

TABLE IV
GRÜNEISEN PARAMETERS FOR THE LONG-WAVELENGTH OPTICAL MODES

	Experimental		Calculated				
	Eq. (1)	Eq. (2)	Born-Mayer ^a	r^{-n} repulsion ^b	Cowley ^c	Model I ^d	Model II ^d
LiF	2.15	2.59	2.44	3.46			
NaF	2.80	2.95	2.43	3.00			
KBr		2.83	2.52	2.95	3.27	~3.0	~2.6
KCl		2.46	2.52	2.92			

^a From Born and Huang (35).

^c From Cowley (37).

^b From Seitz (36).

^d From Cowley and Cowley (38).

transition pressure and both phases appear over a range of pressures. The high-pressure phase (CsCl structure) appears at 16 kbar for KBr and at 24 kbar for KCl. The conversion to the high-pressure phase is complete at 26 and 30 kbar for KBr and KCl, respectively. For a limited average pressure range the TO mode of both the low- and high-pressure phases can be detected, with a gradual decrease in the intensity of the low-pressure phase and an increase in that of the high-pressure phase. With the reduction of pressure, the frequencies of the CsCl phase do not coincide with those determined from increasing pressures (maximum experimental error $\pm 2 \text{ cm}^{-1}$). The low-pressure phase does not reappear until 11 and 16 kbar for KBr and KCl, respectively. Part of these discrepancies can be attributed to the sluggishness of the system and friction within the cell.

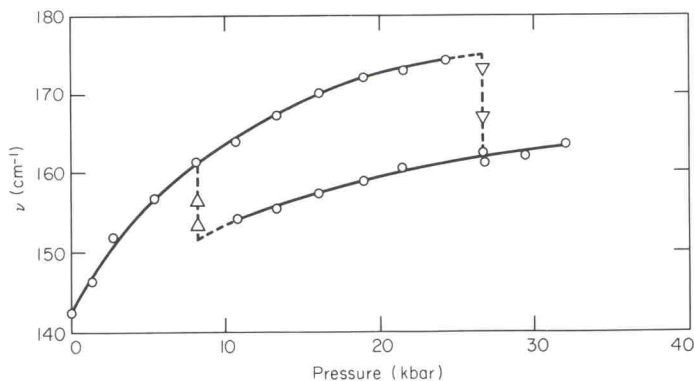


FIG. 4. TO mode of KCl as a function of pressure.

The vibrational frequency decreases at the transition pressure by about 10–12%. The ratio of TO frequency of the CsCl phase to that of the TO frequency in the NaCl phase should equal the square root of the coordination number of each phase; e.g., $\frac{3}{8}^{1/2}$ or 0.87. The observed ratio for KBr is 0.88 and that of KCl is 0.92.

It has been found (39) that the $k \approx 0$ TO frequency of the alkali halides of NaCl structure is proportional to $(a/\chi\mu)^{1/2}$, where a is the lattice constant, μ is the reduced mass per unit cell, and χ is the compressibility. The same is true for the CsCl structure, as illustrated in Fig. 5.

Pressure studies of mixed crystals have recently been reported for $\text{ZnS}_{1-x}\text{Se}$ (40) and $\text{KCl}_{1-x}\text{Br}$ (41). In both the two-mode system $\text{ZnS}_{1-x}\text{Se}$, and the one-mode system $\text{KCl}_{1-x}\text{Br}$, the pressure dependences of the various mixtures of the mixed crystals parallel those obtained for the pure components. Figure 6 illustrates the pressure dependence of the $\text{KCl}_{1-x}\text{Br}_x$ system.

Certain molecular lattice modes were investigated by McDevitt *et al.* (9). The experiments are more difficult to perform since a thicker sample is needed, and spacers must be used to accomplish this. Molecular lattice vibrations have been observed to also shift toward higher frequencies with increasing pressure. Recent Raman experiments (42) have demonstrated that molecular lattice vibrations are more sensitive to pressure than ionic lattice modes, as expected.

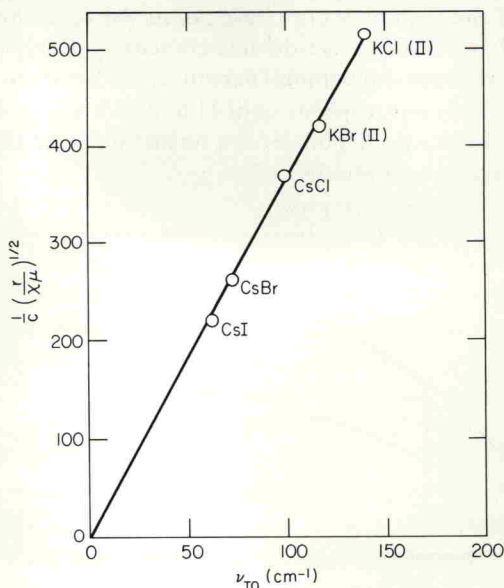


FIG. 5. Plot of TO mode frequency for several CsCl-type salts vs. $1/c(r/\chi\mu)^{1/2}$ (c = velocity of light).