PHYSICAL REVIEW B VOLUME 26, NUMBER 4 15 AUGUST 1982

# Phonon dispersion in $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ mixed crystals

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(Received 18 September 1981)

Phonon dispersion relations in $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ have been measured by coherent inelastic neutron scattering at 300 K. Some of the acoustic phonons and most of the optical phonons are split and show two peaks of nearly equal weight around the mean position. Both the observed maxima show a similar dispersion against the wave vector. The observed phonon frequencies are generally less than the mean of the respective frequencies in the pure crystals. The phonon data have been analyzed in terms of a generalized shell model. The first-neighbor radial force constants and the effective ionic charge are found to be smaller than the mean value for the pure crystals. The elastic constants evaluated by the shell-model fit to the neutron scattering data for $K_{0.5}Rb_{0.5}Cl$ are ($10^{11}$ dyn/cm$^2$)$C_{11}=4.0\pm0.1$, $C_{44}=0.54\pm0.03$, and $C_{12}=0.8\pm0.15$, and for $KCl_{0.5}Br_{0.5}$ are $C_{11}=4.0\pm0.1$, $C_{44}=0.59\pm0.05$, and $C_{12}=0.8\pm0.15$. The values are in agreement with those measured by the sound-echo technique.

## I. INTRODUCTION

The study of lattice vibrations in mixed systems is of considerable interest as they are intermediate between perfect crystals and fully disordered amorphous materials. The mixed alkali halides are a favorable class of such systems, because they have a simple structure and most of them form solid solutions over the entire concentration range. So far phonons in mixed alkali halides have been mainly studied by infrared (ir) and Raman spectroscopy.[1–5] These techniques are restricted to the zone-center optical modes only. Buyer and Cowley[6] have measured some phonons in the mixed crystals of KBr-RbBr in the symmetry directions $[\zeta\zeta\zeta]$ and $[\zeta\zeta 0]$ using the inelastic neutron scattering technique. The only detailed dispersion-relations study by neutron scattering has been done in $K_{0.5}Rb_{0.5}I$ by Aslam *et al.*[7] The phonons were observed in the symmetry directions up to the zone boundary implying that some translational symmetry is preserved in these crystals. The measurements showed a splitting of the transverse-optical zone-center phonon, and the acoustic phonons near the zone boundaries showed a considerable softening as compared to the mean of the respective phonon energies in the pure crystals. A recent neutron elastic-diffraction study[8] of the $K_xRb_{1-x}I$ system showed that the Debye characteristic temperature $\Theta_D$, which represents an effective cutoff phonon energy $h\nu_D$ in the material, does not vary linearly with concentration. The value of $\Theta_D$ is lower than the concentration weighted mean for the mixture and the difference is maximum at $x=0.5$. This confirmed earlier calorimetric measurements on mixed alkali halides.[9,10]

The ir and Raman scattering works on mixed alkali halides show a splitting of the transverse-optical zone-center phonon in $K_{0.5}Rb_{0.5}I$ (Ref. 1), which is termed as a 'two-mode' material, whereas for mixtures like $K_{0.5}Rb_{0.5}Cl$ (Ref. 4) and $KCl_{0.5}Br_{0.5}$ (Refs. 1, 3, 5) only one transverse zone-center phonon is observed and such materials are termed as one-mode materials. Several theoretical models have been put forward[11–15] to explain the frequencies observed in mixed materials. The most significant of these is the one by Chang and Mitra,[13] which categorizes the materials mainly on the basis of the mass ratios of the constituents. Another model by Genzel *et al.*[14] evaluates the optical frequencies by use of the local electric fields.

The present work reports the study of the phonon dispersion relations in mixed alkali halides $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ using the coherent inelastic neutron scattering technique. One of the reasons for the selection of these samples was to compare the results with optical scattering works. For the $KCl_xBr_{1-x}$ system, dispersion-relation calculations are also available.[16] The above two mixed alkali halides are good systems to study because they make solid solutions over the complete composition and a large temperature range.[4] The neutron scattering data has been analyzed in terms of a generalized shell model. In the present work the elastic constants for the above materials were also measured by the sound-echo technique to confirm the neutron scattering results.

## II. EXPERIMENTAL

The single crystals used in this study were grown by the Bridgman technique at a temperature of 800 °C. The starting materials were analytic reagent grade salts. The growth took place in a sealed quartz glass tube under argon atmosphere (20 Torr at room temperature). The inner surface of the container was coated with a carbon film to avoid sticking of crystals to the tube walls. The crystals were annealed at about 70 °C below their melting points for 48 hours. For annealing the temperature was raised at a rate of 1 to 2 °C per minute to avoid any thermal shock to the crystals. Crystals of 1.5-cm diameter and 6-cm length were grown from which good crystals of about 2 cc to 3 cm$^3$ were cleaved. Neutron $\theta$:$2\theta$ scans on these samples gave sharp lines with no shoulders, which indicated the concentration homogeneity of the samples used. Lattice parameters and line shapes were also checked by x-ray powder diffraction. The elastic constants in the mixed crystals were obtained by ultrasonic velocity measurements at room temperature using the "pulse-echo-overlap" method developed by May.[17]

The phonon dispersion relations in single crystals of $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ were measured at room temperature using the $C3$ triple-axis spectrometer at the 44 MW FR2 reactor at Karlsruhe.

