

# Pressure Dependence of the Infrared-Active Phonons in the Mixed Crystal System $\text{KCl}_{1-x}\text{Br}_x$

J. R. Ferraro, C. Postmus, S. S. Mitra, and C. J. Hoskins

The mixed crystal system  $\text{KCl}_{1-x}\text{Br}_x$  shows a one-mode type behavior. The variation of the long-wavelength transverse optical (TO) mode frequency at 1 atm pressure can be understood in terms of the virtual crystal model. The variation of the frequency with pressure or the mole fraction  $x$  can be expressed in terms of volume change alone. The slopes of the  $\nu_{\text{TO}}$  mode vs  $P$  are highest for the end numbers, and are less for intermediate values of  $x$ , and may be understood in terms of a nonlinear variation of the compressibility with  $x$ .

## Introduction

By incorporating<sup>1,2</sup> a high pressure diamond cell<sup>3</sup> with a far ir spectrophotometer it has recently been possible to investigate the effect of pressure on the long wavelength ( $\mathbf{k} \sim 0$ ) optic phonon frequencies of ionic or partially ionic solids. A similar experiment involving the use of a high pressure diamond cell in conjunction with a laser-Raman system has also been accomplished.<sup>4</sup> So far the pressure dependence (up to 40 kbar) of the ir dispersion frequencies of LiF, NaF, KCl, KBr, CsBr, and ZnS has been reported.<sup>2,5,6</sup> In this paper we report the effect of pressure on the lattice vibrations of the mixed crystal system  $\text{KCl}_{1-x}\text{Br}_x$  for a number of compositions. This represents the first experimental study of pressure effects on the  $\mathbf{k} \sim 0$  TO mode of a mixed crystal.

As far as the behavior of the long wavelength optic phonons is concerned, it appears that there exist two types of mixed crystals.<sup>7</sup> In one class of mixed crystals, the "one-mode" behavior type, each of the  $\mathbf{k} \sim 0$  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. Furthermore, the strength of the mode remains approximately constant. In the other class of mixed crystal systems, the "two-mode" behavior type, the two phonon frequencies for each of the allowed optic

modes of the pure crystal are observed to occur at frequencies close to those of the end members. In addition, the strength of each phonon mode of the mixed crystal is approximately proportional to the mole fraction of the component it represents. The  $\text{KCl}_{1-x}\text{Br}_x$  mixed crystal system belongs to the former type.

$\text{KCl}_{1-x}\text{Br}_x$  has previously been investigated by Mitsuishi at STP using thin film deposited on colloidon.<sup>8</sup> There seems to be some doubt about the crystallinity of these films. In certain cases the end member (at  $x = 0$  or  $x = 1$ ) values of the  $\mathbf{k} \sim 0$  TO frequencies do not quite agree with their literature values.<sup>9</sup> In the present paper we present the variation of the TO frequency of  $\text{KCl}_{1-x}\text{Br}_x$  as a function of the mixing ratio. The 298 K, 1 atm pressure data will be discussed in terms of the "pseudo unit cell" or the MREI model developed by Chang and Mitra.<sup>7</sup> Next the effect of pressure on the  $\mathbf{k} \sim 0$  TO phonon frequencies of this system is investigated. The pressure range studied extended from 1 atm to about 17 kbar, just short of the pressure required transition to the CsCl structure.

## Experimental

### A. Mixed Crystal Preparation

The mixed crystals of  $\text{KCl}_{1-x}\text{Br}_x$  were prepared from the pure components KCl and KBr. Mixtures of weighed amounts of each component were fused in a muffle furnace at 810°C for 3-5 min, and quenched quickly. X-ray diffraction patterns were obtained by S. Siegel of ANL, and demonstrated that the fused product was a solid solution. Weighed mixtures were confirmed by analyses of the halogen content for each sample.

