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Phonon force models and surfaces of near degeneracy in the isobaric alkali halides

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A number of near degeneracies occur in the measured phonon spectra of the isobaric alkali halides NaF, KCl, RbBr, and CsI, in which the alkali- and halogen-ion masses are nearly equal. The lattice dynamics of KCl and RbBr are reexamined in terms of several different shell models. It is shown that the observed eigenfrequencies in these materials can be fitted essentially as well by an artificial model in which the two ions are treated as identical except for their charge as by a general 11-parameter model. The calculations indicate the existence of surfaces of near degeneracy in the Brillouin zone, as predicted by Segall and Foldy. Neutron structure factor measurements may be required to distinguish among realistic competing force models.

Neutron scattering experiments on the lattice dynamics of the alkali halides were performed in the 1960s and early 1970s, and interpreted in terms of a variety of shell models.[1] The alkaline earth oxides were studied a few years later within the same framework of ideas.[2-5] Good numerical fits to the neutron data could be obtained with at least one of the many elaborations of the shell model, and in this sense the lattice dynamics of all of these materials are believed to be well understood. However, it is well known that fitted shell model parameters frequently have unphysical values.[1,6] Furthermore, essentially all of the published data on the alkali halides and the alkaline earth oxides consists of eigenfrequencies $\nu(\vec{q},j)$, although the eigenvectors are more sensitive to the phonon force model employed.[7]

Recently, Foldy and co-workers[8-10] suggested that what they term extended symmetry might nearly apply to the isobaric alkali halides, namely, those that have almost equal masses: NaF, KCl, RbBr, and CsI. A rigorous extended-symmetry model is a hypothetical construct in which the two ions in the unit cell are treated as if they are identical except for their (equal and opposite) charge. A number of additional degeneracies occur as a result. Some of these, e.g., degeneracies between optical and acoustical modes at the symmetry point L, are independent of any force model parameters. Other mode crossings vary in location in $\vec{q}$ space with the parameters, reflecting a division of the modes into two groups of three. In one group, the eigenvectors for the two ions in the unit cell are in phase, while in the other, they are out of phase. In the real materials, of course, differences between the two ions split these additional degeneracies and mix the in-phase and out-of-phase eigenvectors.

Only the masses are different[8,9] in one of the first models applied to the lattice dynamics of the alkali halides, the rigid-ion model with first-nearest-neighbor interactions.[11] Because this model gives poor results for the dispersion curves of the nonisobaric compounds, it was abandoned early for shell models. It should also be noted that the rigid-ion model does a poor job of predicting neutron structure factors (phonon eigenvectors) for certain modes.[7] Nevertheless, the rigid-ion model does include most of the physical effects that dominate the lattice dynamics of insulators—the long-range Coulomb forces between charged ions and the short-range repulsive interactions between nearest neighbors—and its primary failing is that ionic polarizabilities are not taken into account.[1,6,7]

In this paper, it is demonstrated that one cannot sensibly distinguish between extended-symmetry[8-10] and more general force models in the isobaric compounds KCl and RbBr solely on the basis of the published measurements of phonon frequencies along high-symmetry directions in the Brillouin zone (BZ). Specifically, it is shown that shell models in which the only differences between the two ions are their mass and charge or their charge alone fit the neutron scattering data essentially as well as more general models with more parameters. The measures for the fits are χ^2 and the standard error ($\mathscr{S}$), defined as follows:

$$\chi^2=\frac{1}{N-K}\sum_{i=1}^{N}\left[\frac{\Delta\nu_i}{\sigma_i}\right]^2 , \quad (1)$$

$$\mathscr{S}=\frac{1}{(N-K)^{1/2}}\sum_{i=1}^{N}(\Delta\nu_i)^2 . \quad (2)$$

Here $\Delta\nu_i$ is the difference between measured and calculated frequencies, σ_i is the estimated experimental uncertainty for the ith phonon, N is the number of measured frequencies, and K is the number of model parameters.

The implications of these calculations for KCl and RbBr, and of other calculations carried out for the mixed compounds RbCl and KBr, are several. First, and already noted, it is known that physical significance cannot be attached to shell-model parameters without caution. The results to be presented reaffirm this conclusion. They do not demonstrate that any of the models tried here are preferred for the isobaric compounds (although a rigorous extended-symmetry model is of course ruled out), but instead indicate a need for more data and perhaps for physically more realistic models. Neutron structure factor (eigenvector) measurements may be required to distinguish between competing force models if the eigenfrequencies allow no distinction to be made.