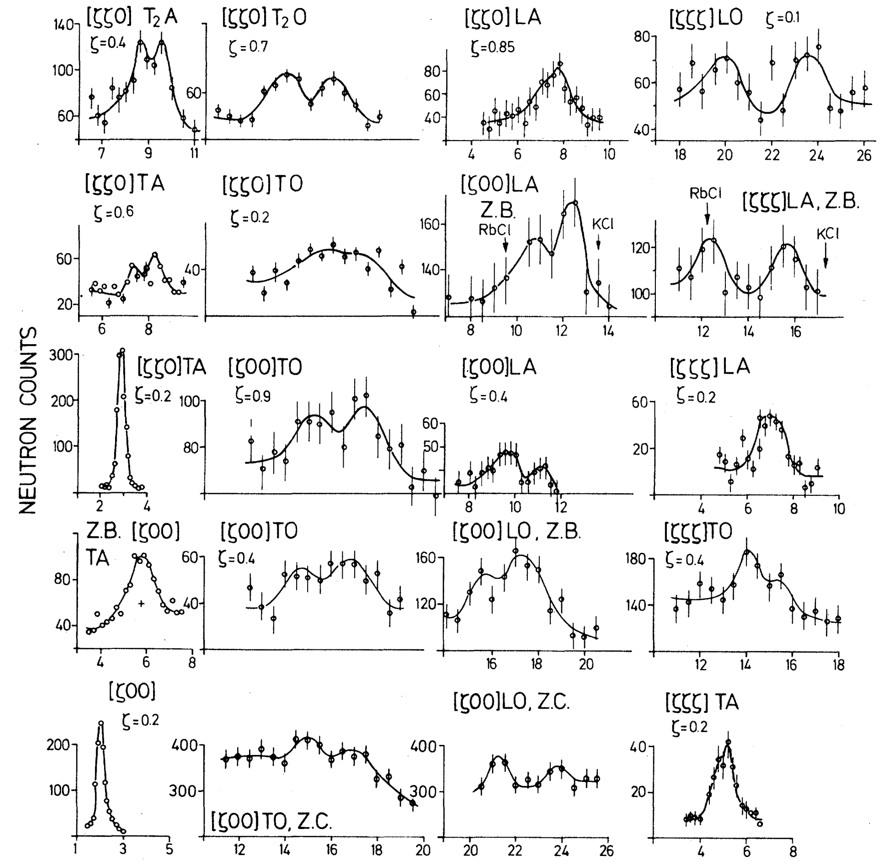

FIG. 1. Some of the phonons observed in three symmetry directions in $K_{0.5}Rb_{0.5}Cl$. Both optical and acoustic phonons are shown. All the optical phonons, transverse as well as longitudinal, have a tendency to have two peaks. Most of the acoustical phonons are also broad. Vertical bars show the statistical errors. The horizontal bars show the instrumental resolution for some of the phonons.

Constant $Q$ method was used for the phonon scans. The neutron incident energy we kept constant either at 14.7 or 25.0 meV.

About 100 phonon scans were made for $K_{0.5}Rb_{0.5}Cl$ and 60 for $KCl_{0.5}Br_{0.5}$ samples in the three symmetry directions $[00\zeta]$, $[\zeta\zeta0]$, and $[\zeta\zeta\zeta]$. Most of the phonons were measured in the $(1\bar{1}0)$ plane and some in the (100) plane. The zone-center phonons and some of the phonons showing a double-peak structure were repeated at many reciprocal points. The inelastic structure factors as used by Raunio *et al.*[18] were followed for the selection of the lattice points for phonon scans.

## III. RESULTS AND DISCUSSION

### A. $K_{0.5}Rb_{0.5}Cl$

The lattice parameter for $K_{0.5}Rb_{0.5}Cl$ has been measured both by the x-ray and neutron scattering, to be equal to 6.443±0.01 Å, which agrees with the mean value for KCl and RbCl.[19] Some of the phonons measured in the three symmetry directions in the mixed crystal $K_{0.5}Rb_{0.5}Cl$ are shown in Fig. 1. Most of the observed phonons are either broad or show a double-peak structure. The mean energy determined from the broad or split peaks was taken to be the phonon energy. The values as ob-

TABLE I. Mean phonon energies (units in meV) obtained by the inelastic neutron scattering technique along three symmetry directions $\langle 00\zeta\rangle$, $\langle \zeta\zeta0\rangle$, and $\langle\zeta\zeta\zeta\rangle$ in $K_{0.5}Rb_{0.5}Cl$.

