

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

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(Received 8 January 1971)

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

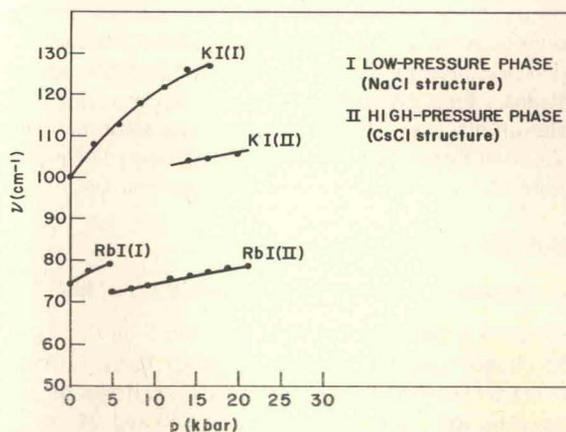


FIG. 1. Long-wavelength transverse-optic phonon frequency of KI and RbI as functions of pressure. Results for both the low-pressure phase (NaCl structure) and the high-pressure phase (CsCl structure) are shown.

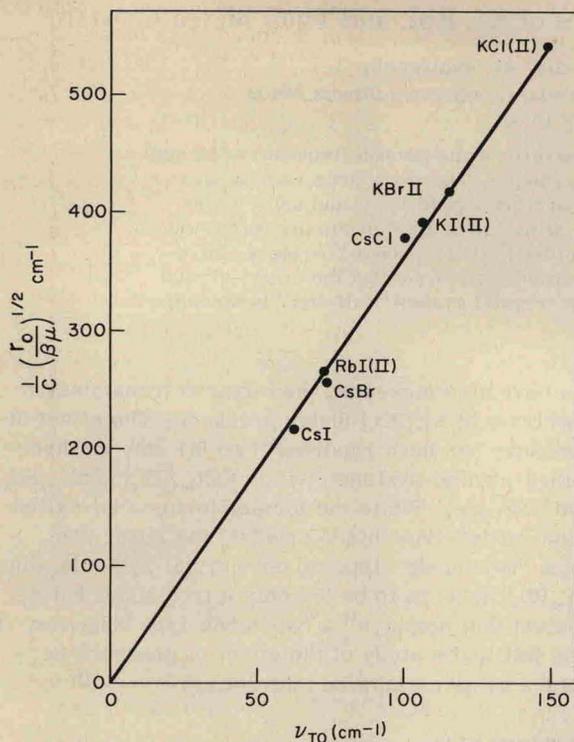


FIG. 2. A plot of long-wavelength TO mode frequency vs $(1/c)(r_0/\mu\beta)^{1/2}$ for CsCl-type crystals.

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.