

Phase behavior of the N₂-Ar system at high pressures: A Raman spectroscopy study

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We have studied the spectral behavior of the Raman Q branch of nitrogen in the binary system nitrogen-argon for nitrogen mole fractions of 0.04, 0.10, 0.25, 0.50, and 0.75 at room temperature. These results have been used to construct the phase diagram. The orientational degrees of freedom of N₂ play an essential role in the shape of the phase diagram. The melting pressure is almost linear dependent on composition although the melting pressures of the pure components are quite different. The amount of nitrogen dissolved in the argon lattice is significantly smaller than the amount of argon in β - and also in δ -N₂. The higher compression of the nitrogen molecule in the argon lattice is reflected in a higher frequency compared to β -nitrogen. The β^* – δ^* transition in N₂-Ar is shifted to higher pressures. The solubility in the δ phase increases rapidly from 4.7 to 6 GPa, but is restricted to about 30% since it is difficult for the argon atoms to occupy the c sites. As a result there is a large solubility gap compared to hard sphere systems with the same diameter ratio (nearly 1). No indication for compound formation was found. In contrast to the pure component, the linewidth in the solid phases strongly increases as a function of pressure.

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INTRODUCTION

In the past decade considerable effort has been put to reveal more insight in the phase behavior of binary mixed systems at high pressure.^{1,2} Theoretical predictions on hard sphere systems generally are used as an indication for the development of the phase diagram of binary mixtures. The ratio (α) of the molecular diameters is an important criterion for the phase behavior. For $\alpha > 0.94$ calculations^{3,4} predict a monotonic incline of the fluid-solid phase lines from the component with the lowest towards the component with the highest solidification pressure. Further, the Hume-Rothery rule states that, for hard spheres, a binary mixed solid is only obtained if $\alpha > 0.85$.

Simple binary mixtures, such as nitrogen with a noble gas, are interesting systems to gain knowledge about the phase behavior and in particular about mutual solubility in solids. Due to the almost spherical shape of the diatomic molecule and the fact that the interaction potential is well known, nitrogen has been the subject of thorough theoretical studies. In addition, extensive experimental research has been done on pure nitrogen and the phase diagram^{5,6} is well known. At room temperature nitrogen solidifies at 2.4 GPa while at 4.8 GPa the β -phase (hcp, orientationally disordered) transforms to the δ phase (cubic, space group Pm3n). The unit cell of the δ phase consists of eight molecules at two distinct sites. Two molecules are located at the corners and in the center of the cell (the a sites) and six are positioned in pairs at the faces of the cell (the c sites). The molecules at the a sites are orientationally disordered while the ones at the c sites rotate in a plane normal to the face.

Studies on the binary systems nitrogen-neon (with $\alpha = 0.73$ and Ne the smaller component) and nitrogen-xenon⁷ ($\alpha = 0.88$, N₂ the smaller component) revealed that the homogeneous mixed fluid region extends to much higher pressures than those of the pure systems. Furthermore, both systems stabilize in stoichiometric compounds at high pressure. Whereas the system N₂-Xe shows mutual solubility, Ne only

dissolves in β - and δ -nitrogen while N₂ does not dissolve in Ne.

Also for the system N₂-He ($\alpha = 0.59$, He the smaller component), a stoichiometric compound⁸ has been identified at room temperature. Further, He dissolves in ε -N₂ (Ref. 9), while no evidence for solubility of He in β - or δ -N₂ could be obtained.

The system N₂-Ar is of particular interest since, although nitrogen and argon have about the same size ($\alpha = 0.94$, Ar the smaller component) and the intermolecular interactions are similar, nitrogen is not completely spherical. Therefore, this system might provide information about the influence of the orientational degrees of freedom on the mutual solubility and other properties of the mixed system. In this respect it is interesting to note that, in contrast to the behavior of hard sphere systems of the same diameter ratio, the solubility of the smaller N₂ molecules in solid xenon is less than vice versa. Research on the nitrogen rich side at high pressure^{10,11,12} showed that the argon atoms dissolve substitutionally into the β as well as the δ lattice of nitrogen. The ratio of the integrated intensity of the two δ modes was found to decrease almost linear with the argon concentration. The authors¹³ explain this phenomenon by arguing that the argon atoms exhibit a preference for the a sites.

