

Pressure Dependence of Infrared Eigenfrequencies of KI, RbI, and Their Mixed Crystals*

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The pressure dependence of the long-wavelength transverse-optic-phonon frequency of KI and RbI was determined by infrared transmission measurements. The mode Grüneisen parameters thus obtained compared well with those calculated from a rigid ion model using Born-Mayer-type potentials. The phase transition to CsCl structure at appropriate pressures was noted for both crystals, accompanied by a lowering of the $\vec{k} \approx 0$ TO phonon frequency. Infrared transmission measurement and its pressure dependence confirms that the mixed-crystal system $K_{1-x}Rb_xI$ forms an intermediate class of mixed-crystal system "half-way" between the "two-mode"- and "one-mode"-type mixed crystals.

INTRODUCTION

Pressure-induced frequency shifts of long-wavelength optic phonons of ionic and partially ionic crystals were first measured¹ by the far-infrared technique for LiF, NaF, and ZnS. Similar measurements have also been made^{2,3} for KCl, KBr, and CsBr. Subsequently, the effect of pressure on the $\vec{k} \approx 0$, where \vec{k} is the phonon wave vector, longitudinal-optic (LO) and transverse-optic (TO) phonons of diamond and a number of zinc blende and wurtzite-type crystals were studied⁴ by Raman-scattering measurements. It was also pointed out that a correlation seems to exist between the effective ionic charge of a crystal and the LO and TO mode Grüneisen parameter, γ_i , defined as

$$\gamma_i(\vec{k}) = - \frac{d \ln \omega_i(\vec{k})}{d \ln V}, \quad (1)$$

where $\omega_i(\vec{k})$ represents the phonon frequency belonging to a branch i and a wave vector \vec{k} and V is the crystal volume.

The experimental data on the pressure dependence of the long-wavelength optic phonons along with the pressure derivatives of elastic constants may be used to calculate the lattice dynamics of crystals as functions of volume. Such calculations have now been performed⁵⁻⁷ for CsCl, CsBr, CsI, LiF, NaF, KCl, KBr, and ZnTe. The resulting dispersion curves for $\gamma_i(\vec{k})$ have been used to obtain the Grüneisen constant and the coefficient of thermal expansion. Remarkable agreement has been achieved between calculated and experimental values of the thermal-expansion coefficient.

In this paper we report the effect of pressure on the long-wavelength TO phonon frequency of two more alkali halide crystals, viz., KI and RbI. Nearly hydrostatic pressure was applied by containing the crystals in an opposed anvil diamond cell, and the phonon frequency measured by infrared transmission. In addition to measuring the pressure-induced phonon frequency shift, a phase transition in both the crystals from NaCl to CsCl structure at the appropriate pressures was also observed. The $\vec{k} \approx 0$ TO phonon frequency of KI (II) and RbI (II) are reported for the first time.

We have also measured the infrared transmission spectrum of $K_{1-x}Rb_xI$ under pressure. The effect of pressure has been reported^{8,9} so far only on three mixed-crystal systems, viz., $KCl_{1-x}Br_x$, $ZnS_{1-x}Se_x$, and $CdS_{1-x}Se_x$. While the former forms a so-called "one-mode"-type mixed crystal, the latter two form "two-mode"-type mixed-crystal systems. Since $K_{1-x}Rb_xI$ appears to be the only mixed alkali halide system that displays¹⁰ a two-mode-type behavior, it was felt that a study of the effect of pressure on such a system would be interesting.

EXPERIMENTAL

The mixtures were prepared from the pure end members KI and RbI by weighing appropriate amounts of each, and heating to melting in a muffle furnace at a temperature of $\sim 750^\circ\text{C}$. The mixtures were cooled, desiccated, and when loaded for the spectral measurements, all sampling was done in a glove box flushed with dry nitrogen. The compositions were checked by analysis for halogen. X-ray diffraction patterns confirmed that the fused materials were a solid solution displaying a unique lattice constant that varied with mole fraction according to Vegard's law.

