FIG. 1. Nitrogen phase diagram partly reproduced from Ref. 6 and more recent data from Refs. 15–17.

Coincidences between Raman and infrared frequencies are not allowed. The Raman spectrum for the α phase has been measured by several workers,[19–23] who obtained librational frequencies which differ by as much as 6%. Four lines have been observed in the lattice region: Three relatively narrow lines which have been assigned to the librational modes and a very broad band around 80 cm^{-1}. In the stretching region two lines with a separation of about 1.2 cm^{-1} have been reported.[21] As the temperature is increased from below 20 °K to just below the α–β transition temperature, the librational frequencies decrease by as much as 15% and the lines broaden considerably.[19,20,22] This temperature dependence of the Raman frequencies and linewidths must be ascribed to anharmonicities. The anharmonicities result from large librational and translational amplitudes. The anomalous increase in the linear coefficient of thermal expansion[16,37] and the heat capacity,[38] and the temperature dependence of the nuclear quadrupole resonance frequency[39] have also been ascribed to large librational amplitudes.[18,39] The rms librational amplitudes calculated from Raman[20] and nuclear quadrupole resonance[17] data range from 14° at 16 °K to 19° near the α–β transition temperature.

The librational frequencies in the α phase have also been the subject of an impressive number of classical and quantum mechanical calculations aimed at elucidating the form of the anisotropic part of the intermolecular potential.[21,34–36,40–49] Several anisotropic potentials have been used in these calculations: quadrupolar, Kohin, and atom–atom interaction potentials. The quadrupolar potential has an r^{-5} dependence on the intermolecular distance r. The Kohin potential adds aniso-

tropic dispersive and repulsive interactions having r^{-6} and r^{-12} dependence, respectively. The atom–atom potential consists of 6–12 interactions between nonbonded atoms.

Quantum mechanical calculations using the quadrupolar interaction potential give the best agreement with the measured librational frequencies.[43–47] Monte Carlo studies of classical free rotors using the quadrupolar interaction potential[48] give good agreement with several experimental quantities. However, a quadrupole-induced mechanism gives poor results for the infrared intensities.[28] Furthermore, the Kohin potential is needed to obtain good agreement between the calculated crystal energy and the measured sublimation energy.[30,35] Unfortunately, classical[35] and quantum mechanical[45] calculations with the Kohin potential yield librational frequencies which are as much as 90% and 50% larger than the measured frequencies, respectively. The general conclusion is that either the forms or the relative strengths of the different terms in the Kohin potential are incorrect.[45]

The atom–atom potential has also been used extensively to calculate librational frequencies and other properties of the α phase.[34,36,40,41,47,49] This potential has yielded good agreement with many experimental properties. Jacobi and Schnepp[47] used a 6–n atom–atom potential and obtained best agreement with experimental properties for $n=9$. Zunger and Huler[36] have studied the effect of zero-point energy and complete relaxation of forces and torques on the properties of α-N$_2$, while Raich, Gillis and Anderson[49] have studied the temperature dependence of the librational and translational lattice modes using the self-consistent phonon approximation. Although both studies are moderately successful in fitting observed properties, the authors conclude that a more complete potential is needed. More recently, Mandell[50] proposed an anisotropic intermolecular potential consisting of a sum of multipolelike interactions and concluded that terms of hexadecapolar symmetry play a significant role in the orientational properties of α-N$_2$ and that these terms are weak in the 6–12 atom–atom potential. Another criticism of calculations using the atom–atom potential is the introduction of a "new parameter," the bond length of the nitrogen molecule, which can then be adjusted to give best agreement with experiment.

The structure of the high pressure γ phase is tetragonal with a $P4_2/mnm(D_{4h}^{14})$ space group and two molecules per unit cell.[14] The molecules are arranged in layers with the molecular axes parallel within a layer and perpendicular in adjacent layers, as shown in Fig. 2. For a molar volume of 24.09 cm^3/mole, x-ray diffraction experiments give lattice constants $a=3.957$ Å and $c=5.109$ Å.[14] The correlation diagram of the γ phase at the center of the Brillouin zone derived from group theoretical considerations[51] is shown in Table I. The numbers in parenthesis indicate the number of modes of that symmetry. The librational and translational modes are separable at the zone center. Two stretching modes of symmetry A_{1g} and B_{2g}, and two librational modes of symmetry B_{1g} and E_g, are expected in the first-order Raman spectrum. One translational mode of symmetry