In this work, in order to study the development of the phase diagram, particularly for small nitrogen mole fractions, we studied the N₂-Ar system at room temperature, using Raman scattering. A detailed analysis of the obtained spectra will be given and the proposed phase diagram is discussed.

EXPERIMENTAL PROCEDURE

The experiments have been performed with a diamond anvil cell (DAC) of the wedge type.¹⁴ The mixtures (research grade nitrogen and argon with a purity of 99.9999%) were prepared in a gas compressor. To allow for proper mixing a mixing time of at least 60 h was taken before loading the cell. The estimated uncertainty in the mole fractions is less

than 0.01. For the Raman experiments, we used the 488 nm line of an argon-ion laser at beam intensities of 400 mW. The pressure in the DAC was determined using the well known ruby fluorescence technique with the scale of Mao *et al.*¹⁵ The absolute uncertainty in the pressure is estimated to be 0.03 GPa in the low pressure range. At high pressures (above 10 GPa) the absolute uncertainty could possibly be a bit higher (up to 0.1 GPa). In order to prevent heating of the ruby chip, during the pressure measurements the laser intensity was minimized.

The detection system consists of a double monochromator and a CCD detector. All measurements have been performed using backward scattering. The N₂ signals have been recorded with an entrance slit width of 20 μm , resulting in an instrumental width (Lorentzian) of 0.15 cm^{-1} and an absolute accuracy of 0.1 cm^{-1} . The spectra have been recorded as a function of pressure at ambient temperature (296 K) in the pressure range 0.2–15 GPa. We used 0.2–1.5 GPa pressure steps and time intervals of 1–3 h, depending on the size of the step. To determine the peak positions all Raman modes have been fitted by a single Lorentzian curve. The full width at half maximum (FWHM) has been calculated by subtracting the instrumental width from the width of the measured spectra.

EXPERIMENTAL RESULTS

In this work the vibrational spectra and phase behavior of the nitrogen-argon system have been investigated by Raman spectroscopy at high pressures in mixtures with nitrogen mole fractions of 0.75, 0.50, 0.25, 0.10, and 0.04. The vibrational frequencies at room temperature as a function of pressure are presented in Fig. 1. For comparison the data of neat nitrogen (Refs. 16,17, and 18) are also given (solid lines)

At low pressures, only a single Raman signal has been observed for all compositions. The frequencies first decrease with pressure and then increase via a minimum at about 0.13 GPa and the redshift changes into a blueshift. The values coincide within experimental accuracy with those of pure nitrogen. The behavior of the linewidth is similar to that of the frequency. Up from 0.3 GPa, the vibrational linewidth (see Fig. 2) increases with pressure as in the pure system but for the mixtures, the values are somewhat higher, in particular for the 25 and 50 mole % samples. The fluid-solid transition has been observed visually for all mixtures except for those with very low nitrogen mole fractions ($x=0.04$ and $x=0.10$). For increasing nitrogen fractions, the coexistence region is entered at 1.7, 2.1, and 2.4 GPa. In this region the Raman signal consists of two peaks as can be seen in Fig. 3. The intensity ratio changes when the laser spot is focussed on a different point in the sample space. Hence, the two modes originate from two different phases. At slightly higher pressures only one single peak, associated with a solid phase is left.

In the pure system at the fluid- β transition, the frequency is shifted 0.95 cm^{-1} upwards and the linewidth is reduced considerably. A frequency jump also occurs at the fluid-solid transition in the binary systems. The shift is only slightly larger for $x=0.75$ and $x=0.50$, but for $x=0.25$ the shift is