The infrared measurements were made using a

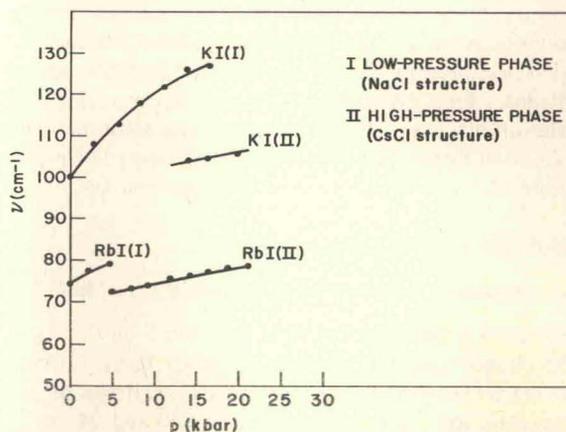


FIG. 1. Long-wavelength transverse-optic phonon frequency of KI and RbI as functions of pressure. Results for both the low-pressure phase (NaCl structure) and the high-pressure phase (CsCl structure) are shown.

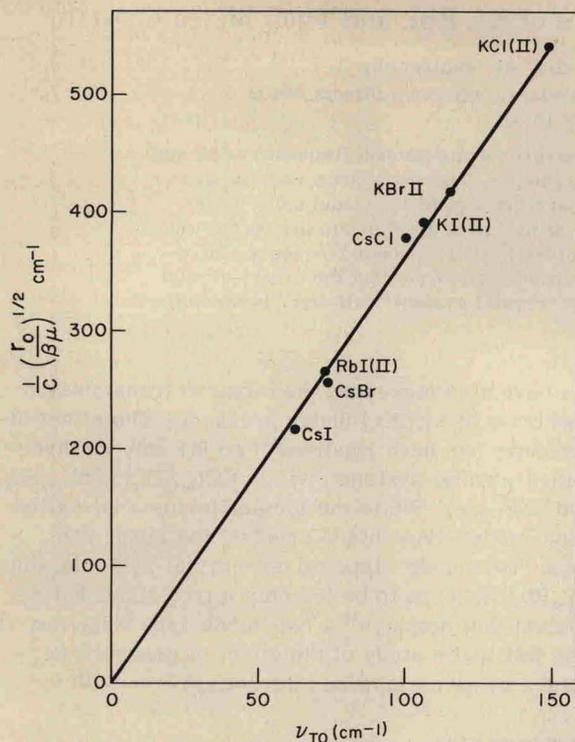


FIG. 2. A plot of long-wavelength TO mode frequency vs $(1/c)(r_0/\mu\beta)^{1/2}$ for CsCl-type crystals.

diamond-anvil high-pressure cell and a Perkin-Elmer Model 301 Far Infrared Spectrophotometer with a $6\times$ beam condenser. The method and apparatus have been previously described.^{3,11}

The powdered samples were placed between the diamond windows of the high-pressure cell. Pressure was alternately increased and decreased until the distribution of the solid appeared uniform across the face of the diamonds, as determined with a microscope. Sample thicknesses used were $1\ \mu\text{m}$ or less. Sample cross sections, depending on the diamond windows used, varied between 300 and $500\ \mu\text{m}$ in diameter. The spectral measurements were made at highest pressures (about 20 kbar) first and then gradually diminished to ambient conditions. This procedure minimized any sample extrusion effects. The pressure-calibration procedure has been described in detail, previously.² Pressures quoted in this paper are average pressures.

RESULTS AND DISCUSSION

Long-Wavelength Transverse-Optic Phonons of KI and RbI

Figure 1 shows the effect of pressure on the $\vec{k} \approx 0$ TO phonon frequency of KI and RbI. The STP values of TO frequency for KI and RbI crystallites measured by the present method are 100 and $74\ \text{cm}^{-1}$, respectively; and they compare well with literature values.¹² As expected, the TO phonon frequencies shifted upward as functions of pressure until the onset of phase transition from the NaCl to the CsCl structure. For RbI this transition is fairly sharp and

occurs at 4.5 kbar. On the other hand, for KI both phases appear to coexist between average pressures of 12–16.5 kbar, and are attributable to the presence of pressure gradients along the face of the diamond windows. These transition pressures are comparable to those measured by Brodman. At the transition pressure, the frequency drops abruptly, as was also the case² with KCl and KBr. Since the near-neighbor central-force constant can be shown to vary as M^{-1} , where M is the coordination number, eigenfrequency is expected to vary approximately as $M^{-1/2}$. Because of the higher coordination number of the CsCl structure the vibrational frequency is expected to decrease at the transition to CsCl structure, as shown in Fig. 1.

