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## Detection of the $\epsilon$ - $\delta$ phase transition in $N_2$ and a $N_2$ -He mixture by Raman spectroscopy: new evidence for the solubility of fluid He in solid $N_2$

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**Abstract.** The vibrons  $\nu_1$  and  $\nu_2$  of  $N_2$  have been measured around the  $\epsilon$ - $\delta$  phase transition by Raman spectroscopy. Thus, for the first time the  $\epsilon$ - $\delta$  transition could be detected in this way. The Raman shift of the  $\nu_1$ -peak has been observed to be larger in the  $\epsilon$ -phase than in the  $\delta$ -phase and the Raman shift of the  $\nu_2$ -peak smaller. More importantly, this feature has also been observed in the mixture  $N_2$ -He with 9.2 mol% He around the phase transition at  $p = 60$  kbar and  $T = 245$  K, which is new evidence for a considerable temperature and pressure shift of the  $\epsilon$ - $\delta$  phase transition line in the mixture and also for the solubility of fluid He in solid  $\epsilon$ - $N_2$  at high pressures.

### 1. Introduction

In the last twenty years the static pressure range has been extended enormously by the development of the diamond anvil cell (DAC) technique [1]. Among other advantages it enables the experimental study of simple molecular substances at high densities, so that phase diagrams and the intermolecular potential at short distances can be investigated. Recently the phase diagram of the helium-nitrogen system [2–4] has been measured in our laboratory (see figure 1). Since small differences from the pure system are sometimes essential the relevant parts of the phase diagrams of nitrogen [5] and helium [6] have been remeasured. This was carried out by quasi-isochoric pressure against temperature scans and by visual observation. In this article we will present a Raman spectroscopic investigation of these systems. First we will discuss the essential properties of the helium-nitrogen system and the various modifications of solid nitrogen.

The study of molecular mixtures at high pressures is a very young and dynamic discipline [7]. Mostly these studies have been concerned with fluid-fluid and solid-fluid phase separations. At our laboratory a systematic study of the binary mixture  $N_2$ -He has been carried out. It was found that the solid-fluid-fluid (SFF) three-phase line persisted up to 100 kbar [2] and that two quadruple points could be detected at 34 and 58 kbar. Later Vos *et al* [3] measured the three-phase lines, which were connected to the quadruple points and showed that the three-phase lines of the lower quadruple point coincided within experimental accuracy with the  $\beta$ - $\delta$  phase transition line in pure  $N_2$ . Recently, Vos and Schouten [4] proved that the upper quadruple point was

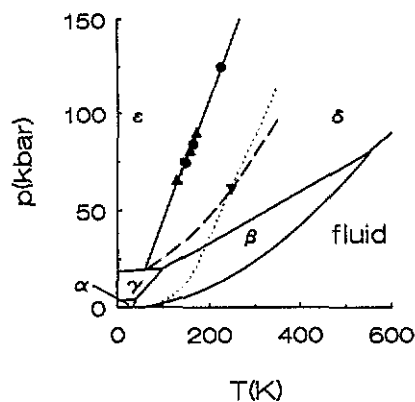


Figure 1. Phase diagram of  $N_2$  and  $N_2$ -He: full curves, phase lines of pure  $N_2$ ; broken curves,  $\epsilon$ - $\delta$ -F three-phase lines (extrapolated towards lower temperatures); dotted curves,  $SF_1F_2$  three-phase lines; ●, [5, 16]; ▲, ▽, this work.

related to the  $\epsilon$ - $\delta$  phase transition in pure  $N_2$ . This phase line was shifted by a factor of two in temperature or pressure and a considerable amount ( $\sim 10\%$ ) of fluid He was dissolved in solid  $\epsilon$ - $N_2$ . As already mentioned the measuring techniques used were 'thermodynamic' methods.

