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 nega-
tive ions. We extend this hypothesis to a relation between phonon pro-
perties 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 monographs[1-4] have summarized
the great advances in understanding the dynamics
of alkali halide crystals as achieved during the
past few decades experimentally through inelas-
tic neutron scattering and theoretically through
simple models (shell, polarization dipole, dis-
tortion dipole, etc.) to describe the response
of the electron distribution to nuclear dis-
placements. Included in these volumes are pre-
sentations of experimental phonon dispersion
curves compared with theoretical predictions
based on macroscopic input data[3] and semi-empir-
ical representations of the data[4]. 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 $\vec{k}$ 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 alka-
line earth oxides) having NaCl structure.

Near degeneracies similar to those of the
first class have been noted and explained pre-
viously 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 iso-
baric alkali halides) whenever the <u>dynamical
matrix</u> yielding the phonon frequencies is in-
variant 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
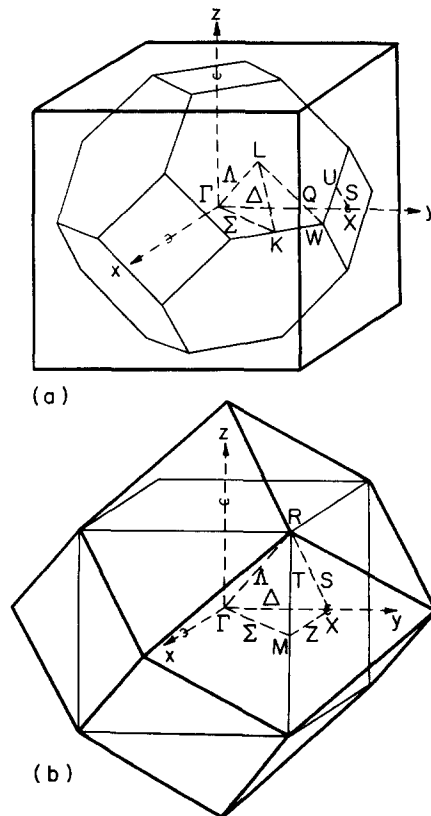(truncated octahedral) BZ (see Fig. 1a). The

Fig. 1. True and extended Brillouin zones for
(a) NaCl and (b) CsCl structure.

optic modes of the NaCl structure are those with
$\vec{k}$ vectors within the extended zone but outside
the true zone. This region can be dissected into
eight congruent subregions, which can be trans-

lated by true reciprocal lattice vectors so as to overlay the true BZ. The continuity of the frequencies associated with a $\vec{k}$-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 $\vec{k}$ vector), there will be an additional degener-- acy at this $\vec{k}$. This will happen if $\vec{k}$ lies at the points L or W or on the straight line Q joining them.[6]

The same considerations hold, mutatis mutandis, 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 generally doubled. The degeneracy patterns predicted under the true and the extended space group symmetry are exhibited in Table I.

Table II shows that the "isobaric" alkali halides indeed have near degeneracies at points

TABLE I. True and extended space group degeneracy patterns.

Structure	Point, Line, etc.[a]	Degeneracy True	Pattern Extended
NaCl	L	(2,2,1,1)	(4,2)
	W,Q	(2,2,1,1)	(2,2,2)
CsCl	R	(3,3)	(6)
	X	(2,2,1,1)	(4,2)
	M,T	(2,2,1,1)	(2,2,2)
	S,B[a]	none	(2,2,2)

[a]BSW notation except that B designates boundary of BZ except for R,X,M, and T.

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 extended 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 interpretation 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], at 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 difference in nuclear charges, however, makes the electronic distributions of anions and cations dissimilar in size, deformability, and polarizability (at least for free ions) and this, together with the nuclear mass differences, breaks the symmetry and splits the degeneracies. Remarkably, the splitting is nevertheless small --

TABLE II. Splittings of extended symmetry degeneracies in alkali halides in units of the longitudinal optical frequency at Γ.[a]

Anion	BSW Pt.	Modes	Cation			
			F	Cl	Br	I
Na	L	LL	0.05	0.20	0.31	0.33
	L	TT	0.05	0.08	0.16	0.13
	W		--	--	--	--
K	L	LL	0.29	0.03	0.33	0.24
	L	TT	0.18	0.04	0.16	0.13
	W		--	--	--	--
Rb	L	LL	0.28	0.27	0.06	0.24
	L	TT	0.19	0.19	0.00	0.09
	W		--	--	0.02	0.11
Cs	L	LL	0.35			
	L	TT	0.18			
	W		--			
Cs	R	all		0.36	0.16	0.03
	X	LL		0.42	0.18	0.04
	X	TT		0.34	0.17	0.02
	M	"4"b		0.37	0.17	0.0?

[a]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 complete 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 dynamical matrix. Thus the dispersion relations for phonons should be similar for the two crystals. Measurements on RbCl and KBr seem to confirm this almost everywhere to better than 5%. For the other such "mirror" pairs, (NaCl,KF), (RbF,NaBr), and (CsF,NaI), 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 computed spectral distributions of the phonons of

"mirror" pairs[4]. This implies a corresponding similarity in the effective Debye temperature θ_D as a function of T for the pairs[9].

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 mode at the point X in the center of 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 LO frequency at Γ), 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[10] 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 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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[3] J.R. Hardy and A.M. Karo, The Lattice Dynamics and Statics of Alkali Halide Crystals (Plenum, New York, 1979).

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[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, R. 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, Phys. Rev. B 17, 4889 (1978); Phys. Rev. B 22 4992 (1980). It was the discovery of the unexpected degeneracy at R in the CsCl lattice of this kind which led to the discovery of

a similar degeneracy in actual CsI and subsequently to the other near degeneracies here reported.

[7] B. 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 Σ in RbBr (Ref. 3, p.190).

[8] The principal difficulties are with the LO 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 θ_D 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.