Mitra and Marshall¹³ have shown that the long-wavelength TO phonon frequency of the NaCl-type crystals is proportional to $(r_0/\mu\beta)^{1/2}$, where μ is the reduced mass per unit cell, r_0 is the equilibrium near-neighbor distance, and β is the isothermal compressibility. A similar relation seems appropriate also for alkali halides of CsCl structure. In Fig. 2 is plotted ν_{TO} vs $(1/c)(r_0/\mu\beta)^{1/2}$ for the CsCl structure which also includes data on the high-pressure phase of KCl, KBr, KI, and RbI (c is the velocity of light). For the K and Rb salts, values of r_0 and β at the transition pressure¹⁴ are used. Indeed, a straight line passing through the origin is obtained.

The mode Grüneisen parameters for the long-wavelength TO phonons of KI and RbI were obtained from the initial slopes of ν_{TO} -vs- P curves of Fig. 1, using Eq. (1) in the form

$$\nu_{TO} = \frac{1}{\beta\nu_{TO}} \left(\frac{\partial \nu_{TO}}{\partial p} \right)_T \quad (2)$$

When the zero-pressure slopes for the ν_{TO} vs pressure of KCl and KBr are used, slightly different values of γ_{TO} are obtained than those reported earlier.² In Table I, the experimental values of γ_{TO} are presented for all the alkali halides measured

TABLE I. Szigei effective ionic charge and the Grüneisen parameter for a number of alkali halide crystals.

Crystal	Szigei effective charge (e^*/e) ^a	γ_{TO} (expt) ^b	γ_{TO} [Eq. (4)] ^c	γ_{TO} [Eq. (5)] ^d
LiF	0.87	2.6	2.44	3.46
NaF	0.93	3.0	2.43	3.00
KCl	0.81	2.9	2.52	2.92
KBr	0.76	2.6	2.52	2.95
KI	0.71	3.1	2.55	3.05
RbI	0.75	2.5	2.59	3.10
CsBr	0.78	2.7	3.20	3.60

^a Reference 12, p. 413.

^b γ_{TO} for KI and RbI are from this study. Other values are collected from Refs. 1–3.

^c Values of the potential constant σ are from M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., New York, 1954), p. 26.

^d Values of the potential constant n are from F. Seitz, *Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 80.

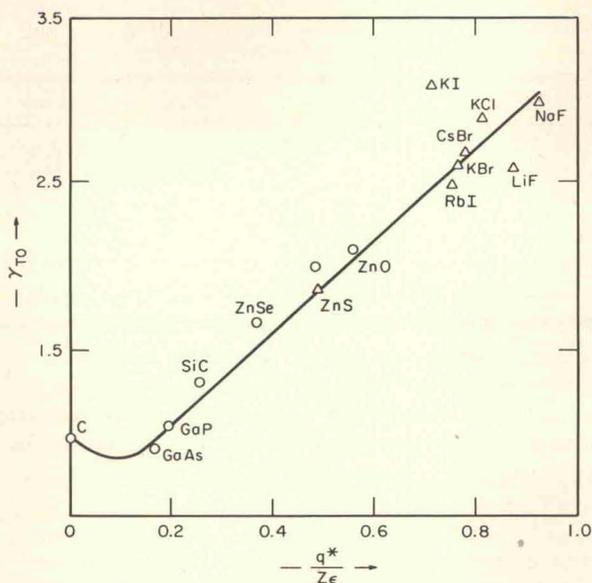


FIG. 3. Transverse-optic mode-Grüneisen parameter at $\vec{k} \approx 0$ vs the effective charge per electron for a number of diatomic crystals. Circles represent Raman and triangles infrared measurements. Sources of data are as follows: KI, RbI, present study; GaAs, unpublished; rest from Refs. 1-4.