Raman spectroscopy has proved to be a very valuable tool for investigations in a DAC. In the case of  $N_2$  at high pressures this technique could be used for detection of phase transitions and for gaining information about the crystal structure [8-10]. Knowledge about the position of the  $N_2$ -phases in the  $P$ - $T$  plane and their molecular vibrational modes is particularly important for the study of  $N_2$ -He, because it provides a unique characterization of the  $N_2$ -phases, which are involved in two-, three- or even four-phase equilibria.

At low temperatures and pressures the modification of  $N_2$  is the cubic and orientationally ordered  $\alpha$ -phase (space group  $Pa3$ ) [11], which possesses two Raman lines in the stretching region with a separation of about  $1.2\text{ cm}^{-1}$  [12]. On pressurizing to about 4 kbar one obtains the  $\gamma$ -phase [13], which is an orientationally ordered phase with tetragonal space group  $P4_2/mnm$  [14]. This shows one molecular vibration line with a slight asymmetry [9], which only appears below  $T = 50\text{ K}$  [15]. Further pressurizing gives  $\epsilon$ - $N_2$  at about 20 kbar [15]. This has been identified as an orientationally ordered rhombohedral structure with space group  $R\bar{3}c$  [10,16]. Here two distinct Raman stretching modes have been determined [15]. The intensity of the higher frequency peak  $\nu_1$  is less than that of the lower frequency peak  $\nu_2$ . Pressurizing once more gives at  $p \simeq 200\text{ kbar}$  [10, 15] a splitting of the lower frequency peak ( $\nu_2$ ). This has been attributed to a phase called  $\zeta$ , the structure of which is suggested to be a lower symmetry  $R3c$  variant of the  $R\bar{3}c$  space group [10].

Upon heating from the  $\alpha$ -phase at about  $T \simeq 35\text{ K}$  one reaches the  $\beta$ -phase, which has a hexagonal close-packed and orientationally disordered structure  $P6_3/mmc$  [17, 18]. In this phase one stretching mode has been observed. At higher temperature this phase is bounded by the melting line.  $N_2$ -fluid has one Raman peak, which is located 1 to  $3\text{ cm}^{-1}$  below that of  $\beta$ - $N_2$  [19]. Compression at room temperature gives a splitting [20] of the Raman peak at  $p \simeq 46\text{ kbar}$ , which is due to a phase transition from  $\beta$ - $N_2$  to  $\delta$ - $N_2$ , an orientationally disordered cubic phase with space group  $Pm\bar{3}n$  [21]. This phase has eight molecules per unit cell. The molecules at the corner and in the body of

the cell are spherically disordered. The six other molecules, which are situated in pairs at the faces of the conventional unit cell, have a disk-shaped orientational disorder in a plane normal to the face. The same Raman modes  $\nu_2$  and  $\nu_1$  mentioned earlier for the  $\epsilon$ -phase can be measured in the  $\delta$ -phase. Again the intensity of  $\nu_2$  is higher than that of  $\nu_1$ . The 'spherical' molecules give rise to  $\nu_1$  and the 'disk' molecules to  $\nu_2$ .

Grimsditch [22] used Brillouin scattering and reported that on pressurizing  $\delta$ - $N_2$  at room temperature a phase transition occurs at 165 kbar. Almost at the same time Reichlin *et al* [23] observed a splitting of the  $\nu_2$  peak above  $p \simeq 200$  kbar, which again was assigned to a new phase and was suggested to be a distortion of the  $\delta$ -phase. Zinn *et al* [19] reported that the Raman spectrum of this phase (called  $\eta$ - $N_2$ ) distinguishes itself in the vicinity of the  $\delta$ -phase by a shoulder at the high-frequency side of the  $\nu_2$  peak. At still higher pressures and at room temperature other distortions of the  $\delta$ -structure may appear [23, 24].

Cooling  $\delta$ - $N_2$  gives  $\epsilon$ - $N_2$  [5, 16]. The  $\delta$ - $\epsilon$  transition can be considered as a freezing out of the rotational disorder of the  $N_2$  molecules together with a small extension of the unit cell along one of the body diagonals, which causes a change of less than  $5^\circ$  in the angle between the axes [16].