The authors are with the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

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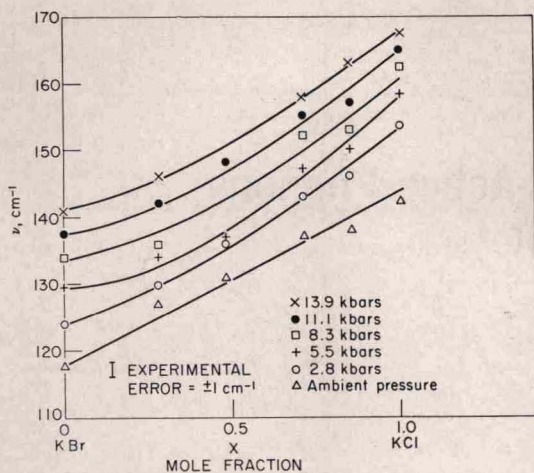


Fig. 1. Variation of the frequency of the TO mode in  $\text{KCl}_{1-x}\text{Br}_x$  system with mole fraction at various pressures.

## B. Instrumentation

Infrared spectra were obtained using a Perkin-Elmer 301 far ir spectrophotometer containing a modified  $6\times$  beam condenser and a high pressure diamond anvil cell. This apparatus has been previously described in the literature.<sup>1,2</sup>

## C. Procedure of Solid Loading

A few milligrams of the powdered sample were placed between the diamond windows of the high pressure cell. Pressure was alternately increased and decreased until the distribution of the sample across the diamond windows appeared uniform, as determined with a microscope. Spectra were obtained at ambient pressure and at intermediate pressures up to  $\sim 17$  kbar, where a phase transition occurred. The pressure was then released and a final spectrum obtained at ambient pressure. Calibration of the pressures obtained has been described previously.<sup>1,2</sup> A pressure gradient existing across the diamond faces, coupled with the sluggishness of the system and friction in the cell, prevented any determination of the half-band width of the  $\mathbf{k} \sim 0$  mode. For these reasons the pressures measured are considered to be only average pressures.

## Results and Discussion

Spectra were recorded at room temperature in the  $100\text{--}200\text{-cm}^{-1}$  region. Pressures covered ranged from  $0.001$  kbar to about  $17$  kbar. For each mixing ratio and at each pressure only one absorption feature was distinctly observable. At any given pressure, the peak position of the absorption band increased in frequency from its value in pure KBr to that in pure KCl as the proportion of KCl increased in the mixed crystal. For a given mixed crystal the peak frequency also went upward as the pressure increased. Data on the peak position of the far ir band in  $\text{KCl}_{1-x}\text{Br}_x$  as a function of  $x$  at

various pressures is shown in Fig. 1. The same data as functions of pressure for various values of  $x$  are plotted in Fig. 2.

Both KCl and KBr belong to the NaCl structure with two particles per Bravais unit cell. The normal modes of a NaCl type crystal are distributed on six branches, three of which are acoustic and three optic. For special directions in the crystal the optic branches can be grouped into transverse and longitudinal types. In ionic crystals the transverse optic (TO) and the longitudinal optic (LO) branches are separated even at  $\mathbf{k} \approx 0$ , where  $\mathbf{k}$  denotes the wave vector. This splitting of the long wavelength optic phonons of ionic crystals into TO and LO types takes place because of the presence of the polarization field due to the motion of charged ions. The characteristic ir absorption in these crystals is mainly associated with the long wavelength TO modes. This is because (1) electromagnetic radiation is transverse in nature; (2) the wave vector of an ir photon ( $\sim 10^3\text{--}10^4\text{ cm}^{-1}$ ) being small compared to the maximum phonon wave vectors ( $\sim 10^8\text{ cm}^{-1}$ ), the former can only interact with phonons of very small (or nearly zero) wave vectors in a one phonon or a first-order process; (3) in ionic crystals large changes in the dipole moment occur during the execution of  $\mathbf{k} \sim 0$  TO modes, which correspond to the vibration of the sublattice composed of the positive ions against that composed of the negative ions.

The absorption feature observed in the present experiments is thus due to long wavelength TO modes. The dependence of the TO mode frequency of  $\text{KCl}_{1-x}\text{Br}_x$  as a function of  $x$  and pressure are given in Figs. 1 and 2. Presently, we shall discuss the data on mixed crystals at STP. Finally, the effect of pressure will be considered.

