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Phase transitions and equilibrium hydrogen content of phases in the water–hydrogen system at pressures to 1.8 kbar

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Using a volumetric technique, the hydrogen solubility X in liquid water (L), low-pressure hexagonal ice (I_h), and high-pressure cubic clathrate ice (sII) is studied at hydrogen pressures up to 1.8 kbar and temperatures from -36 to $+20\,°C$. The triple point of the $L + I_h + s\text{II}$ equilibrium is located at $P = 1.07(5)$ kbar and $T = -10(1)\,°C$. The hydrogen concentrations of phases at the triple point are $X_L = 0.17(5)$, $X_{I_h} = 0.10(5)$ and $X_{s\text{II}} = 2.3(1)$ wt.% H_2. The thermal stability and the process of decomposition of the clathrate phase at ambient pressure are studied by neutron diffraction.

Keywords: Clathrate hydrate; Phase equilibria; Thermal stability

1. Introduction

In 1999, Dyadin *et al.* [1] studied the H_2O–H_2 system by differential thermal analysis (DTA) and observed anomalous behaviours of the melting temperature and the kinetics of melting of ice in a hydrogen atmosphere at pressures from 1 to 3.6 kbar. The authors conjectured that hydrogen clathrate hydrate was formed in this pressure range. Indeed, an sII-type clathrate phase of hydrogen hydrate was synthesized more recently from a liquid at a hydrogen pressure of about 2 kbar [2]. In the cubic unit cell of the sII phase formed by 136 H_2O molecules, there are two types of cages accessible to guest molecules, eight 'large' and sixteen 'small' ones. An *in situ* neutron diffraction (ND) investigation of the D_2O–D_2 clathrate phase showed [3] that the occupancy of the large cages varied from 2 to 4 D_2 molecules depending on the pressure and temperature, whereas the occupancy of the small cages was always close to one D_2 molecule. Accordingly, the composition of the H_2O–H_2 clathrate phase can vary from $H_2/H_2O = 32/136$ to $48/136$, which gives 2.55–3.77 wt.% H_2.

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Recently [4], we studied the H_2O–H_2 system at temperatures from -15 to -36 °C and pressures up to 1.8 kbar using a volumetric technique. The low-pressure hexagonal phase I_h of ice was found to transform into the sII clathrate phase at a pressure of about 1 kbar. The $I_h \leftrightarrow s$II transformation showed a significant baric hysteresis increasing from about 0.1 kbar at -18 °C to 0.4 kbar at -36 °C. We also synthesized the clathrate phase from the liquid and determined the pressure dependence of the synthesis temperature.

In the present work, we completed the T–P diagram of the H_2O–H_2 system at pressures up to 1.8 kbar by constructing lines of the $I_h \rightarrow L$, $L \rightarrow I_h$, and $s\text{II} \rightarrow L$ transitions and specifying the hydrogen content of the condensed phases.

2. Volumetric measurements

The experimental setup is described in ref. [5]. The starting sample of water ice weighing 1.5 g was powdered in an agate mortar under liquid nitrogen in order to speed up the kinetics of hydrogen absorption and desorption. The amount of hydrogen absorbed by the sample was calculated from the volumetric results with an accuracy of ±0.05 wt.% by using published data on the pressure and temperature dependences of the molar volumes of liquid water [6], ice I_h [6], the sII phase [2, 3], and gaseous H_2 [7].

Points of phase transitions were determined from a sudden change in the hydrogen content of the sample. As seen from figure 1, the melting curve of ice I_h in a hydrogen atmosphere (open squares) coincides with that in the absence of hydrogen (dashed line) in agreement with the DTA results of [1] (dash-dotted line). The melting curve of the sII phase (open triangles) lies a few degrees lower than the DTA curve that shifts the point of its intersection with the melting curve of ice I_h to a higher pressure of 1.07 kbar and lower temperature of -10 °C (open star). As the equilibrium line is always much closer to the melting curve than to the curve of solidification, the open star in figure 1 represents the triple point of the $L + I_h + s$II equilibrium.

