Ionic polarizabilities in crystals at high pressures

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Received 12 December 2000; accepted 15 December 2000

Abstract

The pressure dependence of ionic polarizabilities in alkali halides and fluorite-structured crystals has been evaluated via different methods and their results compared. Some methods had to be extended for the fluorite structure. Recent experimental data for cesium halides, together with that for alkali halides, allowed for a more complete analysis of results. When high pressure data were available comparison allows for an evaluation of the validity of the methods themselves; these could then be applied to propose high pressure values for other crystals with measurements only at \( p \neq 0 \).

Keywords: D. Dielectric properties; C. High pressure

In previous works [1,2] we have developed an empirical method for the evaluation of the pressure dependence of anion polarizabilities in crystals starting from data at \( p = 0 \); this is of importance because in general there are no experimental data of dielectric constants at high pressure. A comparison with ab initio calculations for alkali halides was further published [3] showing that for salts with relatively small cations (Li\(^+\), Na\(^+\)) the pressure dependence of the polarizability of the salt can be given by its anion contribution.

In order to go onto the study of salts with larger cations and different structures we have used the following methods:

1. The extension of the empirical method [1] now applied to cations as well as anions, by introducing a cation polarizability function \( \alpha_+(r_+, r_-) \) that can be differentiated with respect to pressure giving:

\[
\frac{\partial \alpha_+}{\partial \rho} = \frac{\partial \alpha_+}{\partial r_+} \frac{\partial r_+}{\partial \rho} + \frac{\partial \alpha_+}{\partial r_-} \frac{\partial r_-}{\partial \rho}
\]

where

\[
\frac{\partial \alpha_+}{\partial r_+} \bigg|_+ = \frac{\partial \alpha_+}{\partial R} \bigg|_+
\]

and

\[
\frac{\partial \alpha_+}{\partial r_-} \bigg|_- = \frac{\partial \alpha_+}{\partial R} \bigg|_-\]

with \( R \) the interionic nearest-neighbor distance, assuming \( R = r_+ + r_- \).

(\( \partial \alpha_+/\partial R \)) should be considered zero because in the calculation of \( \partial \alpha_+/\partial \rho \) we are assuming that for a given cation \( \alpha_+ \) is constant for different salts, and therefore its value is transferable from one salt to another.

We previously described [2] a method of evaluation of \( \partial \rho/\partial \rho \). An alternative way is its evaluation from experimental data of the isothermal volumetric compressibility \( \chi \) and the interionic distance \( R \) of different salts, assuming:

\[
\chi = -\frac{1}{V} \frac{\partial V}{\partial \rho} = -\frac{3}{R} \frac{\partial R}{\partial \rho} \approx - \frac{3}{R} \left( \frac{\partial r_+}{\partial \rho} + \frac{\partial r_-}{\partial \rho} \right)
\]

and using a maximization procedure similar to the one used previously [2]. This last one was applied as a checking procedure. Values of \( \partial \rho/\partial \rho \) used in this work are given in Table 1.
2. When experimental high pressure data are available, an independent evaluation of $\frac{\partial \alpha_+}{\partial p}$ can be obtained by differentiating with respect to pressure the well known relation $(\alpha_+ / \alpha_-) = (r_+/r_-)^3$ giving:

$$\frac{\partial \alpha_+}{\partial p} = \frac{\partial \alpha_-}{\partial p} = 3 \left( \frac{\partial r_+}{\partial p} - \frac{\partial r_-}{\partial p} \right)$$

(3)

and assuming

$$\frac{\partial \alpha_\text{total}}{\partial p} \approx \frac{\partial \alpha_+}{\partial p} + \frac{\partial \alpha_-}{\partial p}$$

(4)

For the fluorite structure one should take into account that the anion contribution to the polarizability is e.g. $\alpha_- = 2\alpha_F$ for CaF$_2$.

$\frac{\partial \alpha_\text{total}}{\partial p}$ is evaluated using the differentiated Clausius–Mossotti equation, when high pressure data of $(-V\alpha_\text{tot}/N)$ is available. $\partial r/\partial p$ are obtained as described previously.

3. When ab initio calculations of $\partial \alpha_+ / \partial p$ are available, this value may be introduced in Eq. 3 giving the corresponding $\partial \alpha_+ / \partial p$ value.

We developed a computation system [4] implemented in Maple V that does the different calculations mentioned above and allows for a comparison of results. For alkali halides, results of $\partial \alpha_+ / \partial p$ obtained with different methods are shown in Table 2. For the fluorite structure the results are shown in Table 3. For CsF and SrCl$_2$ there are no experimental high pressure data, therefore values of $\partial \alpha_+ / \partial p$ (and $\partial \alpha_- / \partial p$) are proposed, assuming the behavior of the anion is similar to the one in alkali halides.

Cesium halides are particularly interesting because there are recent experimental data of $\epsilon_\infty$ at high pressures [5]; in Table 4 the results for these salts (with bcc structure) are given.