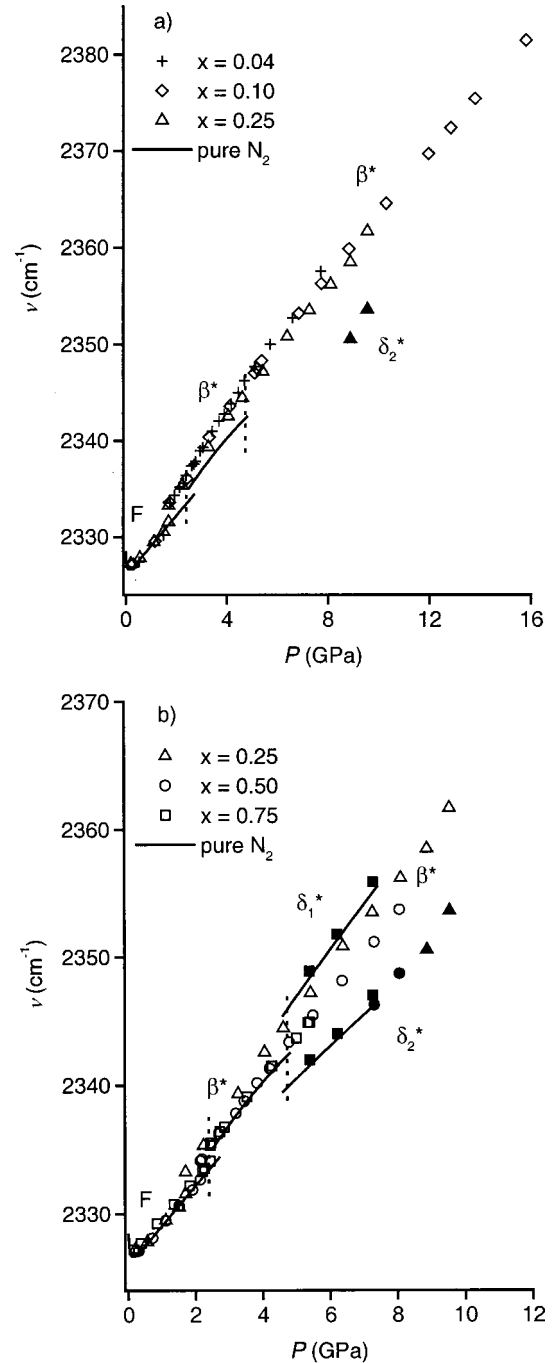


FIG. 1. (a), (b) Vibrational frequency versus pressure at 296 K. Plus signs: $x=0.04$, diamonds: $x=0.10$, triangles: $x=0.25$, circles: $x=0.50$, and squares: $x=0.75$. Full symbols represent the δ^* phase, solid lines: pure nitrogen. The dashed vertical lines indicate phase transitions in pure N₂.

intermediate. Further, the linewidth of the solid is smaller than that of the fluid as in pure N₂ but for all mixtures, the spectra are much broader.

The behavior at high pressures is different for different compositions. Let us first look at $x=0.75$. In this case the linewidth shows very little broadening with pressure in the β phase. At about 5.4 GPa another transition occurs (Fig. 4). The spectrum now consists of two additional vibrational

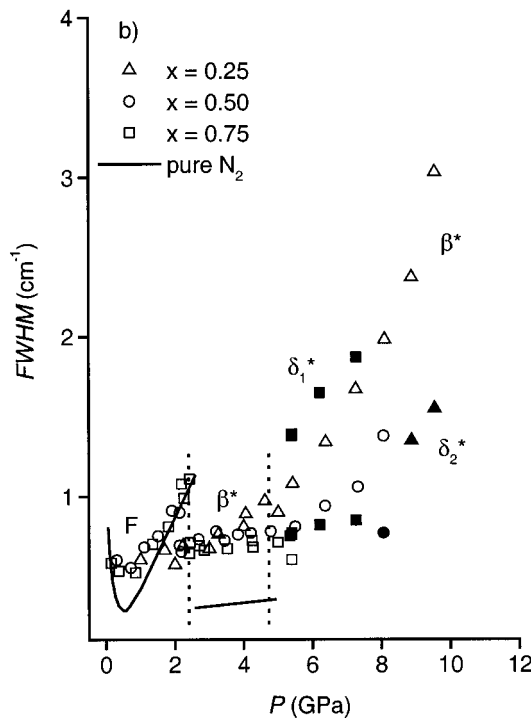
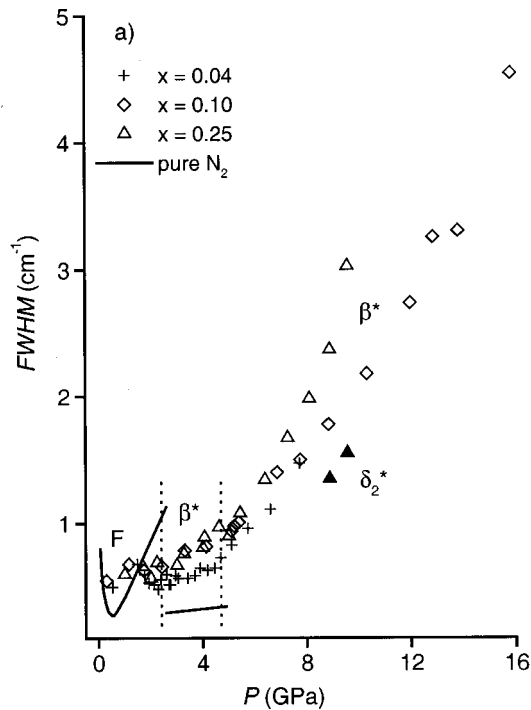


