

pressure diamond cell of High Pressure Diamond Optics, Inc., McLean, Virginia. Certain modifications were necessary. The size of the ellipsoid mirrors on the beam condenser had to be reduced, to accept the diamond cell. To allow for easy alignment of the cell, a machine lathe micrometer attachment was added to give movement in the x,y,z directions. To allow for more energy for operation below 100  $\mu$ , larger diamonds ( $\sim 0.8$  sq. mm. area) were used, although above 100  $\mu$  diamonds of 0.25 sq. mm. can be used. An expansion scale was also built into the No. 301 spectrophotometer, to amplify weak vibrations. This allows for less compensation in the reference beam and the use of narrower slits. For all of the pressure work a microscope is absolutely essential, to determine if one has a good solid load between the diamonds, and if a phase transition is occurring.

In the interferometer tie-up with the diamond cell, a brass cone light pipe is used (angle  $9^{\circ}37'$ ).<sup>9</sup> The infrared radiation comes out of the instrument and enters this cone. The cone bends the radiation toward the small opening in the other end (.060" opening). The cone is machined to accept the diamond cell piston. The energy then passes through the diamonds and enters the detector by means of another light pipe.

#### Calibration of Diamond Cell

It has already been indicated that a pressure gradient exists in the multiple anvil diamond cell. Duecker and Lippincott<sup>17</sup> have demonstrated that the pressure gradient across the diamond face is parabolic, with pressures in the center reaching 1 1/2 times those on the edges. Thus, any measure of pressure in the contact area of the diamond gives only an average pressure.

There are several ways to make a pressure calibration of the cell. These are as follows:

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 micro photographs. One then knows the force per unit area or pressure.
2. The use of solids which undergo phase transformations at known pressures (e.g., KBr - 18 kbars; KCl - 20 kbars;  $\text{NaNO}_2$  - 14 kbars).
3. Calibration can be made by using nickel dimethylglyoxime, which shows a change in spectral properties with pressure.<sup>17-18</sup>

## APPLICATIONS

This paper will attempt to present some of the applications of the far infrared-high pressure technique that have thus far been investigated. It will indicate the newest developments in this area, and further point out other applications that are contemplated.

## Lattice Vibration Studies

Table III lists some ionic lattice frequencies. Most of the frequencies for the transverse optical lattice modes ( $\nu_{TO}$ ) 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. At  $90^\circ$  incident radiation it is not normally observed. Berreman<sup>19</sup> observed the longitudinal mode for a thin film of LiF with an oblique incident radiation. Longitudinal optical modes of the silver halides have recently been studied with similar techniques.<sup>20</sup> With the diamond cell and the highly converging oblique radiation coming from the beam condenser, the longitudinal modes can be observed. 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  $\nu_{TO}$ , and because of the high frequency shift of the  $\nu_{TO}$  band, can no longer be observed. In more covalent solids the  $\nu_{TO}$  is very close to the  $\nu_{LO}$ . In a homopolar covalent crystal,  $\nu_{TO}$  may be equal to  $\nu_{LO}$ . 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  $\text{NaF}$  is shown in Fig. 2. In this system the separation between the  $\nu_{LO}$  and the  $\nu_{TO}$  is sufficiently large to make possible a determination of the pressure dependency of both optical modes.

In all cases studied, ionic lattice vibrations shifted toward higher frequency with increasing pressure. The shifts at pressures up to 50 kbars can be considerable. However, not all ionic lattice vibrations will show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure is given in equation 1,

$$\gamma\chi\nu = \left(\frac{\partial\nu}{\partial p}\right)_T \quad (1)$$

where  $\gamma$  is the Grüneisen parameter,  $\chi$  is the isothermal compressi-