| $\zeta=aq/(2\pi)$ | $\omega$ | $\zeta=(1/\sqrt{2})aq/(2\pi)$ | $\omega$ | $\zeta=(1/\sqrt{3})aq/(2\pi)$ | $\omega$ |
|---|---|---|---|---|---|
| $[00\zeta]$TA | | $[0\zeta\zeta]T_1A$ | | $[\zeta\zeta\zeta]$TA | |
| 0.2 | 2.0 ±0.05 | 0.15 | 2.09±0.05 | 0.15 | 3.75±0.05 |
| 0.4 | 3.63±0.05 | 0.2 | 2.82±0.05 | 0.2 | 5.05±0.05 |
| 0.6 | 4.85±0.05 | 0.3 | 4.2 ±0.05 | 0.3 | 7.3 ±0.2 |
| 0.8 | 5.6 ±0.2 | 0.4 | 5.47±0.05 | 0.4 | 8.7 ±0.2 |
| 1.0 | 5.8 ±0.2 | 0.6 | 7.95±0.05 | 0.45 | 9.1 ±0.5 |
| | | 0.9 | 11.25±0.25 | 0.5 | 9.5 ±0.5 |
| $[00\zeta]$LA | | | | | |
| 0.1 | 2.57±0.05 | $[0\zeta\zeta]T_2A$ | | $[\zeta\zeta\zeta]$LA | |
| 0.2 | 5.15±0.05 | 0.1 | 2.1 ±0.05 | 0.1 | 3.5 ±0.2 |
| 0.4 | 10.25±0.1 | 0.15 | 3.35±0.2 | 0.2 | 7.1 ±0.2 |
| 0.7 | 13.8 ±0.4 | 0.4 | 9.05±0.05 | 0.3 | 10.5 ±0.2 |
| 0.8 | 13.0 ±0.5 | | | 0.4 | 13.2 ±0.5 |
| | | $[0\zeta\zeta]$LA | | | |
| 1.0 | 11.5 ±0.2 | | | 0.5 | 14 ±0.5 |
| | | 0.15 | 4.85±0.05 | | |
| | | 0.2 | 6.35±0.05 | | |
| $[00\zeta]$TO | | | | $[\zeta\zeta\zeta]$TO | |
| | | 0.5 | | | |
| | | 0.4 | 11.8 ±0.3 | | |
| 0.0 | 16.0 ±0.2 | | | 0.05 | 15.8 ±0.3 |
| | | 0.6 | 13.2 ±0.2 | | |
| 0.1 | 16.3 ±0.2 | | | 0.2 | 15.2 ±0.2 |
| | | 0.7 | 12.1 ±0.5 | | |
| 0.2 | 16.0 ±0.5 | | | 0.3 | 14.9 ±0.5 |
| | | 0.8 | 8.7 ±0.5 | | |
| 0.4 | 15.9 ±0.3 | | | 0.4 | 15.0 ±0.5 |
| | | 0.85 | 7.5 ±0.45 | | |
| 0.7 | 17.0 ±0.3 | | | 0.45 | 15.0 ±0.7 |
| | | 1.0 | 5.8 ±0.5 | | |
| 0.9 | 16.5 ±0.2 | | | 0.5 | 14.9 ±0.7 |
| $[00\zeta]$LO | | $[0\zeta\zeta]T_1O$ | | $[\zeta\zeta\zeta]$LO | |
| 0.0 | 21.9 ±0.5 | 0.2 | 16.2 ±0.2 | 0.1 | 21.6 ±0.5 |
| 0.4 | 20.0 ±0.8 | 0.5 | 17.0 ±0.5 | 0.2 | 19.9 ±0.5 |
| 0.6 | 16.9 ±0.5 | 0.7 | 16.7 ±0.5 | 0.4 | 18.5 ±0.4 |
| 0.95 | 17.3 ±0.8 | 1.0 | 16.7 ±0.3 | | |
| 1.0 | 16.7 ±0.3 | $[0\zeta\zeta]T_2O$ | | | |
| | | 0.7 | 14.6 ±0.3 | | |
| | | 0.85 | 15.9 ±0.5 | | |
| | | $[0\zeta\zeta]$LO | | | |
| | | 0.3 | 19.0 ±0.5 | | |
| | | 0.8 | 17.0 ±0.5 | | |

served in fourteen acoustic and optical branches are given in Table I.

The observed phonon energies do not generally correspond to the average of the values in KCl (Ref. 20) and RbCl (Ref. 21) at 300 K. The acoustic-phonon frequencies are found to be weighted more towards the RbCl values. This is understandable if we consider the fact that the acoustic-phonon frequencies are weighted more towards the heavier mass.[22] The energy values for the optical phonons near zone boundaries show less deviation from the respective mean values because they depend on the lighter atom mass (Cl), which is unchanged.

Experimentally observed phonon frequencies are fitted to Cowley's shell model[23] using eleven parameters, with both ions polarizable. The parameters are defined in an earlier work.[7] The parameters evaluated from the shell-model fit are given in Table II. The data of Raunio and Almqvist[20] for KCl and that of Raunio and Rolandson[21] for RbCl were also analyzed for direct comparison with the mixed crystals. The experiments on KCl and RbCl were performed at 80 K but some selected phonons were also measured at 300 K. The difference in phonon energies measured at the two temperatures was found to be small (about 3%) and has been neglected in the present comparison.

Table II shows that the first-neighbor radial force constant $A_{+-}$ and the effective ionic charge $Ze$ are the two most significant shell-model parameters, whereas the other constants have values of the order of standard errors for those constants. For $K_{0.5}Rb_{0.5}Cl$, which is a mixture with mass disorder, the force constants have more similarity with RbCl than with KCl, which has nearly equal masses. Shell-model fit shows that the first-neighbor radial force constant decreases by about 10%, and the effective ionic charge $Ze$ decreases by about 3% for the mixed crystal as compared to the mean values for KCl and RbCl. The present analysis agrees with an earlier study by Angress *et al.*,[5] who found that, to explain the infrared reflection spectra of mixed alkali halides, force-constant reductions were required.

The eleven-parameter shell-model fit to the experimental data for $K_{0.5}Rb_{0.5}Cl$ at 300 K is shown in Fig. 2. The model gives a good overall fit. There is some difference near the $[\zeta\zeta\zeta]$ TO zone boundary. In the model calculations the longitudinal-acoustic and the transverse-optic branches cross each other near the $[\zeta\zeta\zeta]$ zone boundary, but the observed transverse-optic branch lies above the longitudinal branch by about 1 meV. Nair and Walker[4] have observed the TO zone-boundary phonon in $[\zeta\zeta\zeta]$ direction in $K_{1-x}Rb_xCl$ by Raman scattering (RS) at 118 $\text{cm}^{-1}$ (14.64 meV) for $x=0.55$, which is in good agreement with the present observation.

