



Fig. 9. Raman spectra of  $\beta\text{-Ag}_2\text{HgI}_4$  as a function of pressure [159]. (Figure reproduced through the courtesy of the authors and the American Institute of Physics, New York.)

ionic conductors and disorder. The sudden sharpening of the bands at 6.1 kbar is an indication of electronic conduction and a more highly ordered structure. The results are used to determine the anharmonicity in superionic conductors [159]. Both CuI and HgI modes are highly anharmonic, and a highly anharmonic potential may be important in providing a low energy barrier for ion motion and ionic conductivity.

#### (9) Miscellaneous inorganic compounds

(a) *Ammonium halides.* Wong and Whalley [162] have made a Raman study of  $\text{NH}_4\text{F}$  and Ebisuzaki and Nicol [163] have examined  $\text{NH}_4\text{Cl}$  under pressure using Raman spectroscopy. At 10 kbar a disordered-ordered phase transition takes place in  $\text{NH}_4\text{Cl}$ . The lattice mode involving movement of the  $\text{NH}_4^+$  and  $\text{Cl}^-$  sublattices shows a pressure dependency of  $2.65 \text{ cm}^{-1} \text{ kbar}^{-1}$  in the disordered (low pressure) phase. The librational mode behaves similarly. With the exception of the  $\nu_2$  bending vibration in  $\text{NH}_4^+$  the internal modes all show negative pressure dependencies varying from  $-0.1$  to  $-1.2 \text{ cm}^{-1} \text{ kbar}^{-1}$  and are attributed to the increased hydrogen bonding occurring in the ordered high pressure phase.

(b) *Solid nitrogen.* The Raman spectra of the three known phases of solid nitrogen at high pressures (0–10 kbar) and low temperature (8–220 K) were obtained [164]. The high pressure  $\gamma$  phase is tetragonal with  $D_{4h}^{14}$  space group and  $z = 2$ . The observed frequencies and relative integrated intensities were determined. Table 14 tabulates results at various temperatures. By comparing the results with calculated frequencies and relative intensities the low- and high-frequency bands in the lattice region were assigned as librational modes,  $E_g$  and  $B_{1g}$ , respectively.

(c) *Water ice.* In passing I wish to cite the work of Whalley and co-workers on water ices. The IR spectra of water ice II, III, V, VI and VII at appropriate pressures and temperatures were measured [165]. The Raman spectra for ices  $I_h$ ,  $I_c$ , II, III and V were also obtained by Marckmann and Whalley [166].

(ii) *Ionic and pseudo ionic crystals with lattice vibrations*

Considerable interest has developed in examining the pressure dependence of vibrational lattice modes in neat, ionic and pseudo ionic, and mixed crystals. The interest in pressure studies stems from results which can be obtained that can be used for testing lattice dynamics theory. Results are generally reported in terms of a Grüneisen parameter. Both temperature and pressure data provide information on anharmonic contributions to the lattice frequency shift. The temperature dependence of the peak position and half-width of lattice modes consist of the purely volume dependent part of the Grüneisen equation of state and the anharmonic contributions. On the other hand, the pressure dependence of peak position arises chiefly from the volume dependent part of the Grüneisen equation. Comparison of the Grüneisen parameter obtained from both methods can provide some estimate of anharmonicity existing in these solids.

TABLE 14

Observed Raman frequencies and relative intensities for the  $\gamma$ -phase of solid  $N_2$  [164]

Temp. (K)	$\nu(\text{cm}^{-1})$	Relative integrated intensity
35	57.5	2
	95.5	4.5
	2329	1
20	58.2	5.5
	102.5	3
	2330	1
8	58.4	7
	103.6	2.5
	2331	1