

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

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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 ν_{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^{1,2} a high pressure diamond cell³ 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.⁴ 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.^{2,5,6} 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.⁷ 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.⁸ 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.⁹ 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.⁷ 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.

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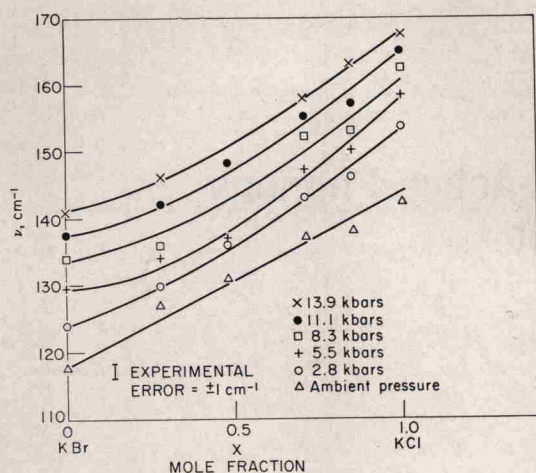


Fig. 1. Variation of the frequency of the TO mode in $\text{KCl}_{1-x}\text{Br}_x$ system with mole fraction at various pressures.

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.^{1,2}

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 ~ 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.^{1,2} 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 sub-lattice 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.

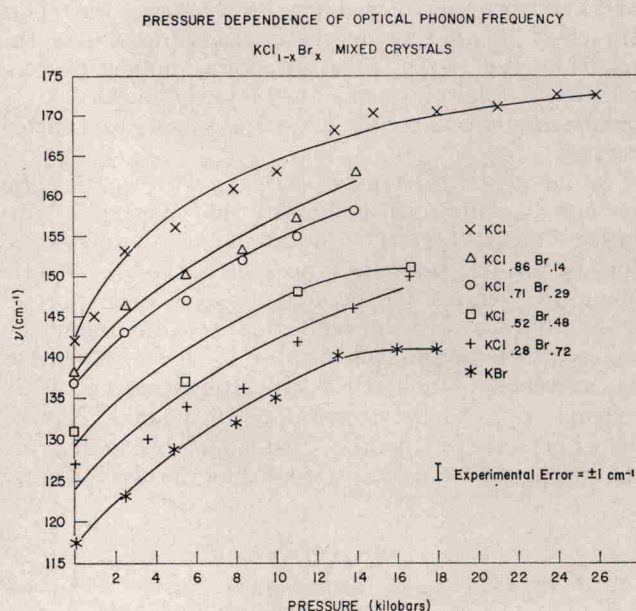


Fig. 2. Pressure dependence of the TO mode in $\text{KCl}_{1-x}\text{Br}_x$ system.