

Fig. 12. Plot of $\ln \nu/\nu_0$ vs. $\ln V/V_0$ for several optic modes [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

assuming a rigid-ion model with central forces incorporating repulsion terms of the Born-Mayer [$\exp(-r/p)$] and inverse-power (r^{-n}) type is good. The results using Cowley's theory give somewhat larger values of γ .

The pressure dependencies of two phases of a solid can be determined by these techniques. Such studies have been made with KBr and KCl [176]. Figure 13 shows the TO mode of KCl as a function of pressure and illustrates the difficulty of studying phase transitions. The pressure gradient across the

TABLE 20

Grüneisen parameters for the long-wavelength optical modes

| | Experimental | | Calculated | | | | |
|-----|--------------|----------|-------------------------|---------------------------------|---------------------|----------------------|-----------------------|
| | Eqn. (1) | Eqn. (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 Ref. 180. ^b Ref. 181. ^c Ref. 182. ^d Ref. 183.

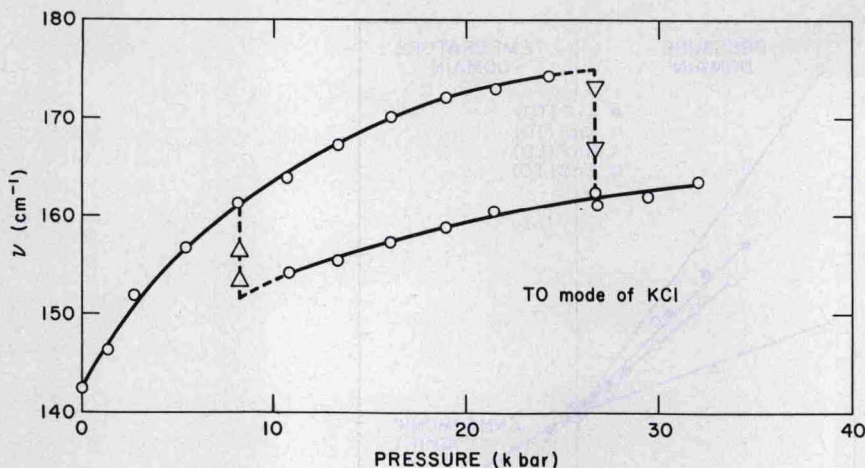


Fig. 13. TO mode of KCl as a function of pressure [139]. (Figure reproduced through the courtesy of the authors and Academic Press, New York.)

diamond anvils prevents the detection of a sharp 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 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. Some of these discrepancies can be attributed to the sluggishness of the system and friction created within the cell.

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 [184] 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. 14.

Pressure studies of mixed crystals have recently been reported for $\text{CdS}_{1-x}\text{Se}_x$, $\text{ZnS}_{1-x}\text{Se}_x$ [185] and $\text{KCl}_{1-x}\text{Br}_x$ [186]. In both the two-mode system $\text{ZnS}_{1-x}\text{Se}_x$, and the one-mode system $\text{KCl}_{1-x}\text{Br}_x$, the pressure dependencies of the various mixtures of the mixed crystals parallel those obtained for the pure components. Figure 15 illustrates the pressure dependence