so far. These values are then compared with those calculated from a rigid ion model using a Born-Mayer potential of the form

$$u = (\alpha e^2/r) + be^{-r/\rho}. \quad (3)$$

γ_{TO} in this model is given by¹⁵

$$\gamma_{TO} = \frac{(\alpha/6)(\sigma^2 - 2\sigma - 2) - 2\pi/C}{\alpha(\sigma - 2) - 4\pi/C}, \quad (4)$$

where $\sigma = r_0/\rho$, r_0 being the nearest-neighbor distance, α the Madelung constant, and C a structure-dependent packing factor given by $v = Cv_0^3$, where v is the unit cell volume. For the NaCl structure $C = 2$ and for the CsCl structure $C = 8/3\sqrt{3}$. If one uses an inverse-power-type repulsive potential of the form b'/r^n instead of the exponential repulsive term in (3), the corresponding γ_{TO} becomes

$$\gamma_{TO} = \frac{(\alpha/6)(n-1)(n-2) - 2\pi/C}{\alpha(n-1) - 4\pi/C}. \quad (5)$$

The experimental values of γ_{TO} of alkali halides and those calculated from Eqs. (4) and (5) are presented in Table I. Considering the approximations involved, viz., (i) neglecting the polarizability and (ii) assuming that the ionic character of the crystal does not change with pressure, the rigid ion model seems to predict the γ_{TO} values of alkali halides rather well, although it appears that the use of an inverse-power-type repulsive energy has a tendency to overestimate.

An examination of Table I will reveal that the experimental data on γ_{TO} vary from 2.5 (RbI) to 3.0 (NaF), and show a definite dependence on the Szegiet effective ionic charge per electron (Z^*), which varies from 0.75 (RbI) to 0.93 (NaF). The only ex-

ception appears to be KI, an explanation for which is not readily available. A correlation between γ_{TO} and Z^* was noted earlier.^{1,4} In Fig. 3 we present such a plot for all available experimental data on diatomic crystals. It is evident that the ionic crystals like the alkali halides have the highest γ_{TO} as expected. However, what is surprising is that some III-V compounds may have a γ_{TO} value lower than that of a covalent crystallike diamond. An explanation for this may be sought in terms of two factors: (i) While $d|Z^*|/dP$ for the alkali halides and the II-VI compounds is negative and zero for group-IV elements, indications¹⁶ are that they are positive for some of the III-V compounds. (ii) The pressure derivative of the "bending"-force constant of some III-V compounds may be comparable and of opposite sign when compared to that of the "stretching"-force constant.¹⁷ A further discussion on this will be reported elsewhere and will not be further elaborated here.

Pressure Dependence of the Transverse-Optic Phonons of the Mixed-Crystal System $K_{1-x}Rb_xI$

As far as the behavior of the long-wavelength optic phonons is concerned, there seem to exist two types of mixed crystals. In one class of mixed systems, termed the one-mode behavior type, each of the $\vec{k} \approx 0$ optic mode frequencies (infrared or Raman active) varies continuously and approximately linearly with concentration from the frequency characteristic of one end member to that of the other end member. Furthermore, the strength of the mode remains approximately constant. Mixed-crystal systems that are known to display this type of behavior are $Na_{1-x}K_xCl$, $KCl_{1-x}Br_x$, $K_{1-x}Rb_xCl$, $(Ca, Ba)_{1-x}Sr_xF_2$, $Ni_{1-x}Co_xO$, $GaAs_{1-x}Sb_x$, $Zn_{1-x}Cd_xS$, etc. On the other hand, in the other class of mixed crystals known as the two-mode behavior type, two phonon frequencies for each of the optic modes of the pure crystal are observed to occur at frequencies close to those of the end members. Moreover, the strength of each phonon mode of the mixed crystal is approximately proportional to the mole fraction of the component it represents. Examples are Si_xGe_{1-x} , $InP_{1-x}As_x$, $GaP_{1-x}As_x$, $CdS_{1-x}Se_x$, $ZnS_{1-x}Se_x$, etc. The crystals belonging to either class are true mixed crystals in the x-ray crystallographic sense, i.e., they display a structure identical with that of the end members with a lattice constant (or lattice constants in case of non-cubic structures) that is approximately linear with concentration.

So far only one alkali halide mixed-crystal system,

TABLE II. Optical-phonon frequencies in mixed crystals of $K_{1-x}Rb_xI$ at ambient conditions (cm^{-1}).