FIG. 2. (a), (b) FWHM versus pressure at 296 K. Symbols: see Fig. 1.

modes, referred to as δ_1^* and δ_2^* as will be explained later. The solid-solid equilibria could not be observed visually since all solids appeared transparent through the microscope. The ratio of the integrated intensities of the δ_1^* and δ_2^* modes is about $\frac{1}{5}$ compared to $\frac{1}{3}$ in pure nitrogen. This ratio does not change when the position of the laser spot is varied, hence both modes belong to the same phase. Comparing the two modes, the δ_1^* signal is about twice as broad as δ_2^* . At

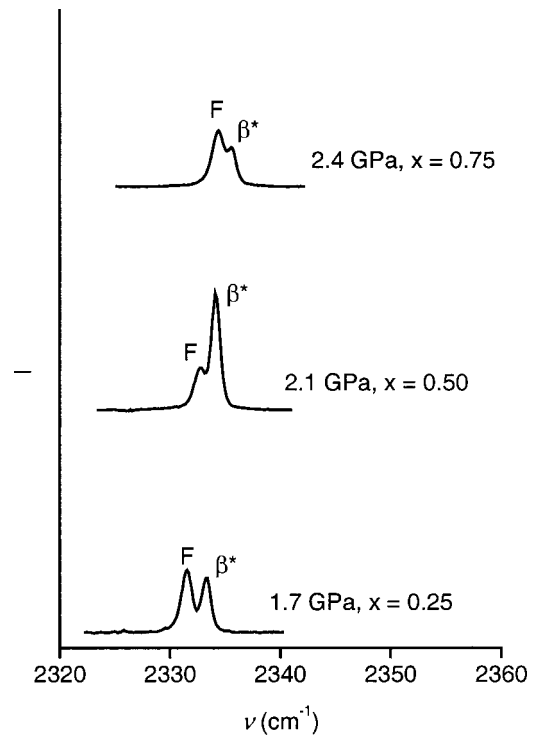


FIG. 3. Raman spectra of nitrogen in N₂-Ar at room temperature, in the fluid-solid coexistence region.

increasing pressure, the β^* peak disappears at 5.4 GPa. Further, the FWHM of the δ_1^* peak increases strongly with pressure, whereas the width of the δ_2^* mode barely broadens as in pure nitrogen.

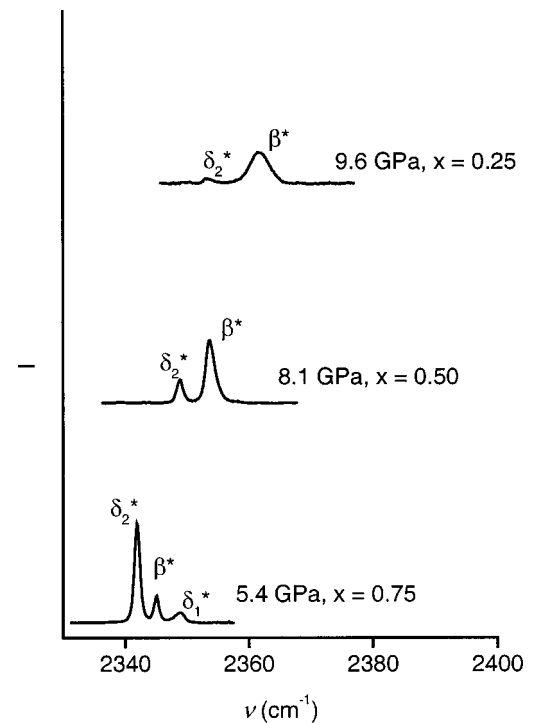


FIG. 4. Raman spectra of nitrogen in N₂-Ar at room temperature, in the solid-solid coexistence region.

