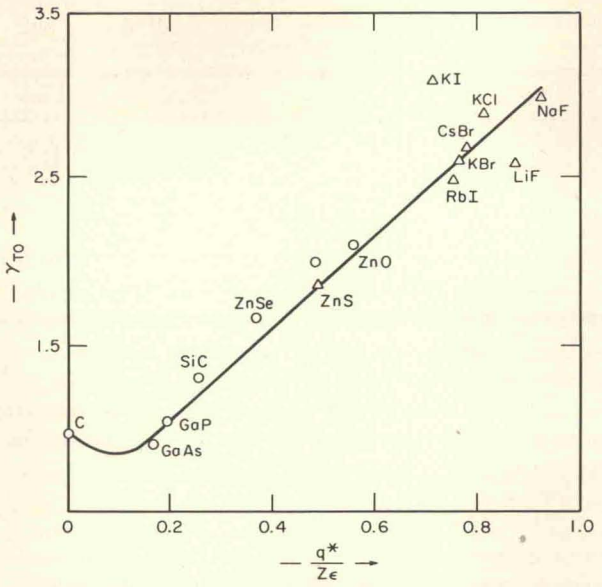

FIG. 3. Transverse-optic mode-Grüneisen parameter at $\vec{k} \simeq 0$ vs the effective charge per electron for a number of diatomic crystals. Circles represent Raman and triangles infrared measurements. Sources of data are as follows: KI, RbI, present study; GaAs, unpublished; rest from Refs. 1–4.

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

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

γ_{TO} in this model is given by[15]

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

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 $v = Cr_0^3$, 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

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

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 polarizibility 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 Szigeti effective ionic change per electron (Z^*), which varies from 0.75 (RbI) to 0.93 (NaF). The only exception 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, indications[16] 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 $\vec{k} \simeq 0$ 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 noncubic 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 $K_{1-x}Rb_xI$. (x is the mole fraction and p the pressure in kbar) (I = low-pressure phase; II = high-pressure phase).

x \ 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., $K_{1-x}Rb_xI$, has been reported[10] 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 $K_{1-x}Rb_xI$, 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 Mitra[19] 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

$$m_B < \mu_{AC}, \tag{6}$$

for a mixed crystal $AB_{1-x}C_x$ is obeyed by a two-mode system, whereas it is not obeyed by a one-mode system. All the examples cited above except for $K_{1-x}Rb_xI$ follow both Lucovsky *et al.* and Chang and Mitra criteria. The latter criterion also predicts a two-mode behavior for $K_{1-x}Rb_xI$. 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's[10] 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.

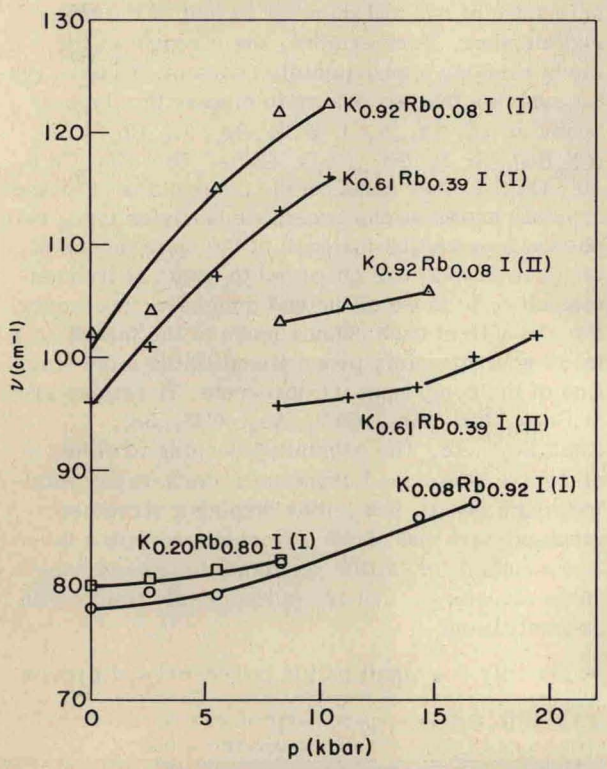

FIG. 4. Pressure dependence of the TO mode frequency in $K_{1-x}Rb_xI$ for four values of x. Phase transitions for $x = 0.08$ and $x = 0.39$ are shown. △ : $K_{0.92}Rb_{0.08}I$; + : $K_{0.61}Rb_{0.39}I$; □ : $K_{0.20}Rb_{0.80}I$; ○ : $K_{0.08}Rb_{0.92}I$. (I = low-pressure phase; II = high-pressure phase).

The Chang and Mitra[19] 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 $K_{1-x}Rb_xI$ 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 reminescent of a two-mode system.

The results are thus indicative that, at best, $K_{1-x}Rb_xI$ is a borderline two-mode system even at ambient conditions. With increasing pressure which