Second, the calculations indicate that extended surfaces of near degeneracy occur in the BZ's of the isobaric crystals, as predicted by Segall and Foldy.[10] This perhaps surprising feature of all models tried can be tested by neutron scattering.

Third, it appears that reasonably good estimates of the phonon spectra of the nonisobaric alkali halides can be obtained from appropriately scaled models for the isobaric compounds. Calculations for the isobars and extensions of these calculations to their mixtures may provide a useful test for phonon force models.

Table I lists parameters for several models fitted to the data of Rolandson and Raunio[12] for RbBr; these data comprise 74 frequencies with a mean experimental uncertainty $\langle \pm\sigma_i \rangle = 0.033$ THz $= 1.2\%$. Model 1 is a general 11-parameter shell model with all short-range forces acting between the shells. In model 2, the ions are the same except for their masses and (equal and opposite) charges, and the mechanical polarizabilities $d_\pm$ go to zero; this last condition ($d_\pm \rightarrow 0$) was imposed after the fitting program gave extremely small values for $d_\pm$ when it was allowed to vary in this model for RbBr. Model 3 is the same as model 2, except that the average mass has been used for both ions. Model 4 is a rigid-ion model in which the ions are the same except for mass and charge. For comparison, Rolandson and Raunio[12] give values of $\chi^2 = 2.39$ and $\mathscr{S} = 0.027$ THz for their best 11-parameter fit to their data. The rather large values for χ^2 in Table I and Ref. 12 do not reflect poor fits to the data, but instead result from the unusually (probably unrealistically) small experimental uncertainties quoted in Ref. 12 and in other papers by the same authors and their co-workers.

Figure 1 compares dispersion curves calculated

TABLE I. Shell models for RbBr fitted to the data in Ref. 12. For models 1, 2, and 4, the atomic masses (a.m.u.) are $M_+ = 85.4678$, $M_- = 79.904$, while for model 3, $M_+ = M_- = 82.69$. K is the number of adjustable parameters.

	Units	1	2	3	4
K		11	6	6	5
χ^2		2.03	2.15	2.17	16.45
$\mathscr{S}$	THz	0.0244	0.0259	0.0272	0.0776
A_{+-}	$e^2/2v = e^2/4r_0^3$	12.30	11.77	11.78	10.82
B_{+-}		−0.699	−0.613	−0.621	−0.743
A_{++}		0.046	0.344	0.335	0.278
B_{++}		0.036	0.064	−0.061	0.047
A_{--}		0.408	0.344	0.335	0.278
B_{--}		−0.142	−0.064	−0.061	0.047
Z	e	0.806	0.757	0.758	0.689
α_+	v	0.0346	0.0242	0.0236	0
α_-		0.0195	0.0242	0.0236	0
d_+	e	0.0178	0	0	0
d_-		0.0653	0	0	0
$a = 2r_0$	Å	6.84			
$e^2/2v$	dyn/cm	1442			

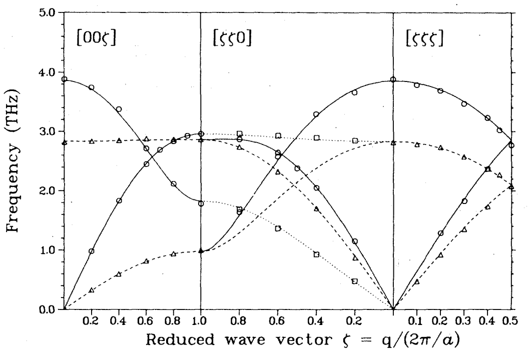

FIG. 1. Calculated (model 3) and observed phonon dispersion curves in RbBr.

from model 3 with experiment. The fit of this model, in which the ions are treated as identical except for their charge, is remarkably good. The same quality of fit is found for KCl. Model 3, because of its strict (and unrealistic) division of the modes into those in which the eigenvectors are perfectly in phase and those in which they are out of phase, permits crossings between modes not decoupled by general symmetry arguments for the NaCl structure. Three of these occur in Fig. 1: the LA-LO (solid lines) crossings along the [001] and [110] directions, and the TA-TO (dashed lines) crossing along [110]. In the real materials KCl and RbBr, these crossings cannot actually occur, but instead are near degeneracies. The data show that the splittings are quite small.