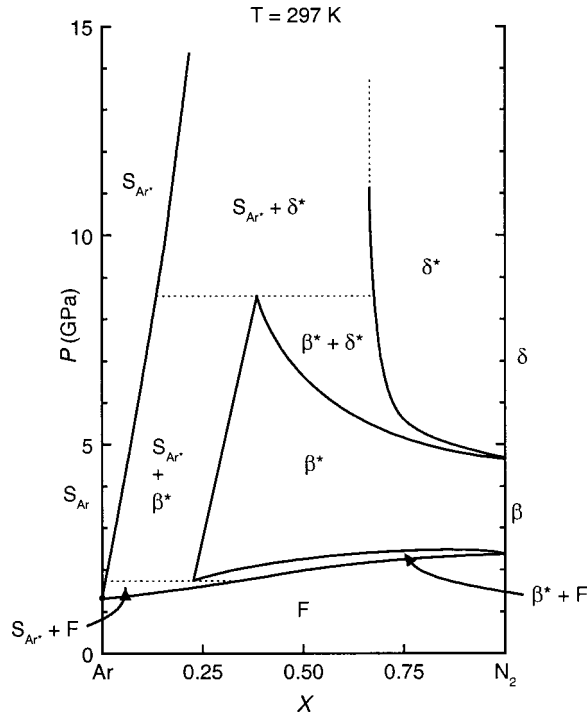


FIG. 5. Proposed p - x diagram at 296 K for the N_2 -Ar system. Solid lines: 2 phase lines, dotted lines: 3 phase lines.

Looking at the results for the sample with $x=0.50$, up to 6 GPa the behavior of the linewidth is comparable with $x=0.75$ but for higher pressures the incline increases strongly. Further, an additional mode appears at about 7.5 GPa. The main peak position and the FWHM coincide within experimental accuracy with δ_2^* of the $x=0.75$ mixture at comparable pressures. Up to the highest pressures investigated, both modes (β^* and δ_2^*) are present. When the position of the laser spot is varied, the intensity ratio of the two peaks changes. In the $x=0.25$ case already up from 3 GPa the widths increase strongly and the δ_2^* mode now appears at 8.8 GPa. For the $x=0.10$ and $x=0.04$ samples only a single peak is present up to the highest pressures investigated (15 GPa). The pressure dependence of the frequency above the fluid-solid transition is stronger compared to the other mixtures. Furthermore, for both samples the pressure dependence of the width grows with pressure. In the $x=0.10$ case up to about 5 GPa the FWHM is similar with the $x=0.25$ sample but above this point the relative increase is less strong. For $x=0.04$ the widths are small compared with all other samples and the increase with pressure is minor up to 5 GPa but similar to $x=0.10$ after this point.

CONSTRUCTION OF THE PHASE DIAGRAM

Based on the experimental results, a cross section of the proposed phase diagram at 296 K for the N_2 -Ar system is presented in Fig. 5. The procedure used in the construction is explained in the following.

For all investigated N_2 -Ar compositions, the fluid turned out to be homogeneous. At room temperature, argon solidifies at 1.3 GPa. For nitrogen, this transition occurs at 2.4

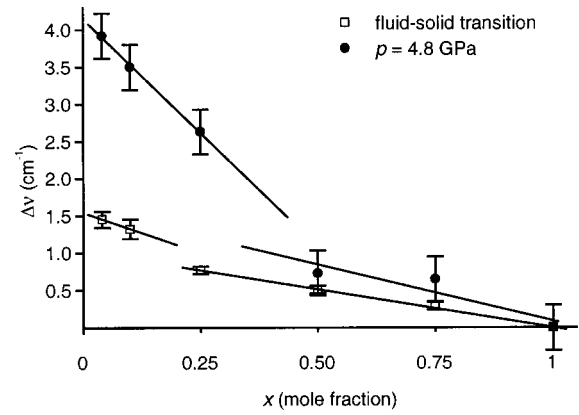


FIG. 6. Squares: frequency shift ($\nu_{\text{solid}} - \nu_F$) relative to the pure system, in the two-phase region just above the fluid area (F). Circles: frequency difference compared with the pure system ($\nu_{\text{solid}} - \nu_\beta$) at 4.8 GPa, lines: guides for the eye.