The shell-model parameters were used to calculate the phonon frequency distribution, using the

TABLE II. Best-fit parameters for shell model in KCl, $K_{0.5}Rb_{0.5}Cl$, RbCl, and $KCl_{0.5}Br_{0.5}$. $A_{+-}$,$A_{++}$,$A_{--}$ are the radial and $B_{++}$,$B_{--}$ are the tangential short-range force constants between near-neighbor ions, in units as shown. $v$ is the volume per unit cell. $B''$ represents the noncentral forces between the nearest neighbors. $\alpha_1$,$\alpha_2$,$d_1$,$d_2$ are the mechanical and electrical polarizabilities of positve and negative ions. $Ze$ is the effective ionic charge.

| | System | | | |
|---|---|---|---|---|
| Parameters Units | KCl (80 K) | $K_{0.5}Rb_{0.5}Cl$ (300 K) | RbCl (80 K) | $KCl_{0.5}Br_{0.5}$ (300 K) |
| $A_{+-}$ $(e^2/2v)$ | $11.0\pm0.1$ | $10.5\pm0.1$ | $12.1\pm0.1$ | $10.9\pm0.1$ |
| $A_{++}$ $(e^2/2v)$ | $0.05\pm0.15$ | $-0.3\pm0.2$ | $-0.4\pm0.2$ | $0.4\pm0.2$ |
| $B_{++}$ $(e^2/2v)$ | $0\ \pm0.1$ | $0.18\pm0.06$ | $0.21\pm0.09$ | $-0.31\pm0.05$ |
| $A_{--}$ $(e^2/2v)$ | $0.5\pm0.15$ | $0.8\pm0.2$ | $1.0\pm0.15$ | $0.1\pm0.2$ |
| $B_{--}$ $(e^2/2v)$ | $0.07\pm0.10$ | $-0.4\pm0.06$ | $-0.2\pm0.1$ | $0.06\pm0.07$ |
| $B''$ $(e^2/2v)$ | $0.03\pm0.03$ | $-0.24\pm0.10$ | $-0.27\pm0.07$ | $-0.21\pm0.05$ |
| $Ze$ $(e)$ | $0.8\pm0.005$ | $0.8\pm0.005$ | $0.84\pm0.005$ | $0.84\pm0.01$ |
| $\alpha_1$ $(1/v)$ | $0.01\pm0.004$ | $0.01\pm0.004$ | $0.01\pm0.004$ | $0.18\pm0.003$ |
| $\alpha_2$ $(1/v)$ | $0.03\pm0.01$ | $0.04\pm0.01$ | $0.04\pm0.005$ | $0.04\pm0.003$ |
| $d_1$ $(e)$ | $0\ \pm0.15$ | $0.04\pm0.02$ | $0\ \pm0.02$ | $0.02\pm0.02$ |
| $d_2$ $(e)$ | $0\ \pm0.15$ | $0.13\pm0.02$ | $0.05\pm0.03$ | $0.04\pm0.02$ |
| $\chi^2$ | 0.056 | 0.07 | 0.169 | 0.054 |

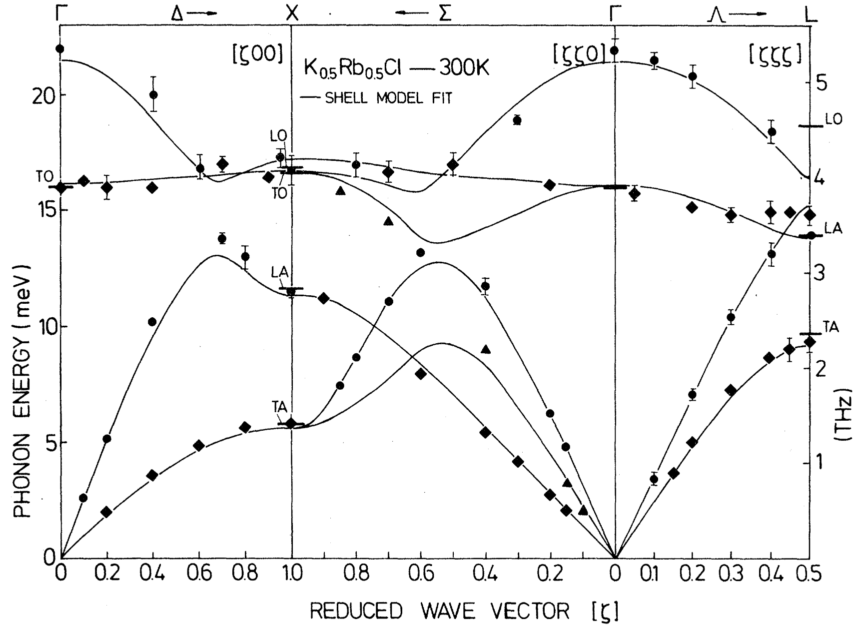

FIG. 2. Phonon dispersion relation at room temperature in the three symmetry directions ⟨ζ00⟩, ⟨ζζ0⟩ and ⟨ζζζ⟩ in $K_{0.5}Rb_{0.5}Cl$. ● and ◆ represent the longitudinal and transverse phonons, respectively. ▲ represent the transverse phonons in (100) plane. The solid lines are eleven-parameter shell-model fit. All the wave vectors are in reduced coordinates. The thick horizontal bars represent mass weighted averages of phonon energies in KCl and RbCl.

interpolation method of Gilat and Raubenheimer.[24] The frequency distribution for $K_{0.5}Rb_{0.5}Cl$ is shown in Fig. 3. The Debye temperature $\Theta_D$ evaluated from the frequency distribution is shown in Fig. 4.