Mole fraction (x)	0	0.08	0.39	0.50	0.80	0.92	1.0
	100(s)	100(s)	96(s)	90(s)	80(s)	78(s)	74(s)
		(?)	(?)	77(m)	99(sh)	101(sh)	

TABLE III. Optical-phonon frequencies (cm^{-1}) as a function of pressure in mixed crystals $\text{K}_{1-x}\text{Rb}_x\text{I}$. (x is the mole fraction and p the pressure in kbar) (I=low-pressure phase; II=high-pressure phase).

$x \backslash p$	0.001	2.7	5.5	8.2	11.3	14.2	14.8	16.7	19.5	Phase
0.92	100	104	115	122	122.5	I
				103.5	104.5	...	105.5	II
0.61	96	101	107	113	116	I
				95.5	96	97	...	100	102	II
0.20	80	80.5	81.5	82	I and II
0.08	78	79.5	79	80	81	84	87	I and II

viz., $\text{K}_{1-x}\text{Rb}_x\text{I}$, has been reported¹⁰ to have displayed a two-mode behavior. Table II records the results at ambient conditions for this system. The present result agrees with that of Fertel and Perry.¹⁰ The mixed crystals also showed phase transitions at higher pressures. For mixtures rich in KI both phases could be followed with pressure. In mixtures rich in RbI, only one phase could be followed, and since the peak indicates an apparent broadening only one absorption feature was followed with pressure. Table III shows the pressure dependencies of the various mixtures of $\text{K}_{1-x}\text{Rb}_x\text{I}$, and Fig. 4 shows the results graphically for the low- and high-pressure phases.

Lucovsky *et al.*¹⁸ have pointed out that the conditions necessary for the existence of localized and gap modes in mixed crystals are fulfilled for two-mode

systems and are not for the one-mode systems. Chang and Mitra¹⁹ have derived a simple criterion for the prediction of one- or two-mode-type behavior of a mixed crystal. The criterion is that the inequality

$$m_B < \mu_{AC}, \quad (6)$$

for a mixed crystal $\text{AB}_{1-x}\text{C}_x$ is obeyed by a two-mode system, whereas it is not obeyed by a one-mode system. All the examples cited above except for $\text{K}_{1-x}\text{Rb}_x\text{I}$ follow both Lucovsky *et al.* and Chang and Mitra criteria. The latter criterion also predicts a two-mode behavior for $\text{K}_{1-x}\text{Rb}_x\text{I}$. However, the application of the criterion proposed by Lucovsky *et al.* to this system is somewhat ambiguous. Whereas KI has a gap between the optic- and acoustic-phonon bands, and Rb impurities in KI indeed produce a gap mode,²⁰ it appears that K impurity in RbI may not produce a localized mode above the optic band of the host lattice. Brodsky *et al.*²¹ have subsequently proposed an intermediate class of mixed crystal, which at the limits of infinite dilution, either displays a local mode or a gap mode but not both. On a closer scrutiny of Fertel and Perry's¹⁰ ambient pressure data on this crystal system, it appears that it indeed may be a weak two-mode system and may conveniently be classed in an intermediate system.

The Chang and Mitra¹⁹ criterion is based on the relative masses of the constituent atoms and neglects the interacting force constants. If these were included, it is possible to reinterpret Fertel and Perry's results as a so-called intermediate case between one-mode-type and two-mode-type systems. We have applied the MREI model of Chang and Mitra to the present data and to that of Fertel and Perry,¹⁰ as shown in Fig. 5. Best results consistent with the idea of an intermediate type for $\text{K}_{1-x}\text{Rb}_x\text{I}$ are obtained by assuming that the local mode due to K in RbI is not distinct and its frequency is coincident or slightly smaller than that of the long-wavelength LO mode frequency of RbI. An inspection of Fig. 5 reveals that as far as the top LO branch is concerned the system acts like a one-mode system. Whereas for the other branches it is reminiscent of a two-mode system.