To date no differences in the Raman stretching features between the  $\epsilon$ - and  $\delta$ -phases have been reported. Therefore, the first aim of this work was to investigate whether subtle changes of this kind exist, in order to make a unique characterization of the  $\delta$ - $\epsilon$  transition.

The second aim of this work was to provide new evidence for the  $\epsilon$ - $\delta$  shift in the  $N_2$ -He mixture by means of Raman spectroscopy, showing that it is possible to shift an interesting phenomenon to a more easily accessible  $pT$ -range by adding gas to the solid sample.

## 2. Experiment

The DAC system, which has been used in this experiment, is of the wedge type [25] and will be described elsewhere in more detail together with the optical system [26]. All experiments were carried out with polished Inconel 718 gaskets, which had been prepressed. Temperature control was accomplished through an electrical coil wound on a 'cold' finger, on which the right balance between heating (electrically) and cooling (by liquid  $N_2$ ) could be set. The complete DAC set-up was thermally isolated, so that the temperature gradients over the sample were very small (they are estimated to be less than 0.1 K). Temperature was measured with a copper-constantan thermocouple, one branch of which was mounted near the gasket and the other one was placed in melting ice.

The usual ruby technique was used to determine the pressure *in situ*. The pressure coefficient was taken as  $0.365 \text{ \AA kbar}^{-1}$  [27]. For the temperature dependence of the ruby lines we used the one in [28]. The ruby was illuminated with the 488 nm line of an argon laser at beam intensities of less than 3 mW.

The Raman spectra were obtained with the same laser as for the ruby luminescence at intensities of 200 to 300 mW. Before entering the DAC, the laser beam was focused by a system of lenses to a spot with a diameter of less than  $30 \mu\text{m}$ . This spot created a clear fluorescent mark on the first diamond. This could be viewed with the help of a microscope, so that it was possible to direct the laser spot to any desired position in the sample space. The forward-scattering geometry was chosen in order to make it

possible to place a microlens against the outer surface of the second diamond. In this manner the divergence of the outgoing Raman signal was considerably decreased before it passed an objective ( $f = 80$  mm) and subsequently the entrance slit of a double monochromator, provided with a photomultiplier tube. The measurements were performed with a resolution ranging from 0.7 to  $2\text{ cm}^{-1}$ . In figure 2 a Raman spectrum is shown of  $\delta\text{-N}_2$  at room temperature and  $p = 83.2$  kbar with a resolution of  $1.5\text{ cm}^{-1}$ . In the normal procedure the region between the  $\nu_2$  and  $\nu_1$  peaks was not scanned in order to save time.

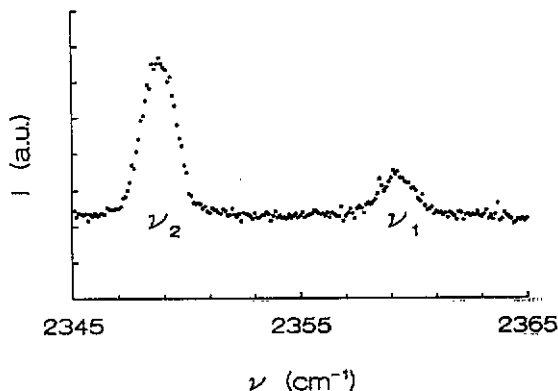


Figure 2. Raman spectrum of vibrons  $\nu_2$  and  $\nu_1$  in  $\delta\text{-N}_2$  at  $T = 294$  K and  $p = 83.2$  kbar.

The gases used were of research grade quality with a purity better than 99.999%. The sample space was loaded by pressurizing the anvil cell in a high-pressure vessel with a homogeneous gaseous mixture or with pure  $\text{N}_2$ . The mixture with a composition of  $9.15 \pm 0.10$  mol% He was previously prepared in a gas compressor. A composition of about 9% was chosen since this is near the estimated maximum solubility and, therefore, results in the best signal. A composition of, for example, 5% gives the coexistence of two solid phases. The anvil cell was closed at a pressure of 2 kbar and placed in the main frame for further pressurization of the sample.