The elastic constants obtained by the shell-model fit and those determined by the ultrasonic sound-echo technique are given in Table III. The elastic constants $C_{11}$ and $C_{44}$ determined by ultrasonic method are in excellent agreement with the mean in pure crystals,[25] also measured by ultrasonic technique. Generally the elastic constants determined by neutron scattering are up to 10% higher than those given by the ultrasonic method, owing to the different interaction times involved in the two methods.[26–28] The elastic constants deter-

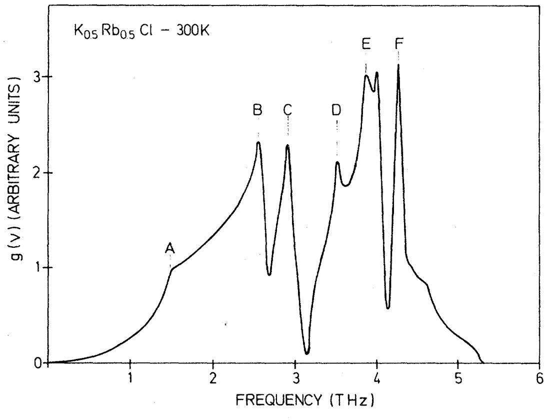

FIG. 3. Phonon density of state for $K_{0.5}Rb_{0.5}Cl$, calculated using the shell-model parameters at room temperature. Peaks *A*,*B*,*C*,*D* in the distribution correspond to the TA⟨ζ00⟩, TA⟨ζζζ⟩, TA⟨ζζ0⟩, LA⟨ζ00⟩, and LA⟨ζζζ⟩ zone boundaries, respectively. Peak *E* corresponds to the TO⟨ζ00⟩ branch and *F* to the LO⟨ζζζ⟩ zone boundary.

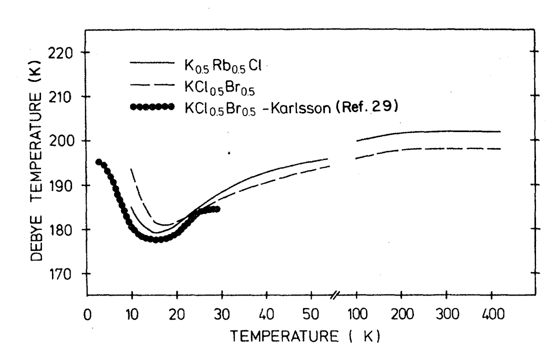

FIG. 4. Debye temperature vs temperature as evaluated from the frequency distribution obtained by inelastic neutron scattering for $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$. The specific heat data ● of Karlsson (Ref. 29) for $KCl_{0.5}Br_{0.5}$ are also plotted.

TABLE III. Elastic constants for $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ at 300 K, determined by the ultrasonic sound-echo method and by the shell-model fit to the neutron scattering data. The values are also compared with the values obtained from the mean of pure crystal ultrasonic data. (Units: $10^{11}$ dyn/cm$^2$.)

| | $K_{0.5}Rb_{0.5}Cl$ | | | $KCl_{0.5}Br$ | | |
|---|---|---|---|---|---|---|
| | Neutron[a] scattering | Ultrasonic[a] | Mean of pure crystals[b] | Neutron[a] scattering | Ultrasonic[a] | Mean of pure crystals[b] |
| $C_{11}$ | 4.0±0.1 | 3.8±0.02 | 3.8±0.06 | 4.0±0.1 | 3.6±0.05 | 3.75±0.05 |
| $C_{44}$ | 0.54±0.03 | 0.53±0.01 | 0.54±0.01 | 0.59±0.05 | 0.55±0.02 | 0.57±0.02 |
| $C_{12}$ | 0.8±0.15 | | 0.63±0.07 | 0.8±0.15 | | 0.6±0.1 |

[a] Present work.

[b] Reference 25.

mined by neutron scattering in Table III lie within 5% of those found by the ultrasonic method. The results also show that the elastic anisotropy $C_{12}/C_{44}$, which is related to the noncentral forces, is much larger for $K_{0.5}Rb_{0.5}Cl$ than for KCl but has a value similar to that for RbCl.

### B. $KCl_{0.5}Br_{0.5}$

The lattice parameter obtained by x-ray and the neutron measurements of 300 K is 6.447±0.008 Å, which is in very good agreement with the mean value for KCl and KBr.[19] The phonon energies observed by inelastic neutron scattering at 300 K are given in Table IV. The observed dispersion relations and the eleven-parameter shell-model fit are shown in Fig. 5. The parameters evaluated from the fit are given in Table II. For comparison, the force constants for KBr were derived from the work of Cowley *et al.*[23] who have measured phonon dispersion relations in KBr at 90 and 400 K. From their analysis at two temperatures the values of $A_{+-}$ and $Ze$ are estimated by linear extrapolation to be 12.6 and 0.975, respectively, at 300 K (in units as given in Table II). The comparison in Table II shows that $KCl_{0.5}Br_{0.5}$ behaves like $K_{0.5}Rb_{0.5}Cl$ in the sense that $A_{+-}$ decreases by about 10% and the effective ionic charge decreases as compared to the mean of KCl and KBr. The other constants have similar behavior as for the $K_{0.5}Rb_{0.5}Cl$ system. The increase in the tangential and noncentral parameters and hence in the elastic anisotropy as observed in the above samples was also observed[7] for $K_{0.5}Rb_{0.5}I$ earlier.