Figure 2 indicates that near degeneracies persist throughout the BZ. What is shown are dispersion curves for KCl along the [0.7,0.5,0.3] direction, calculated from a general 11-parameter model 1 fitted to the data of Raunio and Almqvist.[13] Dispersion curves were calculated in KCl and RbBr along some 26 directions in the BZ with endpoints on the lines connecting $U-X-W-K-L-W$; the results in Fig. 2 are typical in exhibiting several near degeneracies, whose locations vary continuously with direction in reciprocal space and thus map out surfaces of near degeneracy. Calculations were also done with a six-parameter model 2, in which the atoms are the same except for their mass and charge, and the results were very similar.

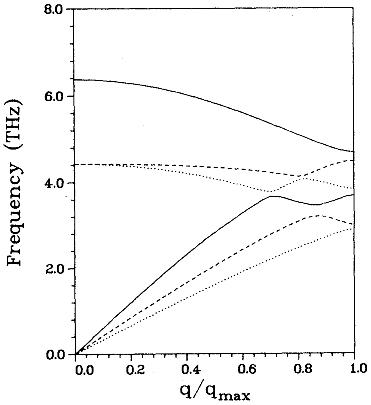

FIG. 2. Calculated (model 1) dispersion curves for KCl along the [0.7,0.5,0.3] direction.

Models 1–3 give comparable fits to the measured frequencies in KCl and RbBr, and the predicted dispersion curves along other directions in the BZ are very similar. However, the eigenvectors calculated in the various models can differ significantly in the region near the zone boundary, around and beyond the $\vec{q}$ values where near degeneracies occur. These differences may be distinguishable in neutron structure factor measurements.[7] In KCl, for example, for scattering wave vectors $\vec{Q}=(2\pi/a)(\zeta,\zeta,2+\zeta)$, the structure factors for the LA and LO modes calculated in model 2 cross at $\zeta\sim0.48$; intensity shifts from the LA to the LO mode beyond this point. In the general 11-parameter model 1, in contrast, the LA mode is much more intense than the LO mode for these scattering wave vectors all the way from Γ to L $(0\leq\zeta\leq0.5)$.

Figure 3 illustrates how models for the isobaric alkali halides might be transferred to the nonisobaric compounds. The curves were calculated for RbCl from a shell model whose parameters were obtained by very simple arguments from the model 2 fits for KCl and RbBr. The electrical and mechanical polarizabilities were assigned the same values $(d_{\pm}\rightarrow0)$ as in KCl and RbBr, and the arithmetic average was used for the charge and the first-neighbor interactions. Second-neighbor in-

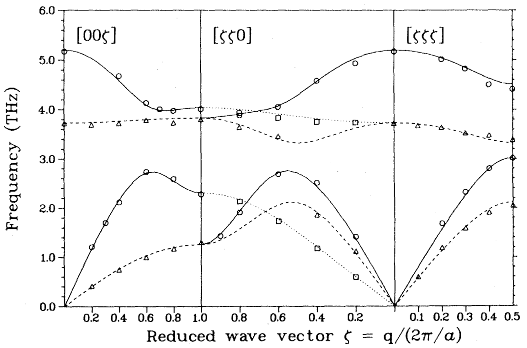

FIG. 3. Calculated and observed phonon dispersion curves in RbCl.

teractions were determined by a Born-Mayer scaling of the form (for Rb)

$$\exp\{-\sqrt{2}[r_0(\mathrm{RbCl})-r_0(\mathrm{RbBr})]/\rho\}\ ,$$

with ρ taken from Table I of Tosi and Fumi.[14] Figure 3 shows that these simple arguments give reasonably good results for RbCl.[15] Applied to KBr, the same procedure gives results that are not quite as good, but are perhaps comparable in overall quality to the model II results of Cowley *et al.*[6]

In summary, a number of calculations have been done that suggest a need to reexamine the lattice dynamics of the alkali halides. Neutron scattering experiments on the isobaric crystals could determine whether the predicted near degeneracies persist throughout the zone. While the measured dispersion curves apparently can be reproduced by several different force models, competing models can give noticeably different eigenvectors for wave vectors near the zone boundary where the near degeneracies occur. Structure factor measurements may therefore be required to determine reliable force models. Experiments on the isobaric alkaline earth chalcogenides CaS, SrSe, and BaTe would be of interest, as Segall and Foldy also note.[10] Further calculations are planned for other alkali halides and the alkaline earth oxides.

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