

TABLE III. Melting parameters and phases studied.

| Sample | Melting temperature (°K) | Melting pressure (kbar) | Molar volume of solid (cm <sup>3</sup> /mole) | Phases studied |
|--------|--------------------------|-------------------------|---|----------------|
| 1      | 112 ± 0.2                | 2.85 ± 0.02             | 26.94 ± 0.06                                  | β, α           |
| 2      | 131 ± 0.2                | 4.28 ± 0.02             | 26.00 ± 0.06                                  | β, α           |
| 3      | 151 ± 0.2                | 6.00 ± 0.02             | 25.15 ± 0.06                                  | β, α           |
| 4      | 189 ± 0.2                | 9.75 ± 0.02             | 23.75 ± 0.06                                  | β, γ           |
| 5, 6   | 125 ± 0.2                | 3.80 ± 0.02             | 26.30 ± 0.06                                  | α              |

the amplified error signal activates either the heaters or a valve that allows the flow of coolant around the cold finger, depending on whether the cold finger is too cold or too hot. Four terminal platinum and germanium thermometers are used to measure the temperature above and below 40 °K, respectively. The resistances of the sensors are measured by a Müller bridge with a reversing mercury switch. In this manner, temperatures can be measured to ± 0.1 °K.

Nitrogen gas from the Matheson Gas Co. of a stated minimum purity of 99.9995% was used to grow samples of the high temperature β phase at several points on the melting curve, depending on which phase was to be studied at low temperatures. Figure 1 was used as a guide and the corresponding melting parameters were then determined from Cheng's data.<sup>15</sup> To grow a particular sample the temperature was maintained constant while the pressure was slowly increased until the solid began to grow. A heating wire was wound around the pressure tubing near the optical cell to prevent the nitrogen from freezing and blocking the tubing. In order to prevent the solid from growing near the pressure inlet another heater was placed on a pressure fitting, maintaining a temperature difference of ~1 °K across the cell. This temperature difference introduced density differences across the samples of less than 0.1%. Samples were grown in periods of up to 12 h and then annealed overnight to remove density gradients. Each sample was then cooled through the β phase and into the α or the γ phase. Table III contains a summary of the samples grown, indicating the melting pressure and temperature, the molar volume of the solid and the phases studied.

The molar volume of each sample remained essentially

TABLE IV. Corrected molar volumes in cm<sup>3</sup>/mole.

| Samples and melting parameters    | Sample 1<br>112 °K<br>2.85 kbar | Sample 2<br>131 °K<br>4.28 kbar | Sample 3<br>151 °K<br>6.00 kbar | Sample 4<br>189 °K<br>9.75 kbar |
|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| T(°K)                             | 26.94                           | 26.00                           | 25.15                           | 23.75                           |
|                                   | cm <sup>3</sup> /mole           | cm <sup>3</sup> /mole           | cm <sup>3</sup> /mole           | cm <sup>3</sup> /mole           |
| 55                                | 26.87 ± 0.08                    | 25.90 ± 0.09                    | 25.05 ± 0.09                    | 23.59 ± 0.10                    |
| 33                                | 26.84 ± 0.08                    | 25.88 ± 0.09                    | 25.02 ± 0.09                    | 23.56 ± 0.10                    |
| 18                                | 26.83 ± 0.08                    | 25.87 ± 0.09                    | 25.01 ± 0.09                    | 23.55 ± 0.10                    |
| 8                                 | 26.82 ± 0.08                    | 25.87 ± 0.09                    | 25.00 ± 0.09                    | 23.55 ± 0.10                    |
| Change from melting curve to 8 °K | 0.4%                            | 0.5%                            | 0.6%                            | 0.9%                            |

constant during the entire run since it is constrained within the optical cell. However, changes in volume of the cell due to changes in temperature and pressure have been estimated using elasticity theory,<sup>67</sup> and Benson's<sup>68</sup> expressions for the volume thermal expansion coefficient, and the modulus of elasticity in tension for maraging steel. Table IV summarizes the corrected molar volumes and estimated errors for samples 1-4 at four different temperatures. These values have been used to trace the path that each sample takes during each run, shown in Fig. 1. For samples 5 and 6 which were grown to study the temperature dependence of the Raman frequencies and linewidths in the α phase, the corrected molar volumes at 40 and 5 °K are 26.18 and 26.17 cm<sup>3</sup>/mole, respectively.

The Raman spectra were excited by the 5145 Å line of an argon-ion laser in the usual 90° scattering geometry. The 4880 Å line was used occasionally as a check. The scattered light was analyzed with a Chromatix DS-40 double monochromator with Bausch and Lomb 1800 lines/mm gratings, blazed at 5000 Å. It was detected and displayed by a Channeltron photomultiplier and a photon counting system with output to a chart recorder.

### III. RESULTS AND DISCUSSION

#### A. Raman spectrum in the γ phase

Sample 4 became nearly opaque when taken into the γ phase in the sense that in the 1 cm long sample essentially the entire exciting beam was attenuated by intergranular anisotropies of the polycrystalline sample. The Raman spectrum of γ-N<sub>2</sub> in Fig. 3 was taken at 8 °K and about 5 kbar and shows two lines in the lattice region with frequencies of 58.4 and 103.6 cm<sup>-1</sup>. These frequencies are in good agreement with those measured by Thiery *et al.*,<sup>23</sup> contrary to the conclusion of Luty and Pawley<sup>68</sup> who did not realize that our sample was grown at 9.75 kbar and cooled nearly "isochorically," not isobarically, to the γ phase. The lattice region was scanned from 25 to 200 cm<sup>-1</sup>, revealing no additional spectral features. However, because of the large amount of elastically scattered light it was difficult to scan within 25 cm<sup>-1</sup> of the laser line. A shoulder was observed on the elastic peak around 20 cm<sup>-1</sup> which could not be resolved. However, this shoulder is located at the base of the laser line more than seven orders of magnitude be-