The results are thus indicative that, at best, $\text{K}_{1-x}\text{Rb}_x\text{I}$ is a borderline two-mode system even at ambient conditions. With increasing pressure which

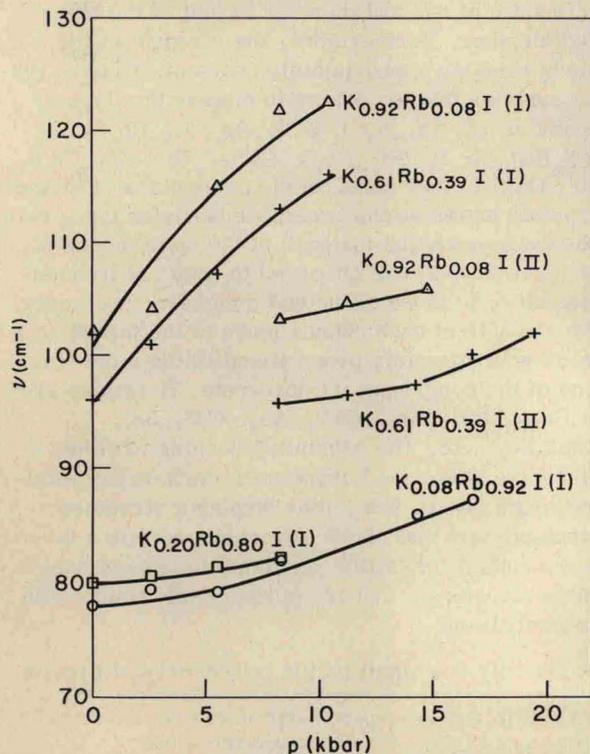


FIG. 4. Pressure dependence of the TO mode frequency in $\text{K}_{1-x}\text{Rb}_x\text{I}$ for four values of x . Phase transitions for $x=0.08$ and $x=0.39$ are shown. Δ : $\text{K}_{0.92}\text{Rb}_{0.08}\text{I}$; $+$: $\text{K}_{0.61}\text{Rb}_{0.39}\text{I}$; \square : $\text{K}_{0.20}\text{Rb}_{0.80}\text{I}$; \circ : $\text{K}_{0.08}\text{Rb}_{0.92}\text{I}$. (I=low-pressure phase; II=high-pressure phase).

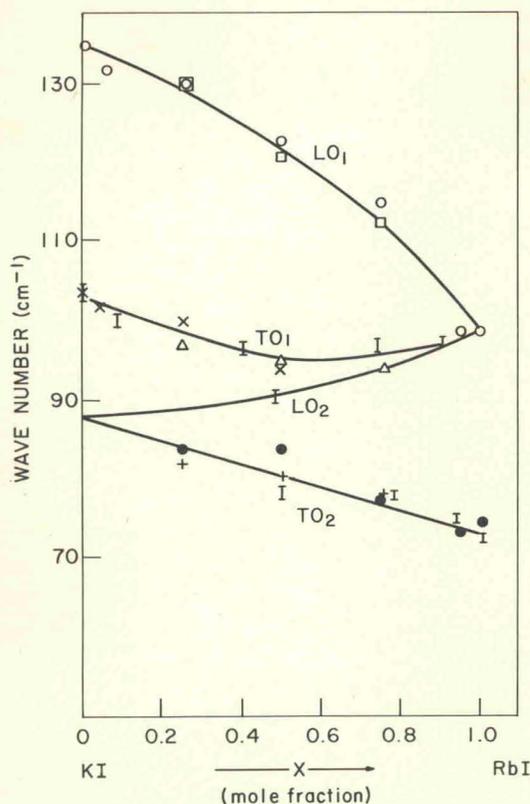


FIG. 5. Variation of long-wavelength LO and TO phonon frequencies of $K_{1-x}Rb_xI$ at STP with composition. Sources of experimental data are LO frequencies from Ref. 10 [\circ (reflection), \square (thin film)] and TO frequencies from Ref. 10 [$+$, \bullet (reflection) and Δ , \times (thin film)]; I [present study (Table II)]. Lines are expected results of MREI model (Ref. 19) assuming that the local-mode frequency is coincident with the LO frequency of RbI (103 cm^{-1}).

changes the force constants, affecting KI and RbI slightly differently, the system probably even becomes entirely a one-mode system. The present experimental data support this view. However, this conclusion may not entirely be true because of the ambiguity in the spectrum arising from the presence of bands corresponding to the high-pressure phase (CsCl structure) as well as the system. It is also not known whether the transition pressure is a linear function of composition for the mixed crystal.

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