The experimental method used was a combination of two types of quasi-isochoric scanning: pressure against temperature [25] ( $pT$ ) and Raman shift against temperature scanning ( $\nu T$ ). That means that the pressure or the Raman shifts of both the  $\nu_2$  and  $\nu_1$  vibrons were measured, varying the temperature in steps of about 1 K. After each step the temperature was stabilized for at least 15 min to obtain equilibrium, so one  $pT$  step took about 20 min, and one  $\nu T$  step about 30 min.

First,  $pT$  runs were performed (cooling as well as heating) in order to position the phase transition and to investigate the metastability. Then,  $\nu T$  runs were carried out (also both cooling and heating). Before and after each  $\nu T$  run the pressure was measured in order to check for consistency.

First, pure  $\text{N}_2$  was investigated along the  $\epsilon$ - $\delta$  transition line at 66, 80 and 90 kbar. Subsequently the  $\text{N}_2$ -He mixture with 9.2 mol% He was studied in the neighbourhood of the solid-solid-fluid three-phase line at  $p = 60$  kbar (just above the upper quadruple point).

In our samples metastability usually occurred in the cooling runs, while in the heating runs it was possible, in most cases, to follow the phase coexistence lines. In the latter case we were able to determine the  $pT$  coordinates of the phase lines, but

the Raman jumps were somewhat less easy to observe than in the case of a transition, which occurs suddenly due to metastability.

### 3. Results and discussion

In figures 3(a)–(d) plots are shown for pure  $N_2$  at about 80 kbar, in the neighbourhood of the  $\epsilon$ - $\delta$  transition and with decreasing temperature. In figure 3(a) the  $pT$  plot is shown; the drop in pressure is at about  $T = 153$  K. When heating we followed the coexistence line in a small range. Then the transition temperature was about 5 K higher. So the metastability turns out to be small. We have also performed  $pT$  scans at  $p = 66$  and 90 kbar, following the coexistence line over a few kelvins. The resulting points of the  $\epsilon$ - $\delta$  phase line are plotted in figure 1. It shows that they are consistent with earlier measurements [5, 16].

