Raman spectrum of solid nitrogen at high pressures and low temperatures[*]

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The Raman spectrum of solid nitrogen has been studied at high pressures and low temperatures using a method of sample preparation that allows the separation of effects due to change of molar volume and of temperature, respectively. Two lines have been observed in the lattice region of the γ phase which are identified as E_g and B_{1g} librational modes on the basis of frequency and relative intensity calculations. An asymmetrical line has been observed in the stretching region of this phase. In the α phase, the measured Grüneisen parameters indicate that neither the quadrupolar nor the 6–12 atom–atom interaction potential has the correct volume dependence. The temperature dependence of the frequency and linewidth of the E_g librational mode is proposed to be due to libron–phonon interactions. Two very broad Raman lines are observed in the lattice region of the β phase. The low- and high-frequency lines are identified with translational and librational modes, respectively. The observations are consistent with a precessing molecule model for the β phase.

I. INTRODUCTION

Considerable experimental and theoretical work has been devoted to molecular solids, such as H_2, N_2, CO, CO_2, CH_4, and others. These solids represent the first step in complexity from the monatomic inert gases. They are among the simplest systems where one can study molecular rotations, i.e., where one can study the anisotropic or orientation-dependent part of the intermolecular potential. Some of these solids are also of interest because they exhibit phase transitions which presumably are associated with the anisotropic part of the intermolecular potential.

Solid nitrogen exhibits such a transition from an orientationally ordered phase at low temperatures to a highly orientationally disordered phase at high temperatures. This transition has been shown to be from a cubic α phase to a hexagonal β phase, as the temperature is increased.[1–11] Another phase, the high pressure γ phase,[12,13] has been found to have a tetragonal structure.[14]

The nitrogen phase diagram is shown in Fig. 1. This diagram covers the temperature range from 0 to 200 °K and the molar volume range from 23.37 to 27.81 cm^3/mole, and includes the fluid, vapor, and three solid phases of nitrogen. The transition lines between the different phases and isobars every 1kbar up to 6 kbar are also shown in this figure. This figure has been partly constructed from a similar figure in Ref. 6. More recent data on the melting parameters[15] and the relative length changes along the solid–vapor line[16] of nitrogen have been used to construct the melting and solid–vapor lines. In addition, the α–β–γ triple point of solid nitrogen used in Fig. 1 has been estimated from the results of nuclear quadrupole resonance studies of the α–β transition.[17]

Studies on the structure of the α phase favor either a $Pa3(T_h^6)$ or a $P2_13(T^4)$ space group. The $Pa3$ structure has four molecules per unit cell with the molecular centers arranged in a face-centered cubic lattice and the molecular axes oriented along one of the four cube diagonals. In the $P2_13$ structure the molecules are displaced along the cube diagonals from the center of inversion symmetry they occupy in the $Pa3$ structure.

The experimental evidence supporting each structure is extensive. In some x-ray[2,3,6] and electron[8–11] diffraction experiments lines which are forbidden for the $Pa3$ structure were not detected. The $Pa3$ structure is further supported by measurements of the optical birefringence that indicate cubic symmetry[18] and the absence of coincidences between the frequencies in the Raman spectrum[19–23] and the infrared absorption spectrum.[24–26] In other x-ray diffraction experiments[1,4,7] lines which are forbidden for the $Pa3$ structure were observed. Further support for the $P2_13$ structure is provided by the detection of piezoelectric resonances[27] and a Raman-active line in the infrared absorption spectrum,[28] since neither is allowed in the centrosymmetric $Pa3$ structure. From an analysis of their data, Jordan *et al.*,[5] and LaPlaca and Hamilton[7] estimate the displacement of the nitrogen molecules from their centers of symmetry to be 0.17 and 0.16 Å, respectively. However, the electron diffraction data of Venables and English[11] can establish an upper limit of 0.05 Å for this displacement. Furthermore, these authors argue that the measurements supporting the $P2_13$ structure can be explained by the presence of twins and other defects.[11]

Finally, the stability of the $Pa3$ structure has been established using different methods and intermolecular potentials.[29–35] In particular, Goodings and Henkelman[35] used the Kohin potential[30] in a classical calculation of the crystal energy as a function of the displacement of the nitrogen molecules along the cube diagonals and found that the lowest energy corresponds to zero displacement or, in other words, the $Pa3$ structure. More recently, Zunger and Huler[36] used the so-called 6–12 atom–atom potential and again determined $Pa3$ as the more stable structure.

Assuming the $Pa3$ structure for the α phase, two stretching modes of symmetry A_g and T_g, and three librational modes of symmetry E_g, T_g, and T_g, are expected in the first-order Raman spectrum. Two translational modes of symmetry T_u are infrared-active.