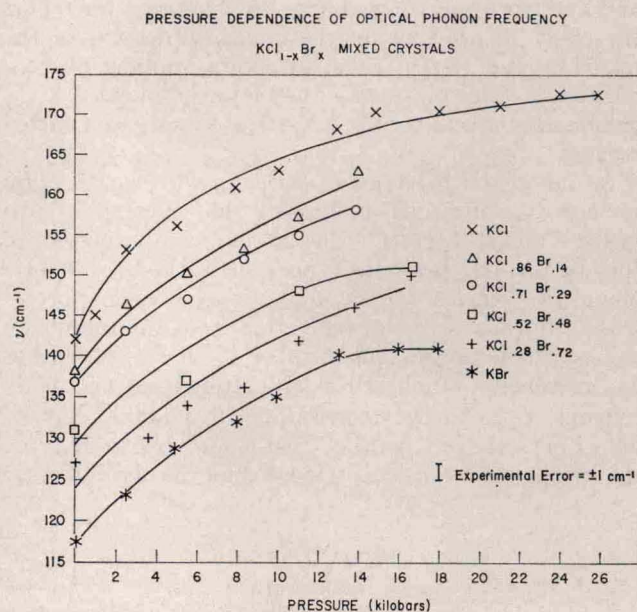


Fig. 2. Pressure dependence of the TO mode in  $\text{KCl}_{1-x}\text{Br}_x$  system.

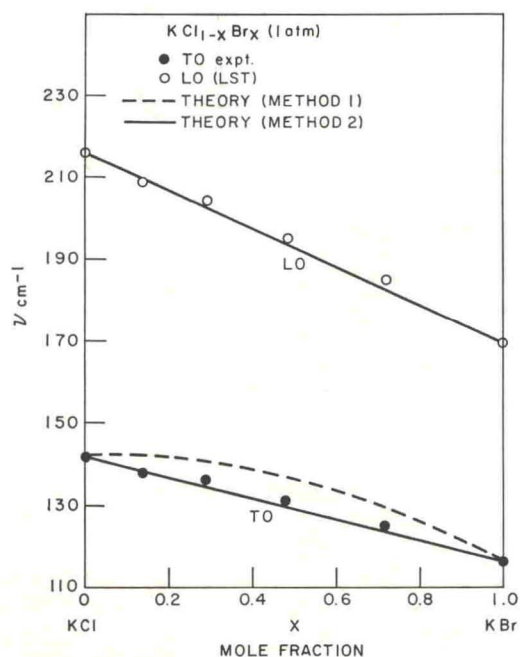


Fig. 3. Comparison of methods 1 and 2 in determining the TO and LO modes of  $\text{KCl}_{1-x}\text{Br}_x$  as a function of mole fraction at 1 atm.

### Behavior of the Mixed Crystal System at Ambient Pressure and Temperature

It has been remarked earlier that the  $\text{KCl}_{1-x}\text{Br}_x$  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  $\text{KCl}_{1-x}\text{Br}_x$  confirm that this system displays a one-mode type behavior, which is predicted according to the Chang and Mitra criterion.<sup>7</sup>

The long wavelength LO and TO modes of a crystal are related by the so-called Lyddane-Sachs-Teller relation:<sup>10</sup>

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

where  $\epsilon_0$  and  $\epsilon_\infty$  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 ( $\epsilon_0$ ) is known<sup>11</sup> to vary approximately linearly with concentration, the same variation expected for the high frequency dielectric constant ( $\epsilon_\infty$ ). The values of  $\epsilon_0$  and  $\epsilon_\infty$  are, respectively, 4.85 and 2.1 for KCl and 4.90 and 2.3 for KBr. Assuming

$$\epsilon_i(\text{KCl}_{1-x}\text{Br}_x) = (1-x)\epsilon_i(\text{KCl}) + x\epsilon_i(\text{KBr}),$$

where  $\epsilon_i$  stands for either  $\epsilon_0$  or  $\epsilon_\infty$ , 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<sup>12</sup> considered a linear diatomic chain model that considers only nearest-neighbor force constants to discuss the one-mode behavior of  $\text{Na}_{1-x}\text{K}_x\text{Cl}$ . This model is idealized with a periodic regular distribution of A ions and B ions in  $\text{A}_{1-x}\text{B}_x\text{C}$ , whereas the true distribution is believed to be random. This treatment dealt with the 50–50 mixed case only. The calculations for  $\text{Na}_{1-x}\text{K}_x\text{Cl}$  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<sup>8</sup> has used this model and calculated the two frequencies for  $\text{KCl}_{0.5}\text{Br}_{0.5}$  and  $\text{K}_{0.5}\text{Rb}_{0.5}\text{Cl}$ . 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<sup>7</sup> 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.*<sup>13</sup> 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  $\text{AB}_{1-x}\text{C}_x$ . 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-