GPa. In a binary mixture, a two-phase region must exist in which the fluid and the solid coexist.

Considering the lower solidification pressure of argon and the fact that the diameter ratio $\alpha=0.94$ to 0.95 it is expected that the fluid-solid transition pressure is a monotonically increasing function of the nitrogen concentrations. Indeed the coexistence region is entered at 1.7, 2.1, and 2.4 GPa for $x=0.25$, 0.50, and 0.75, respectively.

Also, given the fact that $\alpha > 0.85$ considerable mutual solubility is expected; argon atoms dissolve substitutionally into the hcp- β and, at higher pressures, into the cubic δ lattice of nitrogen, forming lattices (β^* and δ^*) with a close resemblance to the pure system. Conversely, the nitrogen molecules are expected to dissolve in the argon fcc lattice, indicated as S_{Ar^*} .

The circles in Fig. 6 represent the difference between the frequency in the mixed solid and in the pure system ($\nu_{\text{solid}} - \nu_\beta$) at 4.8 GPa as a function of the composition. All points have been obtained by linear interpolation between the experimental points and the errors are indicated in the figure. The jump in the frequency at the fluid-solid transition of the mixture ($\nu_{\text{solid}} - \nu_F$) minus that in the pure system is represented by squares. For the mixtures with $x=0.04$, $x=0.10$, and $x=1$ no spectra of coexisting fluid and solid have been recorded. In order to calculate the relative shift, a linear extrapolation of the fluid and the solid line has been applied. For all other mixtures, we made use of the spectra of the coexisting phases and here the errors are smaller than the size of the symbols. From the figure it is clear that, at the fluid-solid transition, for $x \leq 0.10$ the dependence on the composition is different compared to higher values of the nitrogen concentration. For the shift at 4.8 GPa, the breakpoint is situated between $x=0.25$ and $x=0.50$. It is assumed that this behavior is caused by a difference between the vibrational frequency of the nitrogen molecule in the fcc and in the hcp lattice. In that case, for $x=0.25$, first at 1.7 GPa a transition takes place to the β^* phase and then at higher pressures the transition from β^* to S_{Ar^*} . For lower x values we have a transition to the two-phase region $F + S_{Ar^*}$ (no data available for this small region) and, at slightly higher

pressures the three phase line F - β^* - S_{Ar^*} is crossed. At low pressures, the left β^* boundary must then be situated between $x=0.10$ and $x=0.25$ while at 4.8 GPa it is situated at higher nitrogen concentrations.

Another indication for the location of the β^* and also for the S_{Ar^*} boundary is given by the behavior of the linewidth in the $x=0.10$ and $x=0.25$ samples. Figure 2(a) shows that up to about 7 GPa the widths are similar while above this point the increase with pressure is less strong in the $x=0.10$ case. This indicates a transition from the two-phase area $S_{\text{Ar}^*} + \beta^*$ to the S_{Ar^*} area. When both boundaries are steep in the two phase region the amount of S_{Ar^*} increases slowly with pressure. Therefore the widths do not change abruptly at the transition and the assigned location of the boundaries should be considered as an indication.

The location of the upper β^* boundary can be established with more precision since in this case a change from β^* to $\delta^* + S_{\text{Ar}^*}$ is involved and the different modes can be distinguished without difficulties. Regarding the δ phase, the argon atom shows a preference for the a sites and will therefore occupy these sites (almost) completely for argon contents larger than 25%. Thus for compositions with $x < 0.75$ only the δ_2^* mode is expected to be present.

Above 8.5 GPa, for $x=0.25$, the spectrum consists of the combined δ_2^* and the S_{Ar^*} signal. This is the highest pressure at which β^* exists. Therefore the three phase line $S_{\text{Ar}^*} - \beta^* - \delta^*$ must be situated at about this pressure. For $x=0.50$ the two phase $\beta^* - \delta^*$ region is entered at about 6.5 GPa since at this point not only the β^* mode but also the double δ^* signal is present. Finally, for $x=0.75$ this two-phase area is reached at 5.4 GPa. At slightly higher pressures the lower boundary of the δ^* region is crossed since up from 5.5 GPa the β^* signal is not longer present but we only have both delta modes.