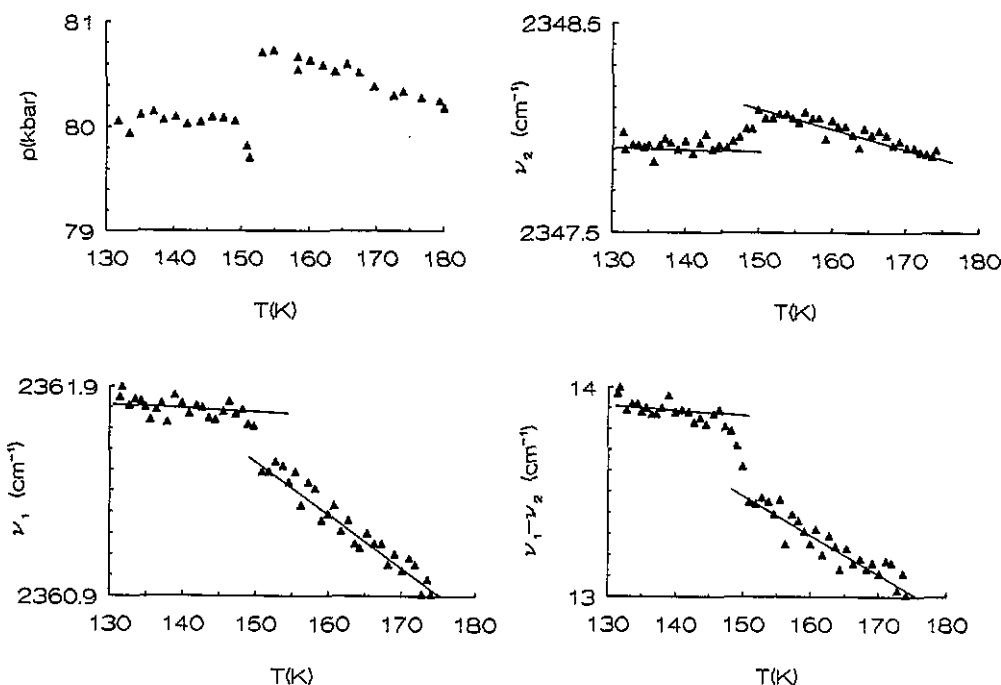


Figure 3.  $pT$  and  $\nu T$  scans at  $p \approx 80$  kbar around the  $\epsilon$ - $\delta$  phase transition in pure  $N_2$ : (a)  $pT$ ; (b)  $\nu_2 T$ ; (c)  $\nu_1 T$ ; (d) resulting  $(\nu_1 - \nu_2)T$ .

In figures 3(b)–(d) respectively the  $\nu_2 T$ ,  $\nu_1 T$  and  $(\nu_1 - \nu_2)T$  plots are shown; these were all measured in one run at  $p = 80$  kbar. In the three figures a jump can be noticed at  $T = 150$  K. This nearly coincides with the pressure drop in the  $pT$  plot. One should realize that these are different runs and due to the metastability the transition does not always occur at exactly the same temperature. The position of the lower frequency peak  $\nu_2$ , which is due to the 'disk' molecules, is lower in the  $\epsilon$ -phase than in the  $\delta$ -phase. That of the higher frequency peak  $\nu_1$ , which is due to the 'spherical' molecules is larger in the  $\epsilon$ -phase than in the  $\delta$ -phase. The jump at

$\nu_1$  is somewhat larger than for  $\nu_2$ . The jump at the transition is more evident if the difference ( $\nu_1 - \nu_2$ ) is plotted against  $T$  (figure 3(d)).

The same features have been measured with increasing temperature at  $p = 80$  kbar, although in this case the jumps were smeared out over a temperature range of a few kelvins. The same aspects have also been recorded at  $p = 66$  and 90 kbar in a cooling run. The jumps in ( $\nu_1 - \nu_2$ ) at the three mentioned pressures were on average  $0.45 \pm 0.05$   $\text{cm}^{-1}$ . This is the first time that the  $\epsilon$ - $\delta$  transition in pure  $\text{N}_2$  has been detected by vibrational Raman spectroscopy.

In the following we note the phases in the mixture by  $\epsilon^*$  and  $\delta^*$ , indicating that we are not dealing with pure  $\epsilon$ - $\text{N}_2$  and  $\delta$ - $\text{N}_2$ . In figures 4(a)-(d) the same sort of plots are shown for the mixture  $\text{N}_2$ -He (9.2 mol% He) at about  $p = 60$  kbar with decreasing temperature. Here, the metastability appeared to be 13 K. In the runs with increasing temperatures we followed the  $\epsilon^*\delta^*F$  three-phase line over a range of 8 K. The resulting point of this phase line is plotted in figure 1. It shows that this is consistent with earlier measurements [3].

