

# Structure of quench condensed $n\text{H}_2\text{-N}_2$ binary alloys: isotope effect

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Structure of quench condensed  $n\text{H}_2\text{-N}_2$  alloys was investigated by powder x-ray diffraction over a wide range of temperatures, compositions, and rates of deposition. The structure of the deposits is shown to depend on the condensation regime. Under mild regime, no solid nitrogen reflections from hydrogen-rich deposits were observed. When the temperature is increased to the hydrogen triple point, nitrogen lines appear at substantially larger angles compared to pure  $\text{N}_2$ , which suggests presence of dissolved hydrogen. The quantum nature of this hydrogen is suppressed in the nitrogen matrix. The samples grown in mild regime exhibit the highest apparent solubility (up to 25%) of hydrogen in solid  $\text{N}_2$ . When  $\text{H}_2$  is substituted by  $\text{D}_2$ , the isotope effect consists in a wider range of mono-phase states based on the nitrogen cubic lattice, which can accommodate up to 70% of deuterium, if grown under mild regime.

PACS: 78.55.Kz Solid organic materials;  
31.50.+w Excited states.

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## 1. Introduction

Solid mixtures of hydrogen with rare gases have been extensively studied within different approaches, ranging from rare-gas diluted matrix-isolation systems [1–8] to high mutual concentrations investigated macroscopically [9–16] and to new stoichiometric compounds formed at very high pressures [17]. Of special interest is the recent high-resolution infrared study [18], in which precise microscopic results are compared with inferences drawn from macroscopic measurements. The results obtained in those papers suggest that not only the behavior of the hydrogen molecules change when placed in the rare gas crystals but that heavy rare gas impurities affect the hydrogen matrix. Hydrogen-containing alloys with molecular alloy components like  $\text{N}_2$ ,  $\text{CH}_4$ , etc. were less studied, in many cases as matrix isolated species. Thus, rotation of heavy molecules in the para hydrogen matrix proved to be appreciably hindered [6]. On the other hand, hydrogen molecules in classical rare gas crystals lose their quantum character [15]. In general, quench condensed solid mixtures of hydrogen and rare gases exhibit many unusual properties, in particular, forming gel-like

amorphous states [13] when the impurity component was the heavier rare gases Ar and Kr. No distinct gel-like states were documented in the case of neon as the impurity. One of the aims of this work was therefore to apply the quench condensation procedure in order to, possibly, produce similar hydrogen-based gel-like states with a molecular impurity component and to study the properties of these states. If the  $n\text{H}_2\text{-N}_2$  system does not form gels, our aim would be to study how the hydrogen impurity affects the structure of the nitrogen-rich alloys.

Previously, we have carried out studies of dilute solutions of nitrogen, oxygen [14], methane, and deuteromethane [19] in solid hydrogen. The unusual behavior of the lattice parameters as a function of temperature and composition was treated, by analogy with the case of neon in solid hydrogen [10], as being due van-der-Waals complexes forming around heavy impurities. Thus, the main aim of this work was to study how hydrogen (deuterium) molecules influence the structural characteristics of solid nitrogen grown under quench condensation conditions, how they change under warmup and with varying condensation rate.

## 2. Experimental

Samples were grown by quench depositing room-temperature gas mixtures of known compositions onto a flat copper substrate kept at a temperature between 6 and 7 K. The mixtures were prepared using the PV method with an uncertainty of about 5% in the hydrogen impurity fraction. Condensation was effected using three deposition regimes: mild (with the rate not exceeding 0.53 ml/s), moderate (the rate 0.6 to 1.0 ml/s), and tough (faster than 1.3 ml/s). We kept the total amount of the mixture deposited in each experiment the same (about millimoles). As the rate was increased, the condensation-related heating of the substrate grew as well. In the mild regime, no recordable heating was observed, while the tough regime resulted in a momentous heating by 1 to 2 K. Hereinafter the concentrations of hydrogen impurities are given in the gas phase prior to condensation. These concentrations of the hydrogen isotopes were varied from 10 to 95%.

