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Vos, W.L.; Schouten, J.A.

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Solubility of Fluid Helium in Solid Nitrogen at High Pressure

Willem L. Vos and Jan A. Schouten

Van der Waals Laboratory, University of Amsterdam, 1018 XE Amsterdam, The Netherlands

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Experiments carried out at high pressures show that the transition of completely ordered solid ϵ -N₂ to orientationally disordered δ -N₂ is shifted over a factor of 2 in temperature or pressure due to the admixture of fluid helium. Between 5.4 and 11.0 mole% helium can be dissolved in ϵ -N₂, favoring the occurrence of this ordered phase. In contrast, the transition from disordered δ -N₂ to disordered β -N₂ is not shifted at all.

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It is only recently that mixtures of molecules have been investigated at high density,¹ although their properties cannot be derived from those of pure substances. Both experimental and theoretical results have been reported on systems such as hydrogen-helium, but these studies are mainly concerned with the phase separations of fluid-fluid and solid-fluid. No investigations have been reported concerning the solubility of a gaseous component in a molecular crystal. Solubility of fluids in solids can be of great interest for the study of the solid state as well as for experiments on solids where gases are used as a pressurizing medium, especially if these solids show ordering transitions.

In this Letter, we present the first experimental investigation of the solubility of a fluid in a solid, in the simple system nitrogen-helium. The experiments were performed at high pressure by comparing the phase transitions in the mixture at various compositions with those in pure N₂. A striking feature of the mixture is the shift of the ϵ - δ transition of pure N₂ (see Fig. 1) by a factor of 2 in temperature or pressure, while the transition δ - β is not affected at all. We show that this shift is due to the solubility of helium in the ϵ phase, which amounts to 5.4–11.0 mole%. We also suggest that the transition from the ϵ phase to an unknown high-pressure phase of nitrogen at about 220 kbar is shifted downward by a factor of about 3 in pressure if some helium is added. The large shift of phase transitions is of interest for modeling the heavy planets.² Among others, the addition of helium might shift the metallization pressure of hydrogen.

Nitrogen is a well studied molecular solid. In spite of its simple molecular structure, it shows a complicated phase diagram (see^{3,4} Fig. 1). The β , δ , and ϵ phases are relevant for this investigation. β -N₂ is a hexagonal phase, where the molecules are disordered.⁵ In the cubic δ phase, the molecules occupy two different lattice sites, on which they can rotate freely or rotate in a plane.⁶ The ϵ phase has a rhombohedral structure, with all molecules having fixed orientations.⁷ Helium, in contrast, does not show any phase transition, except melting, in the p and T range relevant to this study.⁸

An investigation in our laboratory of the system nitrogen-helium revealed that along the solid-fluid-fluid

three-phase line there are two solid-solid-fluid-fluid quadruple points at 34 and 58 kbar (Ref. 9) that correspond to solid-solid transitions in the N₂-rich phases. This can be seen in Fig. 2, where the N₂-rich solids are named β^* , δ^* , and ϵ^* and the distinction between the N₂-rich fluid F_1 and the He-rich fluid F_2 is left out for clarity.¹⁰ The two quadruple points are related to solid-solid-fluid triple points along the melting line of pure nitrogen. However, only one such triple point is known to date, the δ - β -fluid triple point³ at 555 K and 80 kbar (see Fig. 1).

It was shown that the β^* - δ^* - F_1 three-phase line moves from the lower quadruple point to higher temperature and pressure.¹¹ We suggested¹¹ that it was connected to the known δ - β -fluid triple point of nitrogen, though the three-phase line deviated from the δ - β transition line. From phase-theoretical considerations, it then follows that helium is dissolved in either the β phase, the δ phase, or both. If no solubility had occurred, the δ - β

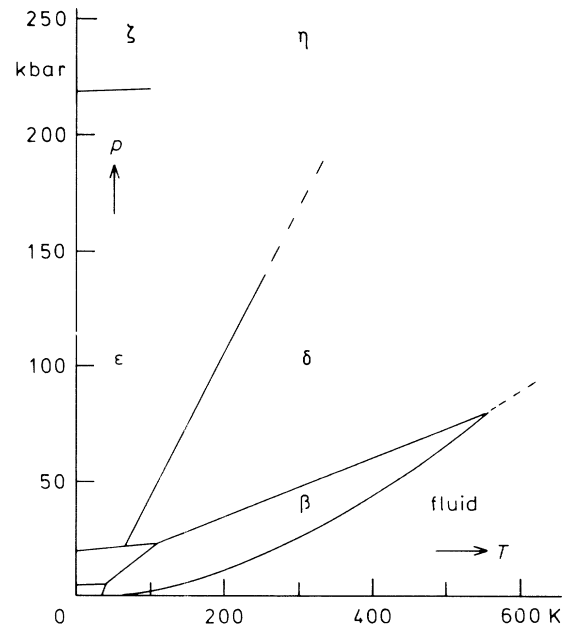


FIG. 1. Phase diagram of nitrogen (Refs. 3 and 4).

