

1. One measures the compression of the spring by means of a Dillon force gauge. The contact area of the diamond is determined by means of microphotographs, which allows one to determine the force per unit area or pressure.

2. Calibration with an internal calibrant is possible, i.e., solids which undergo phase transformation at known pressures (e.g., KBr, 18 kbar; KCl, 20 kbar).

3. Calibrations can be made by using nickel dimethylglyoxime, which shows a change in spectral properties with pressure, as an internal calibrant (23, 24).

### III. Applications

Some of the applications of the far infrared-high-pressure technique that have been investigated thus far will be presented in this section, indicating the newest developments in this area and pointing out other possible applications.

#### A. Lattice Vibration Studies

Table III lists some ionic lattice frequencies. Most of the frequencies for the transverse optical lattice modes ( $\nu_{TO}$ ) in ionic salts are found below  $300 \text{ cm}^{-1}$ . The capability of measuring vibrational spectra in the far-infrared region under pressure allows one to study these vibrations for the first time in this manner. The longitudinal mode ( $\nu_{LO}$ ) is more difficult to study in the infrared. It is not normally observed at  $90^\circ$  incident radiation. Berreman (25)

TABLE III  
LATTICE VIBRATIONS FOR ALKALI HALIDES<sup>a</sup>

Halide	$\nu_{TO} (\text{cm}^{-1})$	Halide	$\nu_{TO} (\text{cm}^{-1})$	Halide	$\nu_{TO} (\text{cm}^{-1})$
LiF	307	NaI	117	RbCl	118
LiCl	191	KF	190	RbBr	88
LiBr	159	KCl	141	RbI	77
NaF	246	KBr	113	CsCl <sup>b</sup>	99
NaCl	164	KI	98	CsBr <sup>b</sup>	74
NaBr	134	RbF	156	CsI <sup>b</sup>	62

<sup>a</sup> S. S. Mitra and P. J. Gielisse (24a).

<sup>b</sup> C. M. Randall *et al.* (24b).

observed the longitudinal mode for a thin film of LiF with an oblique incident radiation, and longitudinal optical modes of the silver halides have recently been studied with similar techniques (26). The longitudinal modes can be observed with a diamond cell and highly converging oblique radiation coming from the beam condenser. They appear as shoulders on the main, intense transverse vibrational bands, and are not easily studied in the infrared, for they are less pressure sensitive than the transverse modes, and because of the high-frequency shift of the  $\nu_{TO}$  band, can no longer be observed. In more covalent solids  $\nu_{TO}$  is very close to  $\nu_{LO}$ . In a homopolar covalent crystal,  $\nu_{TO}$  may equal  $\nu_{LO}$ . In this instance, a very broad absorption is observed, which shows very little frequency shift with pressure.

Figure 1 shows a comparison of several  $\nu_{TO}$  frequencies with pressure. The  $\nu_{LO}$  pressure dependence for NaF is shown in Fig. 2. In this system the separation between  $\nu_{LO}$  and  $\nu_{TO}$  is sufficiently large to make possible a determination of the pressure dependence of both optical modes.

In all cases studied ionic lattice vibrations shifted toward higher frequencies with increasing pressure. The shifts at pressures of up to 50 kbar may be considerable; however, not all ionic lattice vibrations show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure for simple ionic solids, where the three crystallographic axes are equal, is given in Eq. (1):

$$\gamma\chi\nu = (\partial\nu/\partial p)_T, \quad (1)$$

where  $\gamma$  is the Grüneisen parameter,  $\chi$  is the isothermal compressibility of the solid, and  $\nu$  is the frequency of the lattice mode. For noncompressible solids, it is possible that only small shifts will occur. For example, the lattice modes of zirconium and hafnium failed to show significant shifts at 40 kbar (9). It is also possible that the pressure effects may be different in noncubic crystals having different axes parameters, depending on which axis becomes compressible (27, 28).

The data obtained from studies of the pressure dependence of the  $k \approx 0$  lattice vibrations of ionic crystals (29), when combined with data from studies of these modes with temperature (30), may allow one to calculate the anharmonic interactions taking place, and contribute to a better understanding of the lattice dynamics of these solids. It is possible to distinguish between the purely volume-dependent contribution and the contribution from various anharmonic terms in the crystal Hamiltonian (31). Figure 3 shows a plot of  $\ln \nu/\nu_0$  vs.  $\ln v/v_0$  for several optical modes. The data have been obtained from pressure and high-temperature studies (29-31),  $P$ - $V$  data from Drickamer (32), and from Cline and Stephens (33). It can be