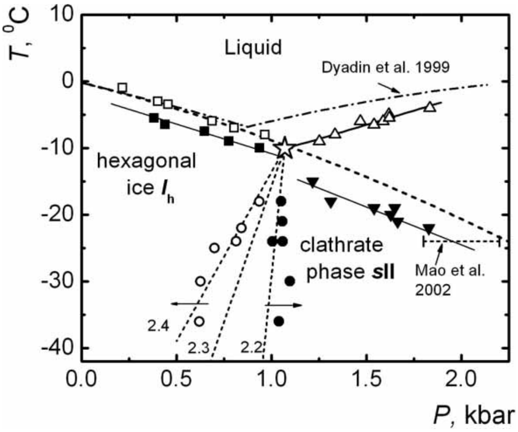

Figure 1. T–P diagram of the H_2O–H_2 system. Open and solid squares indicate, respectively, the points of the $I_h \rightarrow L$ and $L \rightarrow I_h$ phase transition; open triangles of the $s\text{II} \rightarrow L$ transition, and the open star shows the point of the $L + I_h + s$II equilibrium (data of the present work). Solid triangles [4] and the dashed horizontal segment [2] refer to the $L \rightarrow s$II transition. Open and solid circles, respectively, show the points to the $I_h \rightarrow s$II and $s\text{II} \rightarrow I_h$ transition [4]. The dash-and-dot curve shows the melting line of water ices in a hydrogen atmosphere determined by DTA [1]. The dashed curve represents the melting line of ice I_h in the absence of hydrogen [8]. Short dashed lines radiating from the triple point represent the lines of the $I_h \leftrightarrow s$II equilibrium calculated assuming that the sII phase contained 2.2, 2.3, or 2.4 wt.% H_2.

From the slopes of the melting lines and the molar volumes and equilibrium hydrogen concentrations $X_L = 0.17(5)$, $X_{I\mathrm{h}} = 0.10(5)$ and $X_{s\mathrm{II}} = 2.3(1)$ wt.% H_2. of phases at the triple point, the lines of the $I_\mathrm{h} \leftrightarrow s\mathrm{II}$ equilibrium can be calculated by using the Clapeyron equation and the condition that the sum of entropy changes is zero when cycling around the triple point. To illustrate the sensitivity of the calculation to the imprecision of the experimental data used, figure 1 shows the lines calculated for three different values of $X_{s\mathrm{II}} = 2.2$, 2.3, or 2.4 wt.% H_2, each of which agrees with the experimental value $X_{s\mathrm{II}} = 2.3(1)$ wt.% H_2. The calculated lines lying between the experimental $I_\mathrm{h} \rightarrow s\mathrm{II}$ and $s\mathrm{II} \rightarrow I_\mathrm{h}$ boundaries, this suggests the self-consistency of the whole set of the parameters characterizing the $L + I_\mathrm{h} + s\mathrm{II}$ equilibrium.

At temperatures down to −36 °C, the hydrogen solubility in the sII phase decreased from about 2.7 wt.% H_2 at the maximum pressure of 1.8 kbar to 2.2–2.3 wt.% H_2 in the vicinity of the $s\mathrm{II} \rightarrow I_\mathrm{h}$ line, including the triple point. The latter value is lower than the minimum concentration 2.55 wt.% H_2 corresponding to the double and single occupancy, respectively, of the large and small cages by H_2 molecules [3]. Our ND investigation of a high-pressure D_2O–D_2 clathrate sample in the course of its decomposition at ambient pressure showed that the occupancy of the small cages can decrease down to about 0.7 guest molecule that corresponds to 2.2 wt.% H_2 in the H_2O–H_2 clathrate phase.

3. Neutron diffraction measurements

The D_2O–D_2 sample was prepared from powdered D_2O ice and D_2 gas at 1.7 kbar and −20 °C, quenched to liquid nitrogen temperature and repeatedly examined by ND at ambient pressure