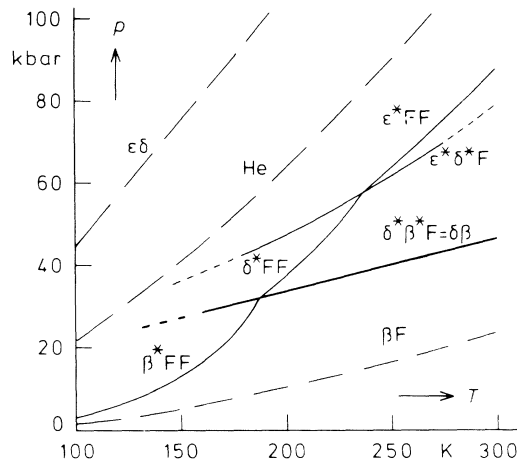


FIG. 2. p - T projection of the phase diagram for nitrogen-helium. Dashed lines are phase lines of the pure components, thin continuous lines are three-phase lines of the mixture, and the thick line is a phase line of both N_2 and N_2 -He. β , δ , and ϵ are solid N_2 phases, with an asterisk denoting solid phases in the mixture, He is the helium melting line, and F denotes fluid phase.

transition would not be shifted. However, because the uncertainty in the position of the δ - β transition of pure N_2 was rather large, we have redetermined the phase diagram of N_2 .⁴ It turns out that the β^* - δ^* - F_1 and β^* - δ^* - F_2 lines in the nitrogen-helium system now coincide within the experimental accuracy with the δ - β transition of pure nitrogen (see Fig. 2). Therefore, helium does not dissolve in either β - N_2 or δ - N_2 near this transition. Furthermore, we can conclude that β^* corresponds to β - N_2 and δ^* to δ - N_2 .

The δ^* - ϵ^* - F_1 line moves from the upper quadruple point to higher temperature and pressure. Since its slope is steeper than that of the melting line of nitrogen, it must be related to a triple point at a much higher pressure than 80 kbar. Since the phase diagram of pure N_2 does not show a phase line near the δ^* - ϵ^* - F_1 and δ^* - ϵ^* - F_2 three-phase lines,³ there are three possibilities: (i) The three-phase lines correspond to a known phase transition of N_2 that is considerably shifted due to solubility of He; (ii) the phase lines correspond to a transition where a stoichiometric solid mixture (SSM) of N_2 and He is formed; and (iii) the phase lines correspond to an unknown phase transition of N_2 . By SSM we mean a solid that exists only at a certain fixed composition. To solve this problem, experiments were performed in order to investigate the nature of the δ^* - ϵ^* - F_1 and δ^* - ϵ^* - F_2 transitions. The experiments are described below. First, the phase diagram of pure nitrogen was further explored to check if δ^* - ϵ^* - F_1 and δ^* - ϵ^* - F_2 are caused by an unknown transition. Subsequently, experiments were performed on mixtures with helium contents of 2.0, 5.4, 11.0, and 31.1 mole% to investigate the possibility of an SSM and to determine the maximum solubility of He in

solid N_2 .

The experiments were carried out in a diamond-anvil cell (DAC) described previously.¹² The usual ruby pressure sensor was used with a pressure coefficient of 0.0366 nm/kbar (Ref. 13) and a temperature coefficient measured by ourselves.¹⁴ The DAC was loaded with samples of known composition. The temperature was measured with a calibrated platinum resistance thermometer with an accuracy better than 0.5 K. The accuracy in pressure is estimated to be 0.3 kbar below room temperature and up to 1 kbar at temperatures up to 550 K, but the relative value of the pressure can be determined much better. The experimental methods used were isochoric temperature scanning¹⁵ and visual observation. In a (quasi) isochoric temperature scan, the pressure is measured as a function of temperature and a phase transition manifests itself as a pressure jump or as a sudden increase of the pressure. This method is suitable for detection of first-order transitions in pure substances and of three-phase lines in binary mixtures. With visual observation, phase transitions involving two solid phases could not be detected.

