APPROXIMATE DEGENERACIES OF ZONE BOUNDARY PHONONS IN ALKALI HALIDE CRYSTALS

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We point out the existence of a pervasive pattern of near degeneracies of phonon frequencies in isobaric alkali halide crystals (NaBr, KCl, RbBr, CsI) which strongly suggests that their dynamical matrices are almost invariant under transformations which exchange positive and negative ions. We extend this hypothesis to a relation between phonon properties of "mirror" alkali halides in which the ions of one crystal are replaced by the oppositely charged isobaric ions of the other, such as RbCl and KBr. Experimental evidence supporting this can also be adduced. Similar near degeneracies universally occurring in NaCl structure alkali halides and alkaline earth oxides are also noted and a possible dynamical basis for understanding these suggested.

Several recent monographs1-4 have summarized the great advances in understanding the dynamics of alkali halide crystals as achieved during the past few decades experimentally through inelastic neutron scattering and theoretically through simple models (shell, polarization dipole, distortion dipole, etc.) to describe the response of the electron distribution to nuclear displacements. Included in these volumes are presentations of experimental phonon dispersion curves compared with theoretical predictions based on macroscopic input data3 and semi-empirical representations of the data4. The results are impressive but it is clear also that further refinement is necessary.

We report here on some surprisingly simple features of the phonon dispersion relation data which to our knowledge have not been previously noted—namely, a pattern of near degeneracies of modes with k vectors on the Brillouin Zone (BZ) boundary. They fall into two classes, one class occurring only in "isobaric" alkali halides (NaF, KCl, RbBr, CsI) in which the two ions are of nearly equal mass, and the other class occurring in all alkali halides (and alkaline earth oxides) having NaCl structure.

Near degeneracies similar to those of the first class have been noted and explained previously in crystals like GaAs and β-brass where the two atomic species are nearly identical.1 Such degeneracies are also to be expected for like mass oppositely charged ions (as in isobaric alkali halides) whenever the dynamical matrix yielding the phonon frequencies is invariant under exchange of the ionic species.5 Under this "extended" symmetry the two species are identical insofar as the dynamical matrix is concerned, and the phonon modes may be considered as those of a monatomic crystal. If the crystal has the NaCl structure, the monatomic lattice is simple cubic and its "extended" BZ is the cube formed by extending the square faces of the true (truncated octahedral) BZ (see Fig. 1a). The optic modes of the NaCl structure are those with k vectors within the extended zone but outside the true zone. This region can be dissected into eight congruent subregions, which can be trans-

Fig. 1. True and extended Brillouin zones for (a) NaCl and (b) CsCl structure.
lated by true reciprocal lattice vectors so as
to overlay the true BZ. The continuity of the frequencies
associated with a k-vector as it
passes through a hexagonal face of the true BZ
means that for a point on the face there will be
an optic mode degenerate with each acoustic
mode. In the reduced zone scheme the optical
mode will be associated with the boundary point
of the true zone into which the original point
is carried by the reciprocal lattice translation,
namely a point on the opposite hexagonal face.
If this point is equivalent to the original
point (i.e. belongs to the "star" of the original
k vector), there will be an additional degener-
cacy at this k. This will happen if k lies at
the points L or W or on the straight line Q
joining them. 6

The same considerations hold, mutatis mutan-
dies, for the CsCl structure, where the cubical
true BZ and the dodecahedral "extended" BZ are
as shown in Fig. 1b. In this case every point on the
surface of the true cubical zone is carried
into an equivalent point by the translation and the
degeneracies of the frequencies are gener-
ally doubled. The degeneracy patterns predicted
under the true and the extended space group sym-
metry are exhibited in Table I.

Table II shows that the "isobaric" alkali halides
indeed have near degeneracies at points
predicted by the extended symmetry and that the
splittings are considerably smaller than those occurring for the corresponding points and modes
in the non-isobaric crystals. In one instance
there is a further degeneracy. At M for CsI ex-
tended symmetry predicts a (2,2,2) degeneracy
pattern while a (4,2) is observed. This could be
accidental, but if the pattern continues to be
(4,2) along the line T joining X and R, the inter-
pretation as an accident would be difficult to sustain.