In our experiments with $x=0.50$ the highest pressure at which the spectra were recorded was just below the upper three phase line ($S_{\text{Ar}^*} + \beta^* + \delta^*$). However, we can conclude that the left border of the δ^* region must be steep since Westerhoff and Feile¹⁰ found coexisting β^* and δ^* phases for $x=0.59$ up to the highest pressures investigated (13 GPa).

DISCUSSION AND CONCLUSIONS

If we define the molecular diameter as the distance at which the exponential-6 potential equals 300 K, using the data of Ref. 19, α equals 0.94 for nitrogen-argon, argon being the smaller component. For $\alpha > 0.94$ calculations^{3,4} for hard sphere systems predict a monotonic incline of the fluid-solid phase lines towards the component with the highest solidification pressure, a small coexistence region and mutual solubility in the solid phase for all concentrations. Consistent with the above, and in agreement with other work¹² on the nitrogen-rich side of the phase diagram, we have found an incline up to high nitrogen concentrations. The fact that for $x=0.75$ the measured pressure at which the solidification starts is a little higher than the solidification pressure of nitrogen is likely an indication of metastability as is the case in the pure systems. On the basis of the size of the

molecules the melting pressure of nitrogen would be similar to that of argon. Due to the orientational possibilities it is much higher (almost twice as high) and the structure of solid N₂ is different from that of solid argon. In the case of hard spheres this difference in melting pressure would result in a eutectic point. Thus, it seems that the orientational degrees of freedom do not have much influence on the fluid-solid transition. In the case of nitrogen-xenon and nitrogen-neon⁷ the fluid region is considerably extended to higher pressures and the mutual solubility in both solid phases is small. In these cases the fluid phase is favored by both the larger orientational and configurational entropy. In β -nitrogen the molecules rotate freely and since argon dissolves easily in β -nitrogen, the fluid phase is not longer favored. For high argon concentrations the nitrogen lattice is too much distorted to allow free rotation of the molecules.

In addition, no fluid-fluid demixing has been observed, in contrast to N₂-CH₄ (Ref. 20) which has about the same diameter ratio.

Considering the fact that the molecular diameter of argon is only slightly smaller than that of nitrogen one would expect the solubility of N₂ in Ar to be almost equal to the solubility of Ar in N₂. However, the experiments show that the amount of argon atoms dissolving in β - and also in δ -N₂ is significantly larger than the amount of nitrogen dissolving in the argon fcc lattice. The lattice parameter of argon is smaller thus hindering the rotation of the nitrogen molecules and apparently the hcp structure is more suitable for rotating molecules, considering the fact that nitrogen crystallizes in this structure. The higher compression of the nitrogen molecule in the argon lattice is also reflected in the higher frequency compared to β nitrogen (Fig. 6). Hence, not only the diameter ratio, the Van der Waals interactions and the Coulomb forces, but also the orientational degrees of freedom play an important role in the solubility in solids at high pressure.

The $\beta^* - \delta^*$ transition in N₂-Ar is shifted to higher pressures, in agreement with the work in Refs. 10 and 12. Previous studies⁷ revealed similar results for the N₂-Ne system whereas for N₂-Xe the $\beta^* - \delta^*$ transition is shifted to slightly lower pressures. It should be mentioned that both the molecular diameters of Ne and Ar are smaller than that of nitrogen while Xe is larger. The solubility in the δ phase increases rapidly as a function of pressure from 4.7 to 6 GPa but is probably more or less constant at still higher pressures. As a result there is a large solubility gap in the system at high pressures. The amount of argon is then about 35%. The solubility limitation is probably related to the fact that the sphere sites are occupied preferentially¹³ due to a decrease in volume and energy of the system. It is less advantageous to occupy the disk sites. That still some disks are occupied is probably an entropy effect.

Stoichiometric compounds have been reported for the N₂-Ne as well as the N₂-Xe system.⁷ As expected, since nitrogen and argon have about the same size, no indication for a compound was found in this work.

Regarding the widths of the spectra, in the fluid phase these are somewhat higher compared with the pure system, especially for $x=0.25$ and $x=0.50$. This effect is probably

caused by composition broadening.²¹ In all solid phases, the slope in the FWHM versus pressure plot increases for all compositions. The origin of this phenomenon is not known but it is suggested that the broadening is associated with more variation in the local composition around the molecules leading to more variation in vibrational frequencies, i.e., line broadening, and possibly also to an increase of the correlation time.²² For $x=0.10$ and $x=0.25$ the increase is largest. It is supposed that this additional effect is due to the fact that the frequencies in the fcc and the hcp lattice lie close together and hence, result in a line broadening rather than in two discrete peaks.