The shell-model fit to the phonon dispersion relations is shown in Fig. 5. The model gives a good overall fit. Massa *et al.*[16] have calculated dispersion relations in $KCl_xBr_{1-x}$ using a pseudounit cell, treating the masses in the virtual crystal approximation and taking the model parameters as the mean for the pure crystals. They employed a breathing shell model for their calculations. Their calculations for $x$ near 0.5 were compared with the present data. The calculations showed a general qualitative fit but gave somewhat lower values for TO branches in all the symmetry directions. The present fit, which allows the parameters to be different from the mean of the end-member values, gives a much better agreement, both with the observed acoustic as well as the optical branches.

The elastic constants determined by the ultrasonic and the shell-model fit are compared with the mean values for pure crystals in Table III. $C_{11}$ and $C_{44}$ agree reasonably well with the mean values. The neutron scattering values are within 10% of the ultrasonic values. $C_{12}$ is higher than the mean value for pure crystals, indicating a higher elastic anisotropy in the mixed system compared to the pure alkali halides.

The frequency distribution evaluated using the shell-model-fit parameters is given in Fig. 6. $\Theta_D$ evaluated from frequency distribution is compared with the specific-heat measurements of Karlsson[29] in Fig. 4. The two works show a reasonable agreement. A maximum difference of 5% at low temperatures can be explained on the fact that in that region $\Theta_D$ depends mainly on the elastic constants and the values for these measured by neutron scattering are generally higher by that amount as compared to those obtained by other methods.

Nair and Walker[3] have measured Raman spectra in $KCl_{1-x}Br_x$. For $x=0.5$ they observe a phonon around 140 cm$^{-1}$ (17.36 meV), which they assign

TABLE IV. Mean phonon energies (units in meV) obtained by the inelastic neutron scattering technique along three symmetry directions $\langle 00\zeta\rangle$, $\langle \zeta\zeta 0\rangle$, and $\langle \zeta\zeta\zeta\rangle$ in $KCl_{0.5}Br_{0.5}$.

| $\zeta = aq/(2\pi)$ | $\omega$ | $\zeta = (1/\sqrt{2})aq/(2\pi)$ | $\omega$ | $\zeta = (1/\sqrt{3})aq/(2\pi)$ | $\omega$ |
|---|---|---|---|---|---|
| $[\zeta 00]$Ta | | $[\zeta\zeta 0]$TA | | $[\zeta\zeta\zeta]$TA | |
| 0.3 | 2.9 ±0.4 | 0.2 | 2.85±0.05 | 0.1 | 2.4 ±0.2 |
| 0.4 | 3.8 ±0.3 | 0.4 | 5.85±0.15 | 0.15 | 3.75±0.25 |
| 0.5 | 4.85±0.4 | 0.6 | 8.3 ±0.4 | 0.2 | 4.9 ±0.4 |
| 0.7 | 5.75±0.5 | 0.8 | 10.7 ±0.3 | 0.3 | 7.5 ±0.3 |
| 0.9 | 5.9 ±0.6 | | | 0.5 | 9.7 ±0.8 |
| 1.0 | 6.0 ±0.6 | | | | |
| $[\zeta 00]$LA | | $[\zeta\zeta 0]T_2A$ | | $[\zeta\zeta\zeta]$LA | |
| 0.1 | 2.5 ±0.1 | 0.15 | 3.75±0.25 | | |
| 0.2 | 5.2 ±0.2 | 0.2 | 4.7 ±0.1 | 0.1 | 3.7 ±0.05 |
| 0.3 | 7.1 ±0.1 | 0.4 | 8.7 ±0.1 | 0.2 | 7.2 ±0.1 |
| 0.4 | 10.1 ±0.2 | | | 0.35 | 12.3 ±0.3 |
| | | $[\zeta\zeta 0]$LA | | | |
| 0.5 | 12.0 ±0.5 | | | 0.5 | 15.0 ±0.1 |
| 0.7 | 14.0 ±1.0 | 0.1 | 3.15±0.05 | | |
| 0.85 | 12.8 ±0.6 | 0.3 | 9.1 ±0.2 | $[\zeta\zeta\zeta]$TO | |
| 1.0 | 12.0 ±0.5 | 0.5 | 13.0 ±0.5 | | |
| | | 0.8 | 9.8 ±0.2 | 0.15 | 15.5 ±0.2 |
| | | | | 0.25 | 15.4 ±0.3 |
| | | | | 0.3 | 15.3 ±0.5 |
| | | $[\zeta\zeta 0]T_1O$ | | | |
| | | 0.2 | 16.2 ±0.5 | 0.4 | 14.5 ±0.5 |
| | | 0.5 | 16.7 ±0.5 | 0.5 | 14.0 ±1.0 |
| $[\zeta 00]$LO | | | | | |
| | | 0.7 | 16.6 ±0.5 | | |
| 0.0 | 23.4 ±1.0 | | | | |
| 0.5 | 20.1 ±0.5 | | | | |
| | | $[\zeta\zeta 0]T_2O$ | | $[\zeta\zeta\zeta]$LO | |
| 0.7 | 15.8 ±0.5 | 0.7 | 14.0 ±0.2 | 0.2 | 22.2 ±1.0 |
| 0.9 | 16.5 ±1.0 | | | | |
| | | 0.85 | 15.3 ±0.5 | | |
| $[\zeta 00]$TO | | $[\zeta\zeta 0]$LO | | | |
| 0.0 | 15.7 ±0.2 | | | | |
| 0.1 | 15.5 ±0.3 | 0.35 | 19.7 ±0.5 | | |
| 0.2 | 15.6 ±0.2 | 0.8 | 16.2 ±0.5 | | |
| 0.8 | 15.8 ±0.5 | | | | |
| 1.0 | 15.7 ±0.5 | | | | |