Structure data were obtained by powder diffraction on a DRON-3M machine equipped with a special liquid helium cryostat, allowing to vary the sample temperature over the range 5 to 300 K. The temperature measurement and stabilization were performed with an accuracy of  $\pm 0.05\%$ . The uncertainty in lattice parameter values did not exceed 0.02%, and that of the integrated reflection intensities, 1%. The setup was completely automatized.

## 3. Results and discussion

### 3.1. Condensation under mild regime (rates not exceeding 0.53 ml/s)

The patterns from fresh quench condensed hydrogen-rich (1 to 30% nitrogen) samples reveal only the (002) reflection from the hexagonal lattice of normal hydrogen; no reflections from solid nitrogen were documented (the lower trace in Fig. 1). This result, which is similar to that obtained earlier [13] for quench condensed  $n\text{H}_2\text{-Kr}$  alloys, suggests that nitrogen is completely dissolved in hydrogen or the nitrogen phase is amorphous or very fine-grained. As the temperature is raised close or above the hydrogen melting point, nitrogen «crystallizes», which can be deduced from a rather broad (111) reflection (the middle trace in Fig. 1) from cubic nitrogen, sharpening upon further warming (the upper trace). This process can be observed within a relatively wide temperature range from 15 to 20 K. As the sample is warmed to the hydrogen triple point, all reflections from the hcp hydrogen phase disappear. The position of the emerging broad (111) nitrogen reflection corresponds to a noticeably smaller (about 3%) lattice parameter of the cubic lattice. As the temperature is raised to 30 K, the (111) nitrogen line becomes narrow and shifts to a position virtually coincident with that

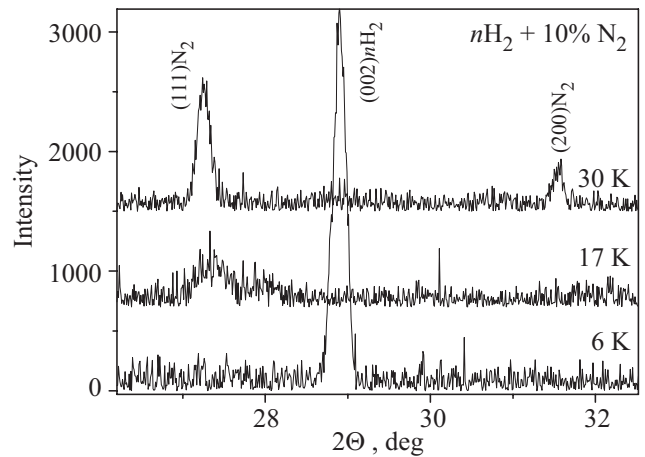


Fig. 1. Typical x-ray diffraction patterns from  $n\text{H}_2\text{-N}_2$  quenched alloys with a nitrogen gas fraction of 10% condensed in the mild regime (see text). The plot shows how the diffraction patterns varies with warmup to 17 K and 30 K.

in pure solid nitrogen; in addition, one more nitrogen reflection (200) grows distinct (see Fig. 1).

If the content of nitrogen in the initial gas mixture exceeds 30%, mild-regime condensation on 6 K results in two x-ray discernable phases based on hcp hydrogen and fcc nitrogen. The nitrogen reflections are strongly broadened and shifted to larger diffraction angles. As the temperature increases, the nitrogen reflections grow narrower and shift to smaller angles (see Fig. 2).