Also in the δ^* phase we find an increase in the width (δ_2^*) as function of pressure. Here the effect is less obvious, since the highest pressure obtained with the 50 and 75 mole % mixtures is about 8 GPa and we only have few data points in the δ^* phase. But when the results for the various

mixtures are compared, the broadening with pressure becomes clear. The same effect has been mentioned in Ref. 10 for the mixture with $x=0.79$. These authors also claim an asymmetry—a shoulder at the high frequency side of δ_2^* —which was not found in our work. For the 75 mole % sample, the ratio of the integrated intensities of the δ_1^* and δ_2^* modes is about $\frac{1}{5}$. Hence, about 50% of the spheres is occupied by argon atoms, whereas in the case of an equal (random) distribution these values would be $\frac{1}{3}$ and 25%. Thus, as already stated by the authors of Refs. 10 and 11, the argon atoms show a strong preference for the a sites. The δ_1^* signal is about twice as broad as that of δ_2^* whereas in pure nitrogen the widths are comparable. The origin of this feature is not yet fully understood but the altered environment in the mixed system obviously plays an important role. In this work, as expected, since nitrogen and argon have about the same size, no indication for a compound was found.

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¹P. Loubeyre, M. Jean-Louis, R. LeToullec, and L. Charon-Gérard, Phys. Rev. Lett. **70**, 178 (1993).

²M. S. Somayazulu, L. W. Finger, R. J. Hemley, and H. K. Mao, Science **271**, 1400 (1996).

³G. T. Kranendonk and D. Frenkel, J. Phys.: Condens. Matter **1**, 7735 (1989); Mol. Phys. **72**, 679 (1991).

⁴D. Kofke, Mol. Simul. **7**, 285 (1991).

⁵A. S. Zinn, D. Schiferl, and M. Nicol, J. Chem. Phys. **87**, 1267 (1987).

⁶W. L. Vos and J. A. Schouten, J. Chem. Phys. **91**, 6302 (1989).

⁷M. E. Kooi and J. A. Schouten, Phys. Rev. B **60**, 12 635 (1999).

⁸W. L. Vos, L. W. Finger, R. J. Hemley, J. Z. Hu, H. K. Mao, and J. A. Schouten, Nature (London) **358**, 46 (1992).

⁹M. I. M. Scheerboom and J. A. Schouten, J. Phys.: Condens. Matter **3**, 8305 (1991).

¹⁰T. Westerhoff and R. Feile, Phys. Rev. B **54**, 913 (1996).

¹¹M. E. Kooi and J. A. Schouten, J. Low Temp. Phys. **111**, 349 (1998).

¹²M. E. Kooi and J. A. Schouten, Phys. Rev. B **57**, 10 407 (1998).

¹³E. P. van Klaveren, J. P. J. Michels, and J. A. Schouten, Phys. Rev. B **61**, 9327 (2000).

¹⁴J. A. Schouten, N. J. Trappeniers, and L. C. Van den Bergh, Rev. Sci. Instrum. **54**, 1209 (1983).

¹⁵H. K. Mao and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

¹⁶B. Lavarel, B. Oksengorn, D. Fabre, R. Saint-Loup, and H. Berger, Mol. Phys. **75**, 397 (1992).

¹⁷M. I. M. Scheerboom, J. P. J. Michels, and J. A. Schouten, J. Chem. Phys. **104**, 9388 (1996).

¹⁸M. E. Kooi, L. Ulivi, and J. A. Schouten, Int. J. Thermophys. **20**, 867 (1999).

¹⁹F. del Río, J. E. Ramos, A. Gil-Villegas, and I. A. McLure, J. Phys. Chem. **100**, 9104 (1996).

²⁰J. A. Schouten, M. G. E. van Hinsberg, M. I. M. Scheerboom, and J. P. J. Michels, J. Phys.: Condens. Matter **6**, A187 (1994).

²¹M. I. M. Scheerboom and J. A. Schouten, Phys. Rev. E **51**, 2747 (1995).

²²M. E. Kooi, J. P. J. Michels, and J. A. Schouten, J. Chem. Phys. **112**, 1404 (2000).