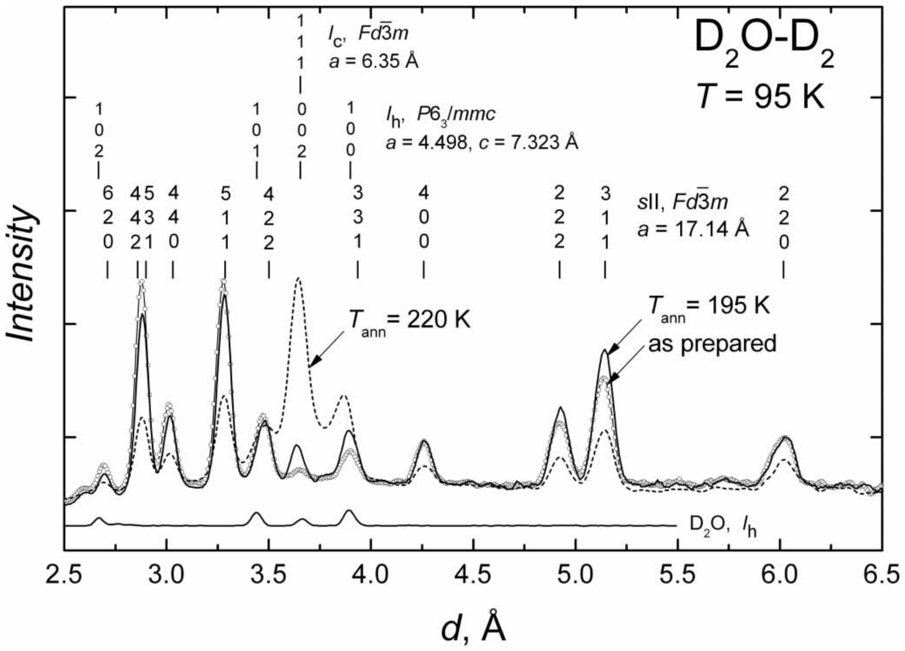

Figure 2. Representative ND patterns of a D_2O–D_2 sample with $D_2/D_2O \approx 32/136$ synthesized under high D_2 pressure and measured with the DN-2 time-of-flight neutron diffractometer (JINR, Dubna) at ambient pressure and 95 K in the as-prepared state (open circles) and in partly decomposed states after a 15 min annealing at 195 K (solid line) and 220 K (dashed line). The solid curve at the bottom shows the calculated contribution of a 1 wt.% admixture of ice I_h found in the as-prepared sample. The rows of vertical bars show the positions of diffraction lines calculated for the structure specified in the corresponding label.

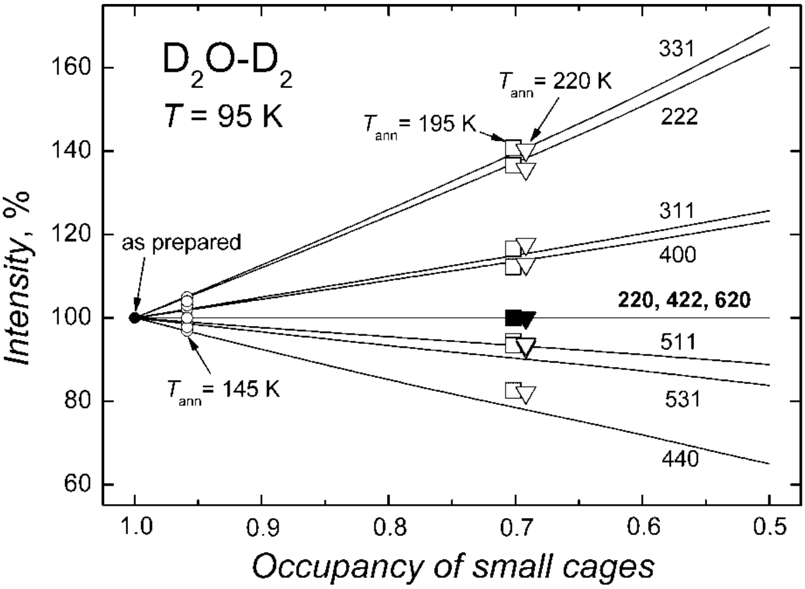

Figure 3. Calculated intensities of diffraction lines of the *s*II-type D_2O–D_2 clathrate phase as a function of the occupancy of small cages by D_2 molecules (solid lines) and the experimental integral intensities of these lines of the *s*II phase in the D_2O–D_2 sample annealed at indicated temperatures (symbols). The invariance of relative intensities of the 220, 422, and 620 experimental lines points to the invariable double occupancy of large cages in the *s*II phase of the studied sample. The occupancies of its small cages are estimated from the best fit of the experimental intensities of other lines to the calculated ones.

and 95 K in the as-prepared state and after successive runs of rapid heating to a chosen temperature (145, 195, 220 and, finally, 250 K), annealing at that temperature for 15 min and rapid cooling back to 95 K.

Three representative ND patterns are shown in figure 2. The starting sample had $D_2/D_2O \approx 32/136$ according to the result of hot extraction, was nearly single-phase and consisted of an *s*II phase with two D_2 molecules in each large cage and one D_2 molecule in each small cage according to the results of profile analysis. After annealing at 195 K, the occupancy of the small cages decreased to about 0.7 D_2 molecules. After further annealing at 220 K, about half of the sample transformed to a mixture of hexagonal ice I_h, cubic ice I_c, and low-density amorphous ice lda. After annealing at 250 K, the sample consisted of I_h, lda, and a smaller fraction of I_c. The changes in the intensities of diffraction lines of the *s*II phase indicating the depopulation of its small cages with increasing annealing temperature are illustrated by figure 3.

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