With pure nitrogen, two p - T scans were performed at about 48 and 84 kbar from 135 to 330 K. The former yielded only a phase transition corresponding with the δ - β transition and the latter yielded only a transition corresponding with the ϵ - δ transition (see Ref. 4). Both transitions showed metastability: The ϵ - δ transition showed a difference of 10 K between the cooling and the heating transition temperature, while the δ - β transition showed a difference of 0 to 20 K. No new phase transitions have been discovered in the region of the three-phase lines. It must be noted that this technique is sensitive enough to detect pressure jumps as small as 200 bars, corresponding to a change in volume of the order of 0.1%. As will be described later, the pressure jumps along the three-phase lines are more than 1 kbar. Therefore, we can exclude the third possibility mentioned above. It is now clear that the δ^* - ϵ^* - F_1 and δ^* - ϵ^* - F_2 three-phase lines correspond to a transition line in pure nitrogen in another part of the phase diagram or to a stoichiometric solid mixture. This proves that helium dissolves in solid nitrogen (but not in the β or δ phases). The most likely candidate is the ϵ phase.

We will now describe the experiments that were carried out to determine the maximum solubility of helium and to discriminate between possibilities (i) and (ii): the formation of a mixed ϵ crystal in a composition interval or a crystal that exists only at a certain composition (SSM). T - x cross sections are very useful to elucidate the results (x denotes composition). In Figs. 3(a) and 3(b) the schematic T - x plots are given for case (i) at pressures below and above the quadruple point, respectively. In Figs. 3(c) and 3(d), the plots are for case (ii). In Figs. 3(a) and 3(c), 1-5 denote the temperatures of the following phase equilibria, respectively: ϵ - δ transition, δ^* - ϵ^* - F_2 or δ^* -SSM- F_2 , δ^* - F_1 - F_2 , β^* - δ^* - F_1 , and

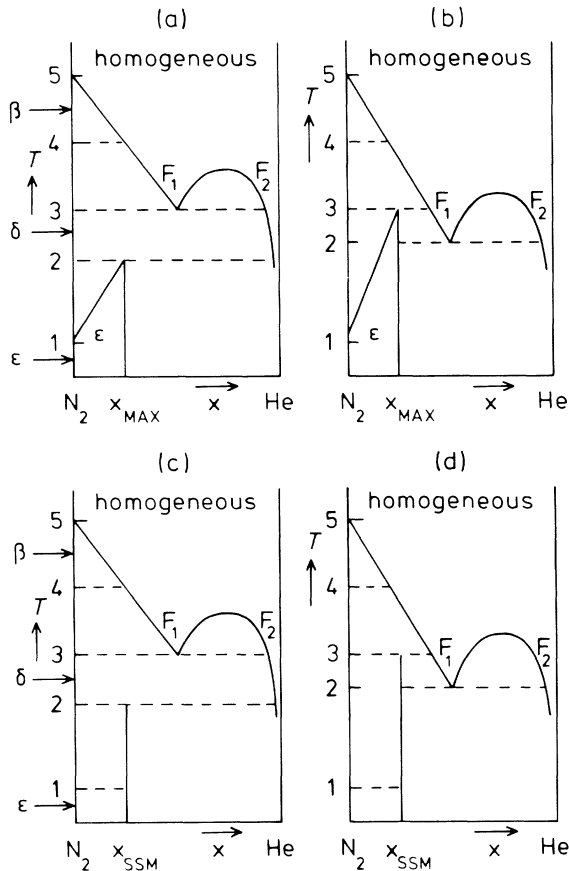


FIG. 3. Schematic isobaric cuts through the phase diagram of nitrogen-helium. See text for explanation.

the melting point of nitrogen. In Figs. 3(b) and 3(d), the same transitions are denoted, except for 2 and 3 which depict the $\epsilon^*-F_1-F_2$ or SSM- F_1-F_2 and $\delta^*-\epsilon^*-F_1$ or δ^* -SSM- F_1 three-phase equilibria. At high temperature, the mixture is in the homogeneous fluid phase. The composition of the nitrogen-rich fluid F_1 at the $\delta^*-F_1-F_2$ and $\epsilon^*-F_1-F_2$ equilibria is about 40 mole% helium. In Fig. 3, it is assumed that the composition x_{SSM} of the SSM and the maximum solubility x_{max} in ϵ -N₂ do not vary with temperature and that the phase boundary between pure ϵ^* and the two-phase region $\epsilon^*-\delta^*$ varies linearly with composition and temperature. Note that these last two assumptions are not essential. For the case of an SSM, it is assumed that no helium is dissolved in ϵ -N₂.

With the mixture containing 31.1 mole% helium, the solid-fluid-fluid transitions could clearly be observed visually both below and above the quadruple-point pressure. This means that the composition x is larger than x_{max} . If $x < x_{max}$, the solid-fluid-fluid transition can be observed only at pressures below the quadruple-point pressure [compare Figs. 3(a) and 3(b)]. At higher pressures, the system forms a homogeneous solid for $T = "3"$ or two solid phases, but there are no fluid phases present.