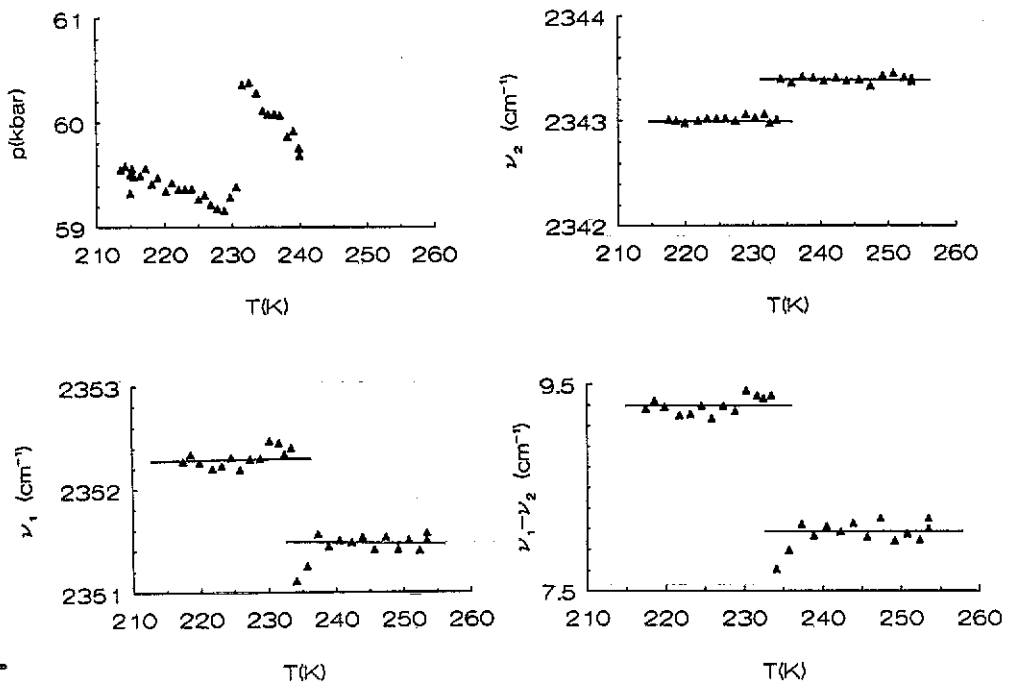
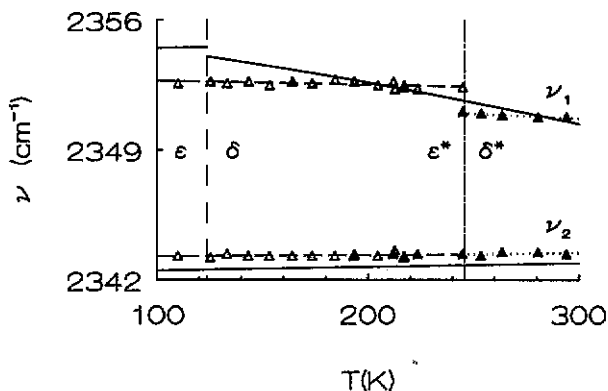


Figure 4.  $pT$  and  $\nu T$  scans at  $p \approx 60$  kbar around the  $\epsilon^*$ - $\delta^*$  phase transition in the mixture He- $\text{N}_2$ : (a)  $pT$ ; (b)  $\nu_2 T$ ; (c)  $\nu_1 T$ ; (d) resulting  $(\nu_1 - \nu_2)T$ .

In figures 4(b)-(d) the same qualitative behaviour can be noticed for both  $\nu_2$  and  $\nu_1$  and thus for  $(\nu_1 - \nu_2)$ . In  $\text{N}_2$ -He the jumps are even larger:  $\Delta(\nu_1 - \nu_2) \approx 1.3$   $\text{cm}^{-1}$ . In the mixture no other jumps in the frequency have been observed on further cooling to  $T = 110$  K. Particular attention was paid to the region of the  $pT$  plane where the  $\epsilon$ - $\delta$  transition should occur in the pure  $\text{N}_2$ . We have also searched with a resolution of 2  $\text{cm}^{-1}$  in other wavenumber ranges for more Raman peaks, but no other peaks were found. Careful measurements of  $\nu_2$  were carried out in the  $\epsilon^*$ - and  $\delta^*$ -phases with a

resolution of  $0.7 \text{ cm}^{-1}$ , in order to search for a weak shoulder at the high-frequency side, but nothing was found. So we have observed a phase transition and in both phases involved we have measured two Raman peaks. Apart from that the distance between the two peaks is about  $10 \text{ cm}^{-1}$  and the intensity of the lower frequency peak ( $\nu_2$ ) is much higher. This situation is present in pure  $N_2$  only at the  $\epsilon$ - $\delta$  transition, as described in the introduction. Moreover, we observe the same qualitative behaviour at the phase transition, as can be noticed in figures 3(b)-(d) and 4(b)-(d). Therefore, we conclude that the  $\epsilon$ - $\delta$  phase transition has been shifted to a higher temperature in the mixture.