either to TO($X$) or to a peak in the density of states. TO($X$) is observed at 15.7 meV in the present work. The phonon observed by Nair and Walker[3] could correspond to the peak $E$ in the density of states (Fig. 5). Fertel and Perry[1] have measured ir reflection spectra in this system at 300 K. From the Kramers-Kronig analysis of the broad spectrum between 100 and 200 $cm^{-1}$ observed by them, they quote 196 $cm^{-1}$ (24.3 meV) and 140 $cm^{-1}$ (17.36 meV) for the LO and TO phonons, respectively, at the zone center. We observe LO($\Gamma$) as a split phonon, centered at $23.4 \pm 1.0$ meV. The value given by Fertel and Perry[1] corresponds to one of the components of this split phonon. The TO($\Gamma$) phonon is observed at $15.7 \pm 0.2$ meV. This energy value does not agree with the work of Fertel and Perry.[1] Mitsuishi[30] from his transmission infrared results on thin films for $x = 0.5$ gives a value of 125 $cm^{-1}$ (15.5 meV) for this phonon, which tends to agree with the present measurements. His work was said to have some uncertainty owing to the difficulty in accurately knowing the composition of the film. There does not seem to be any ambiguity in the present work for this phonon, because the phonons in various dispersion branches starting from $\Gamma$ point, confirm it.

## IV. PHONON WIDTHS

As shown in Fig. 1 for $K_{0.5}Rb_{0.5}Cl$ all the observed optical and some acoustic phonons are

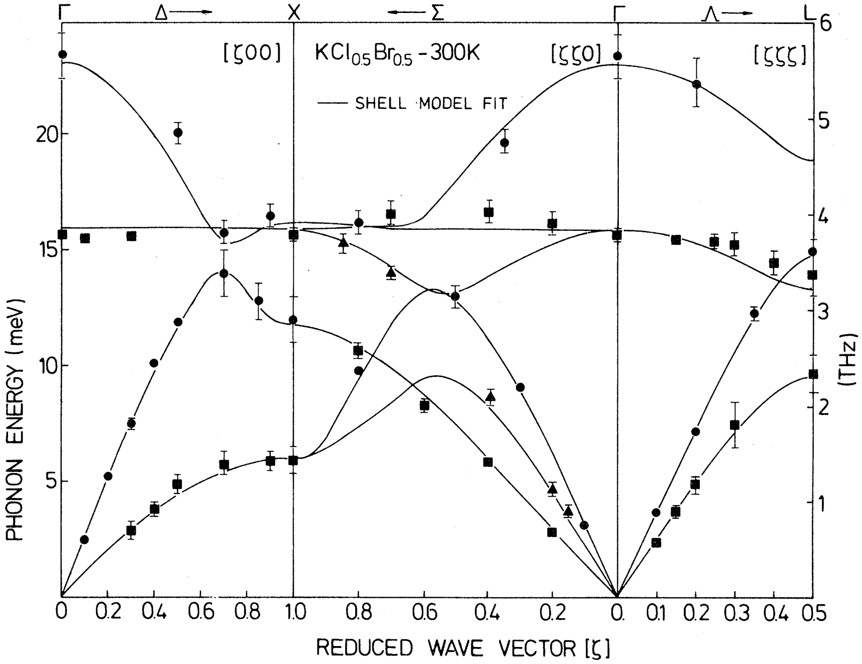

FIG. 5. Phonon dispersion relations in $KCl_{0.5}Br_{0.5}$ at room temperature. The solid lines represent an eleven-parameter shell-model fit.

broad or have two maxima. The phonons in $KCl_{0.5}Br_{0.5}$ also show a similar behavior. In earlier works on $K_{0.5}Rb_{0.5}I$,[7,31] all the optical phonons were also found to be split. In Fig. 7 the [ζ00] TO phonons measured by inelastic neutron scattering are plotted for the above-mentioned three materials. The neutron scattering data show double optical phonons for all the three samples, the only difference being the amount of split for the three samples.

In infrared works at the zone center two TO phonons are observed for $K_{0.5}Rb_{0.5}I$ while one

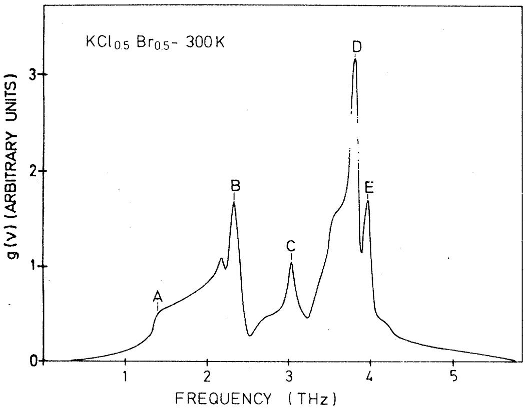

FIG. 6. Phonon density of state for $KCl_{0.5}Br_{0.5}$, calculated using the shell-model parameters at room temperature. Peaks *A*, *B*, and *C* correspond to TA⟨ζ00⟩, TA⟨ζζζ⟩, and LA⟨ζ00⟩ zone boundaries. Peak *D* corresponds to the TO(Γ) and the related branches.