Within the range of low (20–25% or lower) hydrogen contents, mild-regime condensation yields x-ray patterns where only a strongly smeared (111) reflection of the fcc nitrogen is present. As in the case above, this reflection is appreciably shifted to larger diffraction angles compared to pure nitrogen deposited under the same conditions. Again, as the temperature is raised to the hydrogen melt-

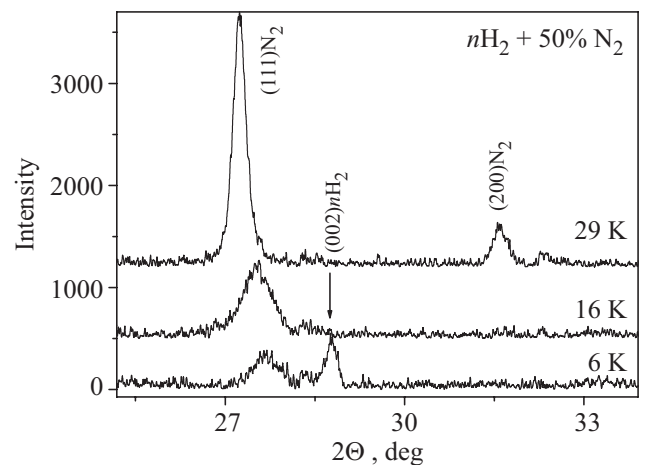


Fig. 2. X-ray patterns from  $n\text{H}_2\text{-N}_2$  alloys with a gas nitrogen fraction of 50% deposited in the moderate regime on 6 K and then warmed up to 16 and 29 K.

ing point, this line narrows and shifts to its position in bulk crystalline nitrogen. No reflections from hydrogen phase(s) appear. Thus, within this content range the hydrogen molecules are dissolved or do not form large crystallites in the nitrogen matrix. The nitrogen lattice is shrunk by the hydrogen present and, therefore, the nitrogen lattice suffers distortions around hydrogen molecules or their small aggregates.

The shift of the nitrogen lines to larger angles, which suggests a shrinking of the fcc lattice, exceeds the value expected from Vegard's rule with account of the intermolecular distances in pure solid nitrogen and hydrogen. Since this effect is likely to be due to isolated or pair hydrogen impurities, the volume per hydrogen impurity is substantially less than the volume per particle in pure H<sub>2</sub> solid. In its turn, this fact suggests the conclusion that the quantum properties of the hydrogen impurity in N<sub>2</sub> matrix are suppressed compared to pure H<sub>2</sub> solid. It should be pointed out that for contents around the equimolar composition the (002) reflection of the hydrogen-rich phase is *also shifted to larger angles*. The reason for this effect can be explained as being due to the suppression of zero-point vibrations of the molecules in the H<sub>2</sub> lattice close to nitrogen impurities, which results in a constriction of the hydrogen matrix.

Summing up, under the mild regime, when no extra heating is present, nitrogen is dispersely distributed in the hydrogen matrix. If the observed boundary of the single-phase region of fcc nitrogen is used, the maximum solubility of hydrogen in solid N<sub>2</sub> for the mild deposition regime will be 25%.

### 3.2. Condensation under tough regime (rates over 1.3 ml/s)

In this case the deposition is carried out by large batches at high rates. Even at low nitrogen contents in the

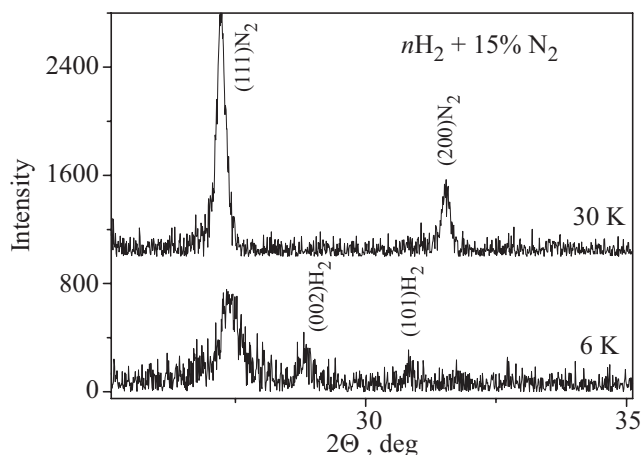


Fig. 3. X-ray patterns from  $n\text{H}_2\text{-N}_2$  alloys with a gas nitrogen fraction of 15% deposited in the tough regime at 6 K and then warmed up to 30 K.