Results show that, in general, the two contributions to $\partial \alpha / \partial p$ ($\partial \alpha_+ / \partial p$ and $\partial \alpha_- / \partial p$) should be taken into account; although for small and compact cations (Li$^+$, Na$^+$, Ca$^{2+}$) $\partial \alpha_+ / \partial p$ can be considered negligible, as has been remarked previously [3]. Tables 2–4 show that for many salts (particularly for Rb, Cs and Ba salts) $\partial \alpha_+ / \partial p$ is an important contribution to $\partial \alpha / \partial p$. Results of $\partial \alpha_+ / \partial p$ for different methods (columns 3 and 5 in Table 2) show a double dependence, on the anion and the cation. The same can be seen for $\partial \alpha_- / \partial p$ (columns 2 and 4 in Table 2). As could be expected, $\partial \alpha_- / \partial p$ changes more with a change of anion than with a change of cation, and vice versa for $\partial \alpha_+ / \partial p$. We can therefore conclude that $\partial \alpha_- / \partial p$ and $\partial \alpha_+ / \partial p$ are not ‘transferable’ between different salts.

Comparison of results (Tables 2–4) shows that for alkali and cesium halides the empirical method gives results of $|\partial \alpha_- / \partial p|$ higher than those obtained by the new method (Eqs. (3) and (4)) or by ab initio calculations; on the other

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\partial \alpha_+ / \partial p$ Eqs. (3) and (4)</th>
<th>$\partial \alpha_- / \partial p$ Eqs. (3) and (4)</th>
<th>$\partial \alpha_+ / \partial p$ Eq. (1)</th>
<th>$\partial \alpha_- / \partial p$ similar to Eq. (1)</th>
<th>Ref. [3]</th>
<th>$\partial \alpha_- / \partial p$ Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>-0.03</td>
<td>-0.87</td>
<td>-0.086</td>
<td>-1.21</td>
<td>-0.86</td>
<td>-0.9</td>
</tr>
<tr>
<td>LiCl</td>
<td>-0.02</td>
<td>-7.48</td>
<td>-0.0017</td>
<td>-11.5</td>
<td>-4.90</td>
<td>-7.5</td>
</tr>
<tr>
<td>LiBr</td>
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<td>-14.2</td>
<td>-0.037</td>
<td>-19.8</td>
<td>-8.56</td>
<td>-14.2</td>
</tr>
<tr>
<td>LiF</td>
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<td>-29.7</td>
<td>-0.089</td>
<td>-37.2</td>
<td>-16.0</td>
<td>-29.7</td>
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<tr>
<td>NaF</td>
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<td>-1.16</td>
<td>-0.89</td>
<td>-1.81</td>
<td>-1.38</td>
<td>-1.5</td>
</tr>
<tr>
<td>NaCl</td>
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<td>-7.04</td>
<td>-1.04</td>
<td>-12.4</td>
<td>-6.27</td>
<td>-7.3</td>
</tr>
<tr>
<td>NaBr</td>
<td>-0.21</td>
<td>-12.3</td>
<td>-1.11</td>
<td>-20.7</td>
<td>-8.99</td>
<td>-12.5</td>
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<td>NaI</td>
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<td>-1.21</td>
<td>-38.6</td>
<td>-18.4</td>
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</tr>
<tr>
<td>KF</td>
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<td>-0.44</td>
<td>-6.80</td>
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<td>-3.3</td>
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<td>-13.7</td>
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<td>-5.75</td>
<td>-42.0</td>
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<td>-25.4</td>
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<tr>
<td>RbF</td>
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<td>-0.97</td>
<td>-12.0</td>
<td>-2.37</td>
<td>-3.37</td>
<td>-5.1</td>
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<tr>
<td>RbCl</td>
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<td>-11.7</td>
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<td>-10.2</td>
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<tr>
<td>Rbl</td>
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<td>-9.82</td>
<td>-44.0</td>
<td>-25.8</td>
<td>-31.8</td>
</tr>
</tbody>
</table>
hand for fluorite structure there is a good coincidence of the three methods. It is interesting to notice that even when there are differences in the results for different methods, they all present similar trends in \( \alpha \) when changing either the anion or the cation.

In conclusion, we have various methods that allow us to evaluate the pressure dependence of ionic polarizabilities. The results show that both anionic and cationic contributions should be considered, and this will be particularly important when more complex ions are studied. \( \alpha \) are not transferable between salts (similarly to what occurs with \( \alpha \)) due to their dependence both on anion and cation nature.

On the basis of this analysis we are proposing values of \( \alpha / \partial p \) and \( \alpha / \partial p \) for CsF and Ca, Sr and Ba chlorides and bromides for which there are no experimental high pressure data at the moment. For Ca, Sr and Ba fluorides there is a good agreement of \( \alpha / \partial p \) values between different methods; \( \alpha / \partial p \) for calcium can be considered negligible, but not so for strontium or barium. For CsF, \( \alpha / \partial p \) presents a higher and lower limit, \(-1.73 \) and \(-3.68 \times 10^{-32} \text{ m}^3 \text{ GPa}^{-1} \), respectively; in this case \( \alpha / \partial p \) is not only non-negligible, but it is a much larger absolute value \((\sim 1.8 \times 10^{-32} \text{ m}^3 \text{ GPa}^{-1})\) than the anionic contribution \((-3.68 \times 10^{-32} \text{ m}^3 \text{ GPa}^{-1})\).

It would be interesting in the future to have measurements of these magnitudes for comparison with the proposed values.

**Acknowledgements**

J.A.O.B. and A.B. acknowledge operating grants from CONICET (PIP 0663/98) and ANPCyT (PICT 98 03611).

**References**