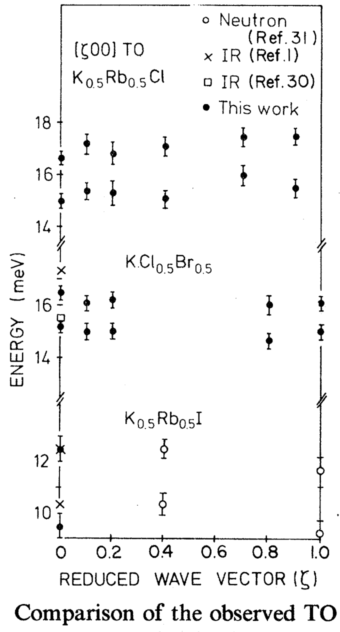

FIG. 7. Comparison of the observed TO⟨ζ00⟩ branch by neutron scattering in three samples $K_{0.5}Rb_{0.5}I$ (Ref. 7), $K_{0.5}Rb_{0.5}Cl$, and $KCl_{0.5}Br_{0.5}$ (present work). The infrared data of Fertel and Perry (Ref. 1) *X* and Mitsuishi (Ref. 30) □ are also given for comparison.

phonon is observed for $KCl_{0.5}Br_{0.5}$.[1,30] Chang and Mitra[13] have used the modified random-element isodisplacement (MREI) model to explain the ir results. They have classified the mixed materials into two groups, according to which $K_{0.5}Rb_{0.5}I$ is classified as the "two-mode" material and $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ as "one-mode" materials. Later on Genzel *et al.*[14] incorporating the local electrical field in the REI model predicated two phonons each for TO and LO branches at the zone center for such mixed materials. In an earlier work Mitsuishi,[30,13] on the basis of a linear-chain model, also predicted two phonons for $KCl_{0.5}Br_{0.5}$ and $K_{0.5}Rb_{0.5}Cl$, one lying between the interval of frequencies of the two pure components and the other outside it. The former had intensity for ir about 1 order of magnitude higher than the latter. The values of the in between modes agreed with the experimental results but the other mode was not observed experimentally in ir works.[13] However, the Raman spectra[4] from $K_{0.5}Rb_{0.5}Cl$ showed that all the observed phonons were broader than 20 $cm^{-1}$ (2.5 meV).

The neutron scattering experiments, which are not inhibited by the optical scattering factors, depending on effective ionic charges, show that all the mixed alkali halides so far studied have similar phonons. Owing to the mass disorder, the lattice vibrations do not have unique frequencies. The phonons have generally two maxima which disperse together. For the acoustic modes the splitting is negligible near the zone center but increases with the increase in the momentum vector (i.e., for vibrations with shorter wavelength) for which the mass disorder is obviously more prominent.

According to Genzel *et al.*[14] the second phonon will have a positive oscillator strength for ir only if the frequency difference in the two longitudinal phonons is large and the lower longitudinal phonon lies in between the two transverse-optic phonons. Taylor[32] has evaluated the ir-active phonon frequencies for $K_xRb_{1-x}I$ and $KCl_xBr_{1-x}$ systems employing the coherent-potential approximation (CPA). For both the samples for $x=9.5$ and $q=0$, two TO and two LO modes are predicted. For $K_{0.5}Rb_{0.5}I$ the energy difference in the respective modes is large and both the modes are ir active, whereas for $KCl_{0.5}Br_{0.5}$ the energy difference is small and only one of the modes has strong ir reflectivity. The two calculated TO phonon energies for $KCl_{0.5}Br_{0.5}$ are around 16.6 and 14.4 meV with a mean energy of 15.5 meV. The values are in good agreement with the present work. The TO phonon observed[1] by ir may be said to correspond nearly to the higher TO phonon energy observed (Fig. 7). Taylor[32] has not included the force-constant changes in his calculations, which are necessary to get the good quantitative value for the split and the energies of the phonons.

## V. SUMMARY

Inelastic neutron scattering measurements on $K_{0.5}Rb_{0.5}Cl$ and $KCl_{0.5}Br_{0.5}$ have been made. No difference has been observed in phonons measured on these materials and $K_{0.5}Rb_{0.5}I$ measured earlier. All these mixed materials show split and broad phonons. The observed differences in these materials in ir may be owing to the optical structure factor for various phonons. The present work also clarifies ambiguities in the assignment of some of the phonons measured by optical techniques.

The shell-model fit to the observed dispersion relations for mixed alkali halides show changes in force constants as compared to the mean of the end members. The elastic constants $C_{11}$ and $C_{44}$ assume a mean value between the end members, whereas the ratio $C_{12}/C_{44}$ is higher than that for the pure crystals. The lattice parameter rigorously follows the concentration weighted mean value.

## ACKNOWLEDGMENTS

One of the authors (M.M.B.) would like to thank the Institute of Applied Nuclear Physics I, Kernforschungszentrum Karlsruhe, W. Germany, for its hospitality and provision of the experimental facilities, without which this work would not have been possible. He would also like to thank the Deutscher Akademischer Austausch-Dienst fellowship for financial support for the visit. Thanks are also due to Dr. W. Reichardt and Dr. L. Pintschovius for help and useful discussions.

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