gas, we observed two distinct phases, from hydrogen and nitrogen as shown in Fig. 3 for a nitrogen gas fraction of 15%. The reflection intensities changed from sample to sample in accord with the nominal condensate composition. The brightest nitrogen reflection (111) even in hydrogen-rich (more than 80%) deposits is clearly seen, though strongly broadened and appreciably shifted to larger diffraction angles. The line narrows as the sample is warmed up to the hydrogen triple point temperature and higher.

### 3.3. Condensation under moderate regime (rates 0.6 to 1.0 ml/s)

The hydrogen-rich samples grown under this regime reveal reflections from the fcc phase of nitrogen at its nominal contents as low as 5%. These lines are rather weak and strongly smeared, unlike the sharp and intense hydrogen ones. As the temperature is increased, the nitrogen lines grow narrower, while the hydrogen reflection disappear above the H<sub>2</sub> melting point.

From the results obtained we draw the conclusion that, if judged from the emerging structural and phase states of the respective samples, the effect of increased condensation rate is similar to that of elevated temperatures. This seems to be quite natural, considering the fact that the higher is the condensation rate the faster the latent condensation heat is released and the higher is the substrate overheating during deposition.

Below we present the effect of the condensation rate on the structural parameters and the characteristics of the reflections involved. As one can understand from Fig. 4, the nitrogen lattice of hydrogen(deuterium)-based samples grown under mild regime shrinks substantially (by

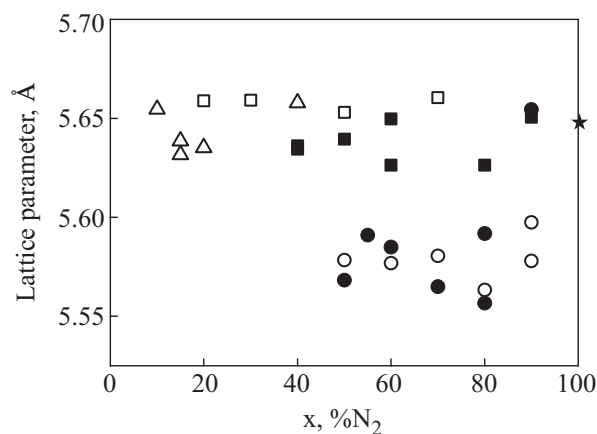


Fig. 4. Effect of the condensation rate on the nitrogen cubic lattice parameter *versus* the nitrogen fraction in the hydrogen-based (empty symbols) and deuterium-based (solid symbols) alloys deposited under mild (circles), moderate (squares), and tough (triangles) regimes. The lattice parameter for pure nitrogen (asterisk) was obtained at a condensation rate of about (0.5–0.6) ml/s.

1.3% on the average). Faster deposition, irrespective of the hydrogen isotope involved, affects negligibly the lattice parameter of the solid nitrogen phase, showing a tendency of a weak expansion. Since the situation for higher deposition rates depends weakly on the nominal composition in the gas, the controlling factor must be the actual concentration of hydrogen impurities in solid  $\text{N}_2$ . One could expect that this concentration will be higher in samples grown at possibly lower temperature, i.e., under mild deposition regime.

The integrated intensities of the reflections from the nitrogen phase, which is understandably little sensitive to condensation rate (especially for the lighter hydrogen isotope), increases linearly with the nitrogen gas fraction, approaching the value found in pure nitrogen, as shown in Fig. 5. However, in mixtures that were grown with sufficiently large deuterium contents an unexpectedly enhanced intensities for the (111) reflections were found in samples grown under mild and moderate regimes. We ascribe this phenomenon to a deuterium-related promotion of textured sample growth.