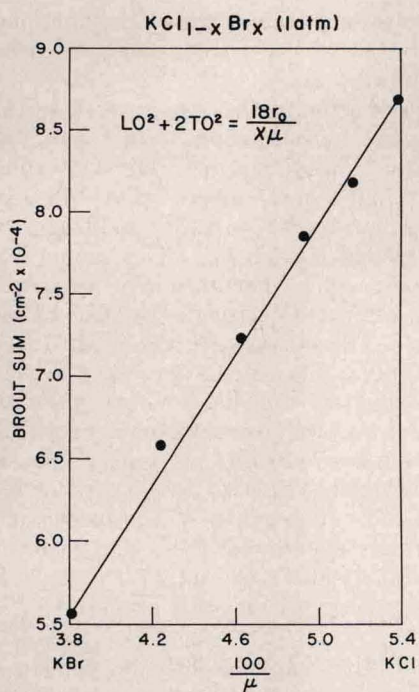


Fig. 4. Plot of the Brout sum vs  $100/\mu$  for  $\text{KCl}_{1-x}\text{Br}_x$  at 1 atm.

quencies. For the TO frequency the latter method yields

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

where  $F$  is the force constant,  $x$  is the mole fraction,  $m$  is the mass, and  $\mu$  is the reduced mass, which is identical with the results of the well-known virtual crystal model.<sup>14</sup> 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  $\text{KCl}_{1-x}\text{Br}_x$  are compared with the calculations based on both the methods in Fig. 3. As usual, the virtual ion model appears to express the data well.

Based on Coulomb attractive forces and nearest-neighbor repulsive forces Brout<sup>15</sup> has given the sum rule,

$$\sum_{i=1}^6 \omega_i^2(\mathbf{k}) = \frac{18r_0}{\mu\chi}, \quad (3)$$

where  $\hbar\omega_i(\mathbf{k})$  is the phonon energy of the  $i$ th vibrational branch at wave vector  $\mathbf{k}$ ,  $r_0$  is the nearest-neighbor distance,  $\mu$  is the reduced mass per Bravais unit cell, and  $\chi$  is the isothermal compressibility. Mitra and Marshall<sup>16</sup> have shown that the zone center ( $\mathbf{k} \sim 0$ ) Brout sum  $\omega_{\text{LO}}^2 + 2\omega_{\text{TO}}^2$  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  $\text{AB}_{1-x}\text{C}_x$  as  $[(1/m_A) + (1-x)/m_B] +$

$(x/m_C)]^{-1}$ , such a plot was made for the  $\text{KCl}_{1-x}\text{Br}_x$  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  $\text{KCl}_{1-x}\text{Br}_x$  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  $\text{KCl}_{1-x}\text{Br}_x$  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  $\text{KCl}_{1-x}\text{Br}_x$  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.<sup>17</sup> 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-

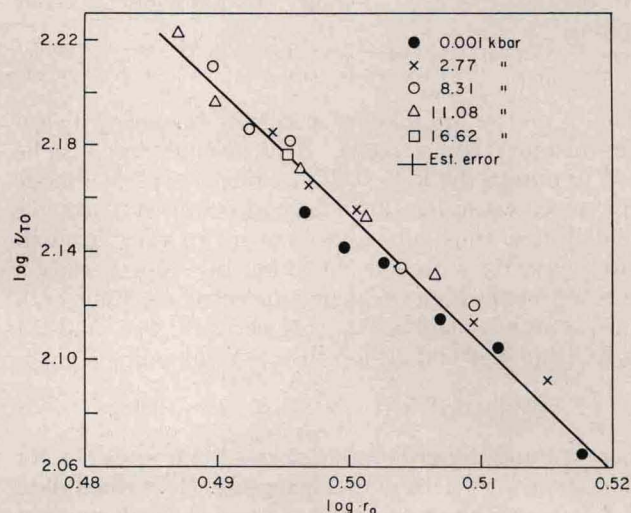


Fig. 5. Plot of  $\nu_{\text{TO}}$  vs  $\log r_0$  for  $\text{KCl}_{1-x}\text{Br}_x$  at various pressures.