The two ions in "isobaric" alkali halides
have nearly the same mass and (in the simpler
models such as the rigid ion model of Kellerman 5,
least) have the same number of electrons. In any model with identical anion-anion and cation-
cations interactions the extended symmetry of
the dynamical matrix would be exact. The dif-
ference in nuclear charges, however, makes the
electronic distributions of anions and cations dissimilar in size, deformability, and polariz-
ability (at least for free ions) and this, to-
gether with the nuclear mass differences, breaks
the symmetry and splits the degeneracies. Re-
markably, the splitting is nevertheless small—

<table>
<thead>
<tr>
<th>Structure</th>
<th>Point, Line, etc.</th>
<th>Degeneracy Pattern</th>
<th>Table I. True and extended space group degeneracy patterns.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>L</td>
<td>(2,2,1,1) (4,2)</td>
<td>(2,2,1,1) (2,2,2)</td>
</tr>
<tr>
<td></td>
<td>W,Q</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>R</td>
<td>(3,3) (6)</td>
<td>(2,2,1,1) (4,2)</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td></td>
<td>(2,2,1,1) (2,2,2)</td>
</tr>
<tr>
<td></td>
<td>M,T</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S,B</td>
<td>none (2,2,2)</td>
<td></td>
</tr>
</tbody>
</table>

Anion BSW Modes F Cation Cl Br I

<table>
<thead>
<tr>
<th>Anion</th>
<th>BSW</th>
<th>Modes</th>
<th>F</th>
<th>Cation</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>L</td>
<td>LL</td>
<td>0.05</td>
<td>0.20</td>
<td>0.31</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>TT</td>
<td>0.05</td>
<td>0.08</td>
<td>0.16</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>L</td>
<td>LL</td>
<td>0.29</td>
<td>0.03</td>
<td>0.33</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>TT</td>
<td>0.18</td>
<td>0.04</td>
<td>0.16</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>L</td>
<td>LL</td>
<td>0.28</td>
<td>0.27</td>
<td>0.06</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>TT</td>
<td>0.19</td>
<td>0.19</td>
<td>0.00</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>L</td>
<td>TT</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>all</td>
<td>0.36</td>
<td>0.16</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>LL</td>
<td>0.42</td>
<td>0.18</td>
<td>0.04</td>
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</tr>
<tr>
<td></td>
<td>M</td>
<td>&quot;4&quot;b</td>
<td>0.37</td>
<td>0.17</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Splittings determined from graphs in Refs. 3 and 4 and from original papers cited therein.

b Splittings quoted are those of two singlets which bracket the doublet.

of order 5 to 10% of the unsplit frequency in each case. Though small splittings are also predicted by more realistic models (deformation and polarization dipole), the observed splittings are often smaller still. 3

Extended symmetry also implies that the group
velocity of degenerate acoustic and optical modes
in the neighborhood of points like L in NaCl
structures and X, R, and M in CsI should have the
same magnitude. Here the data are not com-
plete enough to draw quantitative conclusions,
but what exists roughly confirms what is expected
from a weakly broken symmetry. 7

These features support the ideas that in
isobaric alkali halides phonon properties change little if one simultaneously replaces cations
by their isobaric anions and vice versa. If
this hypothesis is extended to more general
alkali halides it leads to a stronger prediction
in a case such as RbCl one could then replace
both species with their isobaric homologues to
form KBr without substantially changing the dy-
namical matrix. Thus the dispersion relations
for phonons should be similar for the two crys-
tals. Measurements on RbCl and KBr seem to con-
firm this almost everywhere to better than 5%.
For the other such "mirror" pairs, (NaCl,KF),
(RbF,NaBr), and (CsF,Nal), the morphology of the dispersion curves is quite similar (especially when compared to that of nonmirror pairs) but
the numerical differences range up to 25% or
more. 8. Table II also shows some evidence of this "mirror" symmetry, and it can also be recognized in the morphological similarities of the com-
pused spectral distributions of the phonons of
"mirror" pairs. This implies a corresponding similarity in the effective Debye temperature \( \Theta_D \) as a function of \( T \) for the pairs.\(^7\)

The second class of degeneracies which occur in NaCl structure alkali halides irrespective of the mass differences of the ions is a near degeneracy of the degenerate transverse optical modes with what is usually the longitudinal optic "mirror" pairs.\(^4\) This implies a corresponding similarity in the effective Debye temperature \( \Theta_D \).

