Fig. 3. Comparison of methods 1 and 2 in determining the TO and LO modes of $KCl_{1-x}Br_x$ as a function of mole fraction at 1 atm.

Behavior of the Mixed Crystal System at Ambient Pressure and Temperature

It has been remarked earlier that the $KCl_{1-x}Br_x$ crystals display a one-mode type of behavior, in which each of the long wavelength optic mode frequencies varies continuously and approximately linearly with concentration from the frequency characteristic of one end member to that of the other end member, and the strength of the mode remains approximately constant. The present results on $KCl_{1-x}Br_x$ confirm that this system displays a one-mode type behavior, which is predicted according to the Chang and Mitra criterion.[7]

The long wavelength LO and TO modes of a crystal are related by the so-called Lyddane-Sachs-Teller relation:[10]

$$\nu_{LO}/\nu_{TO} = (\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}, \qquad (1)$$

where ϵ_0 and ϵ_∞ are the low and high frequency dielectric constants, respectively. This formula may also be used to obtain the $\mathbf{k} \sim 0$ LO frequencies of one-mode type mixed crystals. For many mixed crystal systems the dielectric constant (ϵ_0) is known[11] to vary approximately linearly with concentration, the same variation expected for the high frequency dielectric constant (ϵ_∞). The values of ϵ_0 and ϵ_∞ are, respectively, 4.85 and 2.1 for KCl and 4.90 and 2.3 for KBr. Assuming

$$\epsilon_i(KCl_{1-x}Br_x) = (1 - x)\epsilon_i(KCl) + x\epsilon_i(KBr),$$

where ϵ_i stands for either ϵ_0 or ϵ_∞, the LO frequencies for the system were determined using Eq. (1). Such data for 1 atm are shown in Fig. 3. The LO frequencies at higher pressures could not be obtained because the

dielectric constants are not known as functions of pressure. Both LO and TO frequencies essentially vary linearly with x.

A number of attempts have been made in the past to account for the concentration dependence of the mode frequencies of a mixed crystal. Matossi[12] considered a linear diatomic chain model that considers only nearest-neighbor force constants to discuss the one-mode behavior of $Na_{1-x}K_xCl$. This model is idealized with a periodic regular distribution of A ions and B ions in $A_{1-x}B_xC$, whereas the true distribution is believed to be random. This treatment dealt with the 50–50 mixed case only. The calculations for $Na_{1-x}K_xCl$ yield two ir active modes: one lies in between the interval of frequencies of the two pure components NaCl and KCl; the other one lies outside. Mitsuishi[8] has used this model and calculated the two frequencies for $KCl_{0.5}Br_{0.5}$ and $K_{0.5}Rb_{0.5}Cl$. The values of the in-between modes agree with the experimental results. However, the weaker mode outside of the interval predicted by this model is yet to be experimentally observed for any crystal.

Chang and Mitra[7] have recently developed a so-called pseudo unit cell model for mixed crystals of either type. In essence the model assumes a complete randomization in which all unit cells of a mixed crystal are identical. For a mixed crystal of AB and AC mixed in the ratio of $(1 - x)$ and x, the pseudo unit cell still contains two particles, maintains its symmetry, and has a unique dimension consistent with the single lattice constant of appropriate value in the case of a mixed crystal made of two cubic crystals. A pseudo unit cell thus contains one atom of A and one atom of $(1 - x)$ B + xC. This model of a mixed crystal is essentially similar to the random-element-isodisplacement model proposed by Chen et al.[13] The model assumes that the cations as well as the anions of like species vibrate as rigid units, i.e., each unit vibrates with one phase and amplitude. This assumption of isodisplacement is strictly true for the reststrahlen frequency in an ordered diatomic crystal, since there is no phase shift from unit cell to unit cell for $\mathbf{k} \sim 0$ modes. The model, thus in essence, considers the vibration of pseudo unit cell containing one unit of $AB_{1-x}C_x$. X-ray diffraction measurements on mixed crystals, whether one-mode or two-mode type, do indeed indicate unique unit cell dimensions throughout the composition range. Each atom, in this model, is subjected to forces produced by a statistical average of its neighbors and no effects of order are actually present. For those cases in which local and/or gap modes are predicted for small impurities of B in AC or C in AB, two-mode behavior for the mixed system is expected. Chang and Mitra obtain a one-mode behavior by assuming the nonexistence of the local and gap modes. This can be achieved in two ways called method 1 and 2, respectively. They are: (1) the triply degenerate local and gap modes of a cubic diatomic system are assumed to split into two modes—a doubly degenerate TO and a nondegenerate LO and finally merge with the like modes of the host lattice; (2) it is assumed that the local and gap modes have vanishing fre-
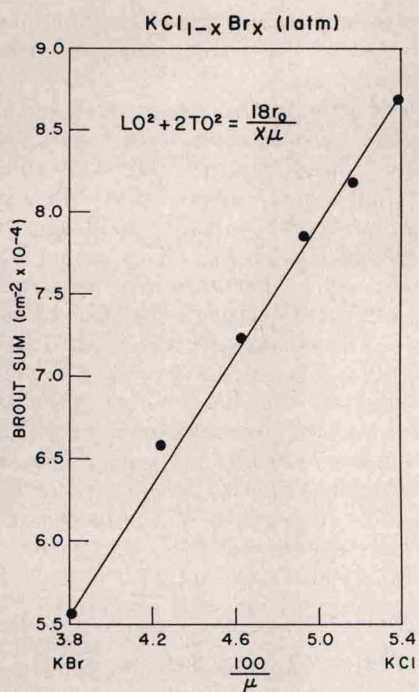
Fig. 4. Plot of the Brout sum vs $100/\mu$ for KCl$_{1-x}$Br$_x$ at 1 atm.