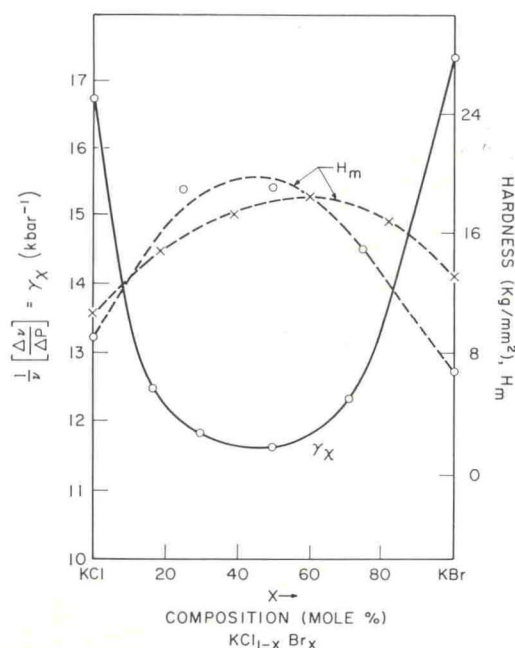


Fig. 6. Plot of  $\Delta\nu/\nu\Delta P$  vs mole fraction for  $\text{KCl}_{1-x}\text{Br}_x$ . For comparison, experimental hardness data<sup>19</sup> after Smakula (solid circles) and Vorobev *et al.* (crosses) are also included.

mental data exist. Since the compressibility of many mixed crystal systems may not be a linear function of the mixing ratio, a point which we shall elaborate upon later, Fig. 5 should only be taken qualitatively; (2) although Fig. 5 establishes that  $\nu_{\text{TO}} \approx \text{const}/V^n$ , not much significance can be attached to the exponent  $n$  of this plot because of the large scatter of points. Furthermore, if at any fixed value of  $x$  one follows the change of  $\nu$  due to change of  $r_0$  (nearest-neighbor distance) one may encounter different slopes than the average slope of the line drawn on Fig. 5.

The pressure dependence of the long wavelength TO frequency may be discussed in terms of a mode Gruneisen parameter defined as

$$\gamma_{\text{TO}} = -d \ln \nu_{\text{TO}} / d \ln V. \quad (4)$$

Since the measurements were done at a constant temperature, this equation may be rewritten as

$$\gamma_{\text{TO}} = \frac{1}{\nu_{\text{TO}}} (\partial \nu_{\text{TO}} / \partial P)_T \quad (5)$$

where  $\chi$  is the isothermal compressibility. Measurements on pure KCl and KBr crystals showed<sup>6</sup> that the experimental values of  $\gamma$  obtained from this relation compared very well with values calculated from a rigid ion model using a Born-Mayer potential.

A plot of  $(1/\nu)(\Delta\nu/\Delta P)$  for the TO mode in the pressure range of 0.001 kbar to 10 kbar is shown in Fig. 6. This curve has a distinct minimum around  $x = 0.5$ . An examination of Eq. (5) reveals that the ordi-

nate of Fig. 6 is proportional to  $\gamma_{\text{TO}}\chi$ . The Gruneisen parameter for the TO mode of most ionic crystals of the NaCl type is known to be around 3. For KCl and KBr,  $\gamma_{\text{TO}}$  is, respectively, 2.9 and 2.6, and appears<sup>18</sup> to depend on the effective ionic charge, which is  $0.81e$  and  $0.76e$ , respectively, for these two crystals. The effective ionic charge for the mixed system is known to vary linearly with composition between these two limits. Thus the nonlinear behavior of  $(1/\nu)(\Delta\nu/\Delta P)$  displayed in Fig. 6 may be understood largely in terms of a nonlinear behavior of  $\chi$ . However, since  $\chi$  and  $\gamma$  are related to the second and third derivative of the cohesive energy with respect to volume, it is entirely possible that both these quantities vary nonlinearly. For comparison, the hardness variation<sup>19</sup> of KCl-KBr system as a function of the mixing ratio is also shown in Fig. 6. It may be noted that hardness, which may be compared<sup>20</sup> to the bulk modulus (reciprocal of compressibility), goes through a maximum in the intermediate mixing range.

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S. S. Mitra of the University of Rhode Island, Department of Electrical Engineering, is a consultant to Argonne National Laboratory. C. J. Hoskins was a CSUI student, September-December 1968.

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