



FIG. 2. Unit cell of the γ phase determined by x-ray diffraction experiments in Ref. 14.

D_{4h}^{14} STRUCTURE

E_u is infrared active. Coincidences between Raman and infrared frequencies are not allowed. The Raman spectrum of the γ phase has been previously reported.²³ Two lines were observed in the lattice region.

At the higher densities corresponding to the γ phase the anisotropic intermolecular potential is likely to be more harmonic and to contain a larger contribution from the repulsive interaction. However, neither the quadrupole, nor the Kohin, nor the 6-12 atom-atom potential is capable of explaining the stability of the D_{4h}^{14} structure.^{33,36,52} Raich and Mills⁵² showed that a Kohin potential where the repulsive term is replaced by a shape-dependent hard-core potential, similar in shape to the calculated electron distribution, accounts for the stability of the γ phase. Finally, Mandell⁵⁰ has shown that hexadecapolar terms in the multipolelike expansion of the intermolecular potential can account for the α to γ transition.

X-ray diffraction studies of the β phase indicate that the molecular centers are arranged in a hexagonal closed-packed structure²⁻⁶ with a high degree of orientational disorder. The molecular axes are inclined at an angle of about 56 deg with respect to the crystal c axis.⁵⁻⁸ Calculations using the quadrupolar^{42,48,52} and 6-12 atom-atom⁵³ interaction potentials can predict a first-order transition from the orientationally ordered α phase to an orientationally disordered phase at higher temperatures. The x-ray diffraction data is equally well fit by having the molecules precessing about the c axis or randomly distributed among the 24 general positions of space group $P6_3/mmc$ (D_{6h}^4). Schuch and Mills⁶ analysed the packing of nitrogen molecules assuming their surface to be defined by the 0.002 electron density contour. They found that the molecules overlap slightly and can not precess freely about the c axis but can take the random orientations of space group $P6_3/mmc$ without overlapping. The c to a ratio has been found to be close to the ideal value of 1.633 for closest packing of hard spheres.³⁻⁶ However, molecular volume data,³ estimates of the rotational specific heat⁵⁴ and the entropy,⁵⁵ and the detection of a small but nonzero nuclear quadrupole coupling constant,⁵⁶ rule out completely free rotation. The results of the nuclear quadrupole resonance experiments are consistent with the molecules being aligned at an angle of 54.7 deg with respect to the c axis while precessing or jumping among different posi-

tions at a rate fast compared to the resonance frequency. These results also rule out the randomly oriented structure.

The Raman spectrum of the β phase in the lattice region has been reported to resemble the wing of the Rayleigh line, whereas in the stretching region a single line with wings has been observed.²⁰ The Raman spectrum expected on theoretical grounds depends obviously on the structure assumed for the β phase. If the $P6_3/mmc$ structure is assumed, the fact that molecules are orientationally disordered means that librational excitations cannot be sustained by the solid. This is the case in the orientationally disordered hexagonal close-packed phases of the solids H_2 , D_2 , and HD , where only a transverse optical phonon has been observed in the Raman spectra.⁵⁷

If the molecules in the β phase are assumed to be precessing at an angle of 56 deg about the c axis, this entails some orientational order and librational excitations can be sustained by the solid. The molecules librate in a plane containing the c axis. Replacing the precessing molecules by some "average" molecules with different polarizability, these new molecules are sitting on sites of D_{3h} symmetry. The correlation diagram can then be worked out, as shown in Table II. One stretching mode of symmetry A_{1g} , one librational mode of symmetry E_{1g} , and one translational mode of symmetry E_{2g} , are expected in the first-order Raman spectrum. None of the modes are infrared-active.

It should be clear from the previous discussions that many questions about solid nitrogen are still unanswered. The most fundamental concern is the form of the anisotropic part of the intermolecular potential. Some detailed subjects of interest are: (1) The structure of the α phase; (2) the Raman spectrum of the β phase; (3) the structure of the β phase; (4) the Raman spectrum of the γ phase; (5) anharmonicities of all solid phases, and others. The present study of the Raman spectrum of

TABLE I. Correlation diagram for the γ phase at the center of the Brillouin zone.

Molecular symmetry	Site symmetry	Factor group symmetry	Activity
$\Sigma_g^+(v)$	A_g	$A_{1g}(1)$	Raman (1)
		$B_{2g}(1)$	Raman (1)
$\Sigma_g^+(T_z)$	B_{2u}	$E_u(2)$	ir(1), acoustic (1)
$\pi_u(T_x, T_y)$	B_{3u}	$B_{1u}(1)$...
	B_{1u}	$A_{2u}(1)$	acoustic (1)
$\pi_g(R_x, R_y)$	$C_\infty \rightarrow C_2(x)$	$B_{1g}(1)$	Raman (1)
		B_{3g}	...
		$A_{2g}(1)$...
$\pi_g(R_x, R_y)$	$C_\infty \rightarrow C_2(y)$	$B_{1g}(1)$	Raman (1)
		B_{2g}	
		$E_g(1)$	Raman (1)