

Determination of the structure of the high-temperature phase of solid H₂

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X-ray investigations of solid hydrogen have been carried out at pressures 80-100 atm. It is shown that the phase transition observed at these pressures in the region of pre-melting temperatures is connected with the transition H₂ from a hexagonal to a cubic face-centered structure.

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It is known that at equilibrium vapor pressure hydrogen crystallizes to form a hexagonal close-packed lattice, which it retains at a low concentration of the ortho-modification down to the lowest investigated temperatures. At an ortho-modification content $c > 0.6$ in solid hydrogen and at temperatures 1.5-3°K, a phase transition from the hcp to the fcc lattice is observed,^[1] due to the orientational ordering of the molecules. A number of recent experimental studies offer evidence that one more phase transition seems to exist in solid hydrogen near the melting point at pressures above several dozen atmospheres.^[2,3] It has been established^[3] that at $P \approx 30$ atm the molar volume of the high-temperature phase is smaller by 0.15% than that of the low-temperature phase, and the transition temperature is practically independent of the ortho-para composition. A hypothesis was advanced^[3] that this transition is analogous to a transition from the hcp to the bcc structure observed at low pressures in solid He⁴.^[4] Taking into account the presence of a negative volume jump, this conclusion seems quite doubtful. It is more probable that the high-temperature phase of H₂, just as the low-temperature phase, is close-packed but with an fcc lattice, which is realized in both solid isotopes of He at pressures $P > 1000$ atm.^[5,6] Only direct structure investigations can answer this question unequivocally. To this end, we have carried out an x-ray structure study of solid hydrogen in the region of pre-melting temperatures at pressures 80-100 atm. We investigated approximately 50 polycrystalline samples obtained in a cylindrical beryllium ampoule with inside diameter 8 mm and wall thickness 0.5 mm. The measurements were made with the US-20 apparatus with copper K_{α} radiation in a cryostat which made it possible to stabilize the given value of the temperature in the sample cell with accuracy ± 0.1 °K. A high-power BSV-11 x-ray tube was used. The pressure on the H₂ sample was maintained with the aid of helium gas with accuracy ± 1 atm.

Owing to the low ability of hydrogen to scatter x-rays, and also owing to the considerable amplitude of the zero-point vibrations of the molecules in the lattice, reliable structure investigations in the case of hydrogen are a technically complicated experimental problem. In the best case it is possible to observe on the x-ray patterns not more than three lines drawn at small angles, and the large crystal dimensions typical of solid hydrogen and the texture possessed by the samples greatly limit the possibility of a reliable analysis of its structure.^[7] In our investigations we succeeded in developing a procedure for ob-

taining finely-dispersed samples that were stable with respect to recrystallization, the better among which gave distinct Debye lines up to $\theta \sim 40^\circ$. This made it possible to confirm the presence in solid hydrogen of a phase transition in the pre-melting temperature region and to determine reliably the structure of its high-temperature phase.

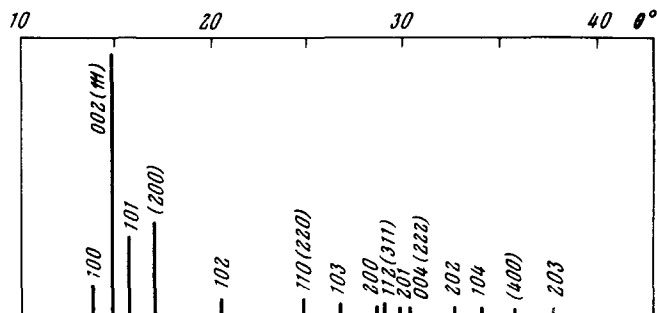


FIG. X-ray line pattern of solid H_2 ($T = 13^\circ K$, $P = 90$ atm). The indices of the fcc lattice are indicated in parentheses.

The x-ray line pattern corresponding to actual photographs of samples obtained by condensation of a gaseous steam-hydrogen mixture compressed to 900 atm (H_2 concentration $\sim 5-10\%$) in a beryllium ampoule cooled to helium temperatures is shown in the figure.

All the x-ray patterns obtained in similar fashion show only the lines characteristic of two close-packed lattices—hcp and fcc. Altogether we succeeded in observing on the x-ray patterns obtained from these samples up to 13 individual reflections. A comparison of the relative intensities of the reflections, which do not coincide for the hcp and fcc structures, indicates that the amount of the hcp phase was as a rule several times smaller than fcc. When the samples were heated to $13^\circ K$, all the lines became less distinct, but the ratio of the hcp and fcc phases remained practically unchanged. Annealing the samples at a temperature $16.2^\circ K$, which at $P = 100$ atm is $0.7^\circ K$ lower than the melting temperature of the hydrogen, led to an appreciable redistribution of the line intensities in favor of the fcc structure. Although in the performed experiment the reflections typical of the hcp lattice did not disappear completely even once their behavior patently indicated that near melting, at pressures on the order of 100 atm, the hcp phase is not thermodynamically stable, but exists alongside the fcc phase as a metastable component. This conclusion was clearly confirmed in experiments performed on samples obtained at $T = 16.2^\circ K$ from hydrogen previously liquified in a beryllium ampoule suddenly flooded with helium compressed to 100 atm. The finely dispersed samples obtained under conditions of fast crystallization revealed on the x-ray patterns only lines characteristic of the fcc lattice. At the same time, even the intense hcp lattice reflections were completely missing from all such x-ray patterns.

According to our measurement data, the possible difference between the molar volumes of the two crystalline phases does not exceed 0.5%. The absolute values of the molar volume of the solid H_2 , at pressures 80–100 atm, are in good agreement with those indicated in^[8].

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