follows:

\( A_3 \) mode

\[
\left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) K_1 + 4F_1 + \left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) K_3 + \left( \frac{ab}{8} + \frac{bc}{8} + \frac{ac}{2} \right) F_3 = 0
\]

\( B_{1g} \) mode

\[
\left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) K_1 + 4F_1 + \left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) K_3 + \left( \frac{ab}{8} + \frac{bc}{8} + \frac{ac}{2} \right) F_2 + 2K_3 + \left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) F_2 - m_a\omega^2 = 0
\]

\( B_{2g} \) mode

\[
m_a\omega^2 = \left( \frac{a^2}{8} + \frac{b^2}{8} + \frac{c^2}{2} \right) K_3 + \left( \frac{a^2}{16} + \frac{b^2}{16} + \frac{c^2}{4} \right) K_4 + 2\left( \frac{a^2}{16} + \frac{b^2}{16} + \frac{c^2}{4} \right) F_2
\]

\( B_{3g} \) mode

\[
m_a\omega^2 = \left( \frac{a^2}{16} + \frac{b^2}{16} + \frac{c^2}{4} \right) K_4 + \left( \frac{a^2}{16} + \frac{b^2}{16} + \frac{c^2}{4} \right) K_3 + 2\left( \frac{a^2}{16} + \frac{b^2}{16} + \frac{c^2}{4} \right) F_2
\]

Here \( a, b, c \) are the lattice constants and \( m_a \) is the mass of the \( X \) atom.

### RESULTS AND DISCUSSION

If one uses the values of Raman active modes as given in Table 4 of Ref. [5] to find the various interatomic force constants of Li\(_2\)MnBr\(_4\) and Li\(_2\)CoCl\(_4\), then the values of the force constants \( K_1 \) and \( K_2 \) obtained are too small when compared with the similar values in the case of spinel-type Li\(_2\)ZnCl\(_4\) [6]. Also, it is found that with the use of these force constants, the calculated infrared transversal optic (TO) frequencies for these compounds are also less when compared to infrared TO frequencies in spinel-type Li\(_2\)ZnCl\(_4\) [8]. The reason for obtaining smaller values is the assignment of a lower value to \( A_3(2) \) in comparison to \( B_{1g}(1) \) in Table 4 of Ref. [5].

<table>
<thead>
<tr>
<th>Internal coordinate</th>
<th>Force constant</th>
<th>Li(_2)MnBr(_4)</th>
<th>Li(_2)CoCl(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M-X(1) )</td>
<td>( K_1 )</td>
<td>0.735</td>
<td>0.794</td>
</tr>
<tr>
<td>( M-X(2) )</td>
<td>( K_2 )</td>
<td>0.840</td>
<td>0.965</td>
</tr>
<tr>
<td>Li(_-)X(1)</td>
<td>( K_3 )</td>
<td>0.109</td>
<td>0.136</td>
</tr>
<tr>
<td>Li(_-)X(2)</td>
<td>( K_4 )</td>
<td>0.114</td>
<td>0.113</td>
</tr>
<tr>
<td>X(1)-X(1)</td>
<td>( F_1 )</td>
<td>0.000</td>
<td>0.037</td>
</tr>
<tr>
<td>X(1)-X(2)</td>
<td>( F_2 )</td>
<td>0.037</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Table 1. Experimental values of the Raman active phonons (cm\(^{-1}\)) for SnMn\(_2\)S\(_4\)-type halide [5]

<table>
<thead>
<tr>
<th></th>
<th>( A_3(1) )</th>
<th>( A_3(2) )</th>
<th>( B_{1g}(1) )</th>
<th>( B_{1g}(2) )</th>
<th>( B_{2g} )</th>
<th>( B_{3g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)MnBr(_4)</td>
<td>145</td>
<td>126</td>
<td>98</td>
<td>66</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Li(_2)CoCl(_4)</td>
<td>240</td>
<td>210</td>
<td>150</td>
<td>126</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Calculated short-range force constants (N cm\(^{-1}\))
Furthermore, the $K_1$ and $K_2$ force constants should be nearly the same as they are acting between similar ions at nearly the same distance. Similarly, the $K_3$ and $K_4$ force constants will be nearly the same. Hence, the two $A_k$ values and the two $B_k$ values should be closer to one another. Therefore, the correct assignment of the frequencies will be a higher value for $A_k(2)$ mode in comparison to $B_k(1)$ mode. The new assignments are given in Table 1 for the lithium ternary halides (SnMn$_2$S$_4$ phase).

With these assignments, the calculated force constants are presented in Table 2. One can observe now that the force constants $K_1$ and $K_2$ are quite comparable to $M-X$ interactions in similar spinel or Suzuki phase compounds [8, 9]. With the force constants of Table 2, the calculated zone centre frequencies are shown in Table 3 along with the available experimental results with the correct assignments. When the calculated infrared frequencies for these compounds are compared with the infrared frequencies of spinel or Suzuki-type ternary lithium halides [8, 9], we infer that the calculated infrared frequencies of the SnMn$_2$S$_4$-type compounds under investigation are of the right order of magnitude.

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REFERENCES