The $\delta^*-\epsilon^*-F_1$ and the $\delta^*-\epsilon^*-F_2$ three-phase lines could be detected with the isochoric scanning method.

The experiments with a mixture containing 11.0 mole% helium revealed that the $\delta^*-F_1-F_2$ and $\epsilon^*-F_1-F_2$ three-phase lines could be observed both visually and by p - T scans. Therefore, again $x > x_{max}$. However, visually the amount of fluid seemed to be much less at the $\epsilon^*-F_1-F_2$ transition than at the $\delta^*-F_1-F_2$ transition. Thus, the composition of ϵ^* seems close to 11 mole%. The $\delta^*-\epsilon^*-F_1$ and $\delta^*-\epsilon^*-F_2$ transitions showed large pressure jumps of more than 1 kbar.

In the experiment with 5.4 mole% helium, it was possible to detect the $\delta^*-F_1-F_2$ transition both visually and by p - T scans. It was barely visible and the pressure jump was only 0.15 kbar, due to the small amount of fluid phases. However, the $\epsilon^*-F_1-F_2$ transition could not be observed at all with either method. This implies that no fluid phases are present. This proves that the amount of helium dissolved in the solid or present in the stoichiometric compound is somewhere between 5.4 and 11.0 mole%. The $\delta^*-\epsilon^*-F_1$ transition could be observed visually and by scanning, showing a pressure jump of about 1 kbar.

In the experiment with 2.0 mole% helium, the $\beta^*-F_1-F_2$ transition could be detected visually. It is uncertain whether the $\delta^*-F_1-F_2$ three-phase line could be observed. Furthermore, the $\epsilon^*-\delta^*-F_1$ and $\epsilon^*-\delta^*-F_2$ transitions could not be observed. This implies that the 2.0 mole% helium may just be dissolved in δ -N₂ at higher pressures than the δ - β transition. Nevertheless, we stress that ϵ^* is certainly another phase, either ϵ -N₂ or an SSM.

The main question left is whether the crystal composition is stoichiometric or not. Figures 3(c) and 3(d) show that, in the stoichiometric case, the ϵ - δ transition should be observed if $x < x_{SSM}$. With the 2.0-mole% mixture, two scans were performed between 120 and 170 K at 70 and 73 kbar. Although the mixture contains 98% nitrogen, the ϵ - δ transition was not observed. Therefore, in the mixture the ϵ - δ transition is shifted. Furthermore, the $\epsilon^*-\delta^*-F_2$ line extrapolates to the ϵ - δ - γ triple point in pure N₂. We conclude that ϵ^* corresponds to ϵ -N₂ and that the $\epsilon^*-\delta^*-F_1$ and $\epsilon^*-\delta^*-F_2$ transitions correspond to the ϵ - δ transition of pure nitrogen. In the 5.4-mole% mixture, a phase transition was observed at 170 K and 83 kbar, which is probably a three-phase line corresponding to the ϵ - ζ or ϵ - η transitions in pure N₂. The reasons for this assumption are that it showed a flatter slope than the ϵ - δ transition (30 bars/K vs 600 bars/K), it undercooled much more than the ϵ - δ transition (35 K vs 10 K), and a scan at 92 kbar revealed no phase transition near the locus of the ϵ - δ transition in pure nitrogen.

We propose that the helium atoms are dissolved interstitially in solid nitrogen for two reasons: first, the size differences between the species (0.26 and 0.37 nm for a Lennard-Jones potential) and second, the large pressure jumps and consequently large volume jumps on the ϵ^* -

δ^*-F_1 and $\epsilon^*-\delta^*-F_2$ transitions, compared to the $\epsilon-\delta$ transition, which means that the partial molar volume of helium is small in the solid phase. Note that this is consistent with solubility in ϵ -N₂ but not with an SSM.

In conclusion, it is proven that between 5.4 and 11.0 mole% fluid helium dissolves in solid nitrogen. It is consistently shown that helium is dissolved in the ϵ phase. This leads to a shift of the $\epsilon-\delta$ line to the $\epsilon^*-\delta^*-F_1$ and $\epsilon^*-\delta^*-F_2$ lines in the mixture by a factor of 2 in temperature or pressure (see Fig. 2). Because ϵ is ordered and δ is disordered, this means that the ordering transition in solid nitrogen is enhanced under the influence of fluid helium. In contrast, near the $\beta-\delta$ transition in pure nitrogen no helium is dissolved in either phase, but at higher pressure or lower temperature about 2.0 mole% helium may be dissolved in δ -N₂. We have also observed a three-phase line in the mixture at 83 kbar that probably corresponds to the $\epsilon-\zeta$ or $\epsilon-\eta$ phase line of pure nitrogen at more than 200 kbar. Thus, nitrogen can be studied at much lower pressure due to the admixture of helium.

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