Note that even if we had not observed any frequency jumps at the  $\epsilon$ - $\delta$  and  $\epsilon^*$ - $\delta^*$  transitions, the results would still prove the temperature shift. The existence of the same two Raman peaks in both phases involved as well as the fact that these spectra are similar to these of  $\epsilon$ - and  $\delta$ - $N_2$  is sufficient evidence. In that case a  $pT$  run is needed to detect the transition. In our case the observation of the jumps in the Raman spectra gives independent evidence of the temperature shift and thus for the solubility of fluid He in solid  $\epsilon$ - $N_2$ . In this case the  $pT$  runs, which we present here, are a check for consistency.



**Figure 5.** Raman shifts of  $\nu_2$  and  $\nu_1$  peaks against  $T$  at the isobar  $p = 60.0$  kbar: full lines represent  $\nu_2$  (lower) and  $\nu_1$  (upper) for pure  $N_2$ ; the triangles represent the results of the mixture  $N_2$ -He; open symbols in the  $\epsilon^*$ -phase, full symbols in the  $\delta^*$ -phase; the broken and dotted lines are linear fits through the data of the mixture. The two vertical lines mark the temperatures of the phase transitions in pure  $N_2$  and the mixture.

In order to look at these described phenomena in more detail, the positions of the  $\nu_2$  and  $\nu_1$  peaks have been plotted in figure 5 as a function of temperature at constant pressure ( $p = 60.0$  kbar). This figure has been based on measurements, in which the peak positions have been determined simultaneously with the pressure. In the pure component we have only performed measurements above 66 kbar, so the positions, indicated with full lines in the figure, are extrapolations of the high-pressure results. The measurements on the mixture have been performed at nearly constant pressure around  $p = 60$  kbar. Minor differences in pressure have been corrected with the known isothermal  $\nu p$  relations for the  $\epsilon$ -phase [10, 15] and the  $\delta$ -phase [20]. These corrected mixture data have been plotted in the figure, together with their linear fits. The  $\epsilon^*$  points have open symbols while the  $\delta^*$  points have full symbols. This figure shows that both in pure  $N_2$  and in the mixture the position of the  $\nu_2$  peak remains constant



at the isobar even at and beyond the  $\epsilon$ - $\delta$  or  $\epsilon^*$ - $\delta^*$  transition. This indicates that the drop in  $\nu_2$  in figures 3(b) and 4(b) is due to the pressure jump at the transition. It can also be seen that  $\nu_2$  for pure  $N_2$  is not very different from that of the mixture: the accuracy of the extrapolated pure  $N_2$  values is of the same order. This indicates that the forces of the surrounding molecules on the 'disk-shaped' molecules are almost similar in both cases.

In pure  $N_2$  the Raman shift of the  $\nu_1$  peak in the  $\delta$ -phase increases along the isobar with decreasing temperature. This suggests that the jump in going from  $\delta$  to  $\epsilon$  can be regarded as a consequence of the density jump at the isobar, while passing the  $\epsilon$ - $\delta$  transition (this is estimated to be 0.5% [16]). Both in  $\epsilon$ - $N_2$  and in  $\epsilon^*$ - $N_2$ -He almost no temperature dependence of the  $\nu_1$  peak position could be detected within measuring accuracy ( $0.3 \text{ cm}^{-1}$ ). The Raman shift was about  $1.8 \text{ cm}^{-1}$  lower in the  $\epsilon^*$ -phase than in the  $\epsilon$ -phase, confirming that a large amount of He has been dissolved in that phase [4]. In the mixture the position of the  $\nu_1$  peak in the  $\delta^*$ -phase is nearly the same as in  $\delta$ - $N_2$ , indicating that not much He has been dissolved in that phase, as found in [4].

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