Deformation dipole theory (which predicts the deviation is 0.017. The mean splitting in the square BZ face. Space limitations preclude a complete listing of these but the results may be summarized by noting that the mean of the splittings in the 14 such alkali halides is less than 0.035 (in units of the \( \omega_0 \) frequency at \( \Gamma \)), the largest splitting is 0.06, and the standard deviation is 0.017. The mean splitting in the deformation dipole theory (which predicts the smallest mean splitting and the best fit to the frequency itself) is 0.054, maximum 0.09, and standard deviation 0.039. Results for the polarization dipole model are not substantially different. The same near degeneracy is found also in the alkaline earth oxides (CaO, MgO, SrO, BaO) with a mean splitting of 0.06, a maximum of 0.11, and a standard deviation of 0.04. The degeneracy is not found in LiH, LiD, MnO, FeO, CoO, or AgCl.

We know of no simple argument like extended symmetry by which these degeneracies can be understood but the following observation may have some relevance to why the splittings are small: The three modes in question have very similar motions of the ions. The longitudinal "optic" mode at (001) and the transverse "optic" mode at (100) have identical motions in every x-z plane except that alternate planes have opposite phases in the two modes. Thus interactions between ions lying within such planes cannot contribute to the splitting. The splitting due to nearest neighbor central forces between planes is also small since the relative motion of these neighbors is transverse.

For the isobaric compounds one can easily understand the essential features of the dispersion curves on the basis of extended symmetry\(^11\) and it may be possible to produce a simple theoretical treatment of these by taking the extended symmetry into account \textit{ab initio} and treating the effects which break the symmetry as perturbations. An investigation of experimental data has been undertaken in connection with mirror symmetry, not only between "mirror" alkali halide crystals, but their melts as well, with encouraging results.\(^11\) Since extended symmetry predicts further relations between phonon frequencies which have not yet been measured, a program of more comprehensive and accurate measurements of phonon modes would help to quantify better the degree to which a weakly broken extended symmetry is indeed a useful concept in understanding these crystals and perhaps open the possibility of bringing more powerful group theoretical techniques to bear on the subject.

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\textbf{REFERENCES}


\(^3\) J.R. Hardy and A.M. Karo, \textit{The Lattice Dynamics and Statics of Alkali Halide Crystals} (Plenum, New York, 1979).


\(^5\) The letters L, W, Q and others used here and below for points or lines in \( k \) space refer to the standard notation of L.P. Bouckaert, B. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936), hereafter referred to as BSW, See Fig. 1.

\(^6\) It is also exact for Wigner-Dyson lattices with equal charge and mass species. See F.J. Dyson, Ann. Phys. (N.Y.) 63, 1 (1971); T.A. Witten, Jr., Astrophys. J. 188, 243 (1974); and L.L. Foldy and B. Segall, Phys. Rev. B 17, 480 (1978); Phys. Rev. B 22 4992 (1980). This was the discovery of the unexpected degeneracy at R in the CaCl lattice of this kind which led to the discovery of a similar degeneracy in actual CsCl and subsequently to the other near degeneracies here reported.

\(^7\) G. Segall has pointed out to us that extended symmetry also gives degeneracies within the true BZ, e.g. when longitudinal acoustic and longitudinal optic branches cross as at reduced \( k = 0.6 \) on \( \Sigma \) in RbBr (Ref. 3, p.190).

\(^8\) The principal difficulties are with the \( \omega_0 \) branch. The larger errors here suggest ionic properties do change in different crystal environments, perhaps particularly for Na and F.

\(^9\) These can be observed in theoretical results for \( \varepsilon_2 \) vs \( T \) curves and spectral moment functions in Ref. 3, again comparing mirror and non-mirror pairs. Experimentally they may be seen for two mirror pairs (KBr vs RbBr and NaCl vs KF) for which adequate specific heat data is available (L.L. Foldy and B. Segall, to be published).

\(^10\) The optical modes are here identified as those in which some pairs of nearest neighbor ions move directly towards and away from one another.

\(^11\) L.L. Foldy and B. Segall, to be published.