quencies. For the TO frequency the latter method yields

$$\omega_{TO}{}^2 = F\left(\frac{1}{m_A} + \frac{(1-x)}{m_B} + \frac{x}{m_C}\right) = F\left(\frac{1-x}{\mu_{AB}} + \frac{x}{\mu_{AC}}\right),$$

(2)

where F is the force constant, x is the mole fraction, m is the mass, and μ is the reduced mass, which is identical with the results of the well-known virtual crystal model.[14] The force constant F in the above equation varies linearly from its value for AB to that for AC. Experimental data on LO and TO of KCl$_{1-x}$Br$_x$ are compared with the calculations based on both the methods in Fig. 3. As usual, the virtual ion model appear to express the data well.

Based on Coulomb attractive forces and nearest-neighbor repulsive forces Brout[15] has given the sum rule,

$$\sum_{i=1}^{6} \omega_i{}^2(\mathbf{k}) = \frac{18r_0}{\mu\chi},$$

(3)

where $\hbar\omega_i(\mathbf{k})$ is the phonon energy of the ith vibrational branch at wave vector $\mathbf{k}$, r_0 is the nearest-neighbor distance, μ is the reduced mass per Bravais unit cell, and χ is the isothermal compressibility. Mitra and Marshall[16] have shown that the zone center ($\mathbf{k} \sim 0$) Brout sum $\omega_{LO}{}^2 + 2\omega_{TO}{}^2$ varies linearly with $1/\mu$ for a homologous series of closely related compounds like the II-VI or the III-V compounds, where one may assume that the nearest-neighbor force constant is nearly constant. It is of interest to see whether such a relation holds for the mixed crystal system. Expressing the reduced mass of a crystal AB$_{1-x}$C$_x$ as $[(1/m_A) + [(1-x)/m_B] +$

$(x/m_C)]^{-1}$, such a plot was made for the KCl$_{1-x}$Br$_x$ system, which is shown in Fig. 4. Indeed, a linear plot is obtained approximately passing through the origin. Thus, it appears that going from KCl to KBr the nearest-neighbor force constant does not change substantially.

Effect of Pressure

At constant temperature the change of frequency due to change of pressure is only due to a volume change. However, in the mixed crystal system KCl$_{1-x}$Br$_x$ volume also changes due to the mixing process, namely, the lattice constant of KCl changes monotonically to that of KBr with increasing x. If it is assumed that the phonon frequency is primarily a function of volume at constant temperature thus keeping the anharmonic effects unchanged, one may expect to arrive at the same phonon frequency for a certain unit cell volume, irrespective of whether the volume change was achieved by changing pressure or changing the mixing ratio. There is, however, a problem in testing this hypothesis rigorously. Although we have lattice constant measurements at one atm pressure on KCl$_{1-x}$Br$_x$ as a function of x and also the P-V data on the end members, no lattice constant measurement for a mixed crystal at elevated pressures is available. It has been found that for the mixed crystal KCl$_{1-x}$Br$_x$ at the atmospheric pressure, the lattice constant varies approximately linearly with x, a fact which is true for most mixed crystals and is known as the Vegard's law.[17] Assuming that the Vegard's law also holds good at elevated pressures, one may replot the data on Figs. 1 and 2 on a volume scale alone. Such has been done in Fig. 5. Indeed one obtains an approximate straight line on a log–log plot, confirming our original contention that in closely related crystals like KCl and KBr the frequency is primarily a function of volume. Two points are worth noting: (1) Vegard's law was assumed to hold good at elevated pressures for which to date no experi-
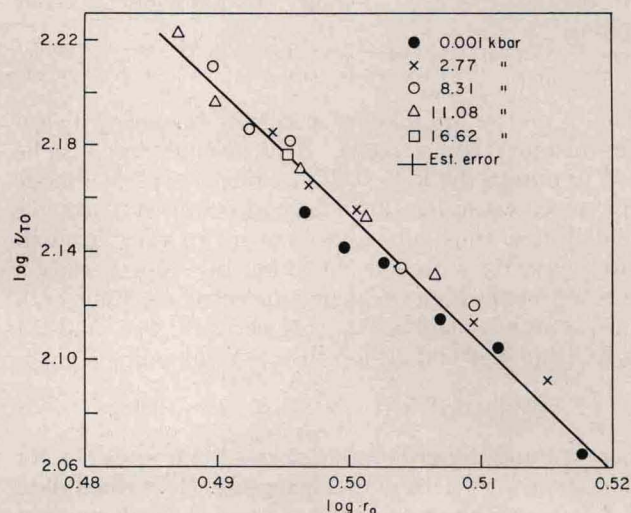

Fig. 5. Plot of ν_{TO} vs log r_0 for KCl$_{1-x}$Br$_x$ at various pressures.