As shown in Fig. 6, the (111) nitrogen reflection from samples deposited under mild regime is an order of magnitude broader than in pure nitrogen and no other reflections are present; as the gas fraction of hydrogen decreases, the (111) reflection narrows. Two factors could explain the above finding: a strong lattice distortion or/and a small average size of crystallites. Since the relevant deposition was the most smooth and the actual deposition temperature was the lowest, there is no reason to think that such a procedure could bring about abnormally large lattice distortions. On the other hand, this procedure does not expel light and loosely bound hydrogen molecules from the growing deposit, thereby promoting a uniform nucleation of the emerging nitrogen-rich phase, which inevitably results in small-size crystallites. Under higher condensation rates the nitrogen reflections are

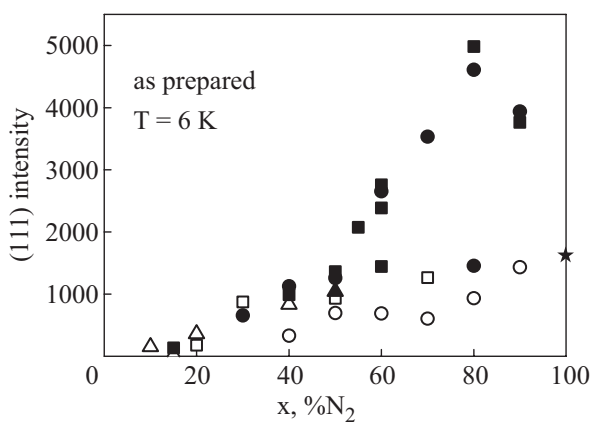


Fig. 5. Effect of the condensation rate of the same samples as in Fig. 4 on the integrated intensity of the (111) reflection from the nitrogen-rich phase. The notations are the same as in Fig. 4.

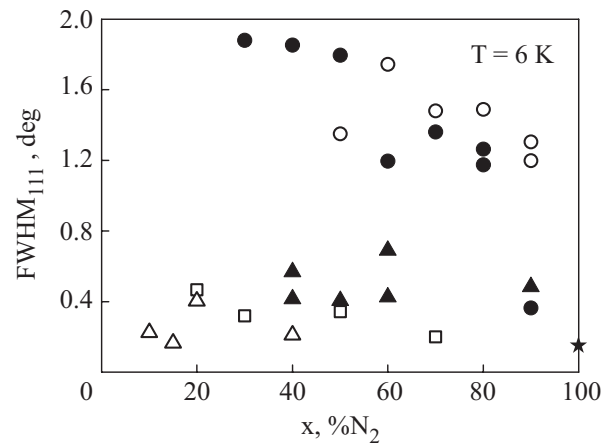


Fig. 6. Effect of the condensation rate on the full width at half maximum of the (111) reflection from the nitrogen-rich phase of the same samples as in Fig. 4. The notations are the same as in Fig. 4.

much narrower (see Fig. 6), likely because the warmup due to latent heat comes not only from deposition itself but also a faster (compared to mild condensation) aggregation of nitrogen. It should be added here that both the sticking parameter in physisorption of hydrogen is very sensitive to the local temperature close to 10 K and above.

The results reported above prove that, in line with the general concepts of crystal growth physics, deposition procedure is a very important factor that determines the morphology and structure of emerging quench condensed  $n\text{H}_2\text{-N}_2$  alloys. The range of (quasi)-uniform solid solutions of the hydrogens in solid nitrogen is the largest when the deposition is sufficiently slow. In this case, one could expect observation of highly amorphous condensates as in the  $\text{Kr-H}_2$  system [13].

