TABLE II. Correlation diagram for the β phase at the center of the Brillouin zone.

Molecular symmetry $D_{\infty h}$	Site symmetry D_{3h}	Factor group symmetry D_{6h}	Activity
$\Sigma_g^+(\nu)$ ——	A_1' ——	$A_{1g}(1)$	Raman (1)
		$B_{1u}(1)$	...
$\pi_g(R_x, R_y)$ ——	E'' ——	$E_{1g}(1)$	Raman (1)
		$E_{2u}(1)$	Acoustic (1)
$\Sigma_u^+(T_z)$ ——	A_2'' ——	$B_{2g}(1)$	...
		$A_{2u}(1)$	Acoustic (1)
$\pi_u(T_x, T_y)$ ——	E' ——	$E_{2g}(1)$	Raman (1)
		$E_{1u}(1)$	...

solid nitrogen at various temperatures and pressures was undertaken with the hope of shedding light on some of these questions.

The experimentally measured quantities serve as a check of the anisotropic part of the intermolecular potential used in a particular theory. Pressure dependence studies can provide a severe test for any theory. This is particularly true since most infrared and Raman experiments on nitrogen have been done along the solid–vapor line, the exception being the Raman scattering experiments of Thiery et al., recently reported.[23] However, these experiments were done at only one temperature and under nonhydrostatic pressure that made quantitative results less reliable. The present high pressure experiments are unique because of the use of a novel method of sample preparation that allows the separation of temperature and volume effects on the Raman spectrum. This is accomplished by constraining the sample inside a high pressure optical cell and hence assuring that the molar volume changes only slightly as the temperature is lowered.

In the present work the experimental techniques used in obtaining Raman spectra of the three known phases of solid nitrogen are described. Results for the three phases are presented. Calculations of the librational frequencies and relative intensities are compared to the experimental results in the γ phase. The volume dependence of the Raman frequencies in the α phase is discussed in relation to the form of the anisotropic part of the intermolecular potential within the context of the quasiharmonic approximation. The temperature dependence of the Raman spectrum is discussed in relation to the cubic and quartic anharmonic terms in the Hamiltonian of a perturbative treatment of the lattice dynamics of the α phase. Finally, the Raman spectrum of the β phase is discussed and its structure is identified.

Preliminary reports on the Raman spectrum of the γ phase and the volume dependence of the Raman frequencies in the α phase have already appeared in the literature.[58,59]

II. EXPERIMENTAL DETAILS

Samples used in Raman scattering studies are usually grown by condensation from the gas phase on a substrate. This method has several disadvantages: (1) Strains are usually present in the samples during growth, leading to sample cracking and defects and the resultant loss of optical quality; (2) the external surfaces are of poor optical quality; and (3) as the temperature of the sample is changed, changes in the frequencies of the Raman lines result from changes in both temperature and volume. These effects cannot be separated in a single such experiment.

The experimental method used in this work remedies the above mentioned disadvantages. Samples of solid nitrogen are prepared by growth within an optical cell at high pressures on the melting curve. Samples are then cooled nearly isochorically to the temperature of observation. The optical cell is equipped with sapphire windows[60,61] so that the sample may be studied in situ within its high pressure jacket. The method has been used in inelastic neutron scattering studies of neon[62,63] and krypton.[64] The method has the following advantages: (1) The high pressure prevents sample cracking and the resultant loss of optical quality; (2) for the same reason the external optical surfaces remain flat and of high optical quality; (3) the shifts of spectral lines with temperature directly represent temperature-dependent anharmonic self-energies; and (4) growing samples of different densities allows the determination of the volume dependence of the Raman frequencies which can then be compared to the volume dependence calculated with various anisotropic intermolecular potentials.

The pressure generating system is a standard research tool in our laboratory and has been extensively described.[65,66] The gas under investigation, in this case nitrogen, is used as the pressure transmitting fluid. Prepressurization is accomplished by a 2 kbar air-operated pump. The main valve is closed and the pressure is further increased using an intensifier with an area ratio of 15:1. The intensifier piston is driven by a hand-operated oil pump. The pressure is transmitted to the optical cell and pressure gauge through hard drawn stainless steel pressure tubing. In this manner, pressures of 10 kbar are easily reached. Pressure is measured by a high precision manganin gauge constructed and calibrated in this laboratory.[65] Pressures measured with this gauge are estimated to be accurate to better than 5 bars in the 0–10 kbar range.

The high pressure optical cell used in this study has been designed by one of the authors (WBD) and will be described elsewhere. It is constructed from maraging steel and has an estimated bursting pressure well above 10 kbar. It is attached to the cold finger of a cryostat capable of operation at liquid helium temperature. Two radiation shields and a vacuum jacket are placed around the cell.

The temperature is controlled to better than $0.1\,^\circ$K by a Kelvin resistance bridge arrangement having a temperature sensor as one arm and a variable resistance as the balance arm. When the bridge is not balanced,