#### 4. Isotope effect

Using the same sample preparation procedure and the same three deposition regimes we carried out similar studies on nitrogen-deuterium quench condensed alloys. After condensation the alloys were warmed in a stepwise manner by 2 to 5 K till the final temperature of 20 to 30 K, depending on the composition. Typical x-ray diffraction patterns are plotted in Fig. 7.

Summing up our findings, the substitution of  $\text{H}_2$  by the heavier isotope  $\text{D}_2$  renders the range of single-phase solid mixtures with the fcc nitrogen lattice broader. Under mild condensation regime, the nitrogen lattice can accommodate up to 70%  $\text{D}_2$ . The nitrogen reflections from as-prepared samples are strongly broadened and shifted to larger diffraction angles (the lower trace in Fig. 7). The reasons behind these findings are the same as discussed above. It is interesting that the pattern retains its shape up to 15 K up to as high as 20 or 22%, which might suggest a

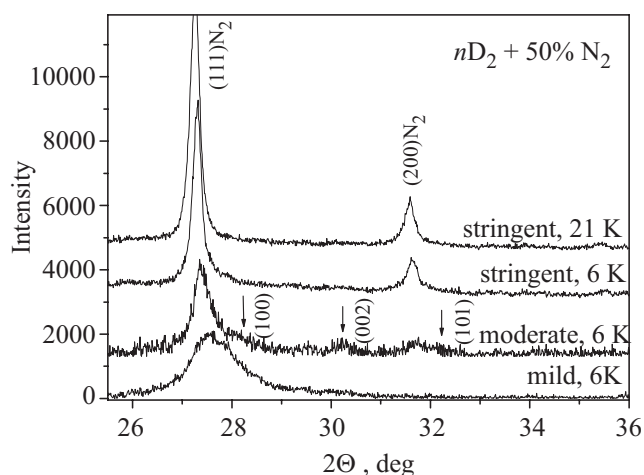


Fig. 7. Typical x-ray diffraction patterns from quenched deuterium-nitrogen alloys with a nitrogen gas fraction of 50% condensed in various regimes as shown in the plot. The arrows indicate reflections from the hexagonal deuterium-rich phase.

more pronounced (compared to  $H_2$ ) reluctance of the heavier isotope to migrate during warmup. Again, as the temperature is raised higher, the reflections from the deuterium hexagonal lattice disappear while those from the nitrogen matrix grow narrower and more intensive. When the nominal fraction of deuterium was large enough, no reflections from the nitrogen phase were recorded.

The apparent solubility of deuterium in nitrogen decreases at higher deposition rates. In this case, single-phase samples with the nitrogen lattice grew when the nitrogen fraction in the gas exceeded approximately 50%. The lines were broad and shifted to larger angles. As the temperature or the nominal nitrogen fraction were increased, the reflections became narrower.

## 5. Conclusions

1. A dramatic influence of the hydrogen quantum impurity on the low-temperature  $\alpha$ - $N_2$  phase has been observed. Condensation of strongly supercooled hydrogen-rich mixtures results in an amorphous or fine-grained nitrogen phase, which recrystallizes only when hydrogen molecules leave the sample upon warming. Quenching of nitrogen-rich mixtures yields reflections from solid hydrogen as well as strongly broadened lines from a distorted nitrogen-based phase.

2. Direct evidence of a suppression of the quantum nature of hydrogen molecules in the nitrogen matrix has been observed: dissolving of hydrogen entails an abnormally strong shrinking (up to 3.5% of the volume) of the  $\alpha$ - $N_2$  lattice.

3. It is shown that under certain conditions (moderate and mild regimes) the hydrogen impurity promotes highly

textured matrices, the (111) plane arraying parallel to the substrate surface. Presence of hydrogen impurities leads to a considerable broadening of the reflection, suggesting fine grains or strong distortions of the  $\alpha$ - $N_2$  lattice.

4. A considerable isotope effect in the solubility of hydrogen in solid nitrogen has been observed. Under tough regime the solubility of deuterium is 2.5 higher than that of hydrogen.

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