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NEUTRON DIFFRACTION STUDY OF THE CRYSTALLINE STRUCTURE OF SOLID HYDROGEN AND DEUTERIUM

V. S. KOGAN, B. G. LAZAREV, R. P. OZEROV and G. S. ZHDANOV

Physico-Technical Institute, Academy of Sciences, Ukr. SSR; L. Ya. Karpov Physico-Chemical Institute

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Neutron diffraction analysis at 12°K has confirmed the structure of deuterium and the tetragonal variant of the hydrogen structure, as found by x-ray diffraction methods. For neutrons, the diffraction patterns were found to be considerably richer than for x-rays, for both hydrogen and deuterium. This is due, in the first place, to the appearance of interferences at angles greater than those for which the intensity of the x-ray interferences, which falls rapidly with increasing scattering angle, decreases to zero, and, in the second place, to the occurrence in the neutron diffraction patterns of interferences having odd index sums, which are forbidden for body-centered structures made up of identical particles. The latter may be accounted for, if it is assumed that the ortho- and para-molecules are distributed through the lattice in an ordered manner, and have different neutron scattering cross-sections. In certain cases interferences were observed at small angles, to which indices may be assigned by proceeding from the assumption that the ortho- and para-molecules are ordered within a volume containing eight cells.

X-RAY structural analysis of polycrystalline samples of hydrogen and deuterium has shown that at 4.2°K these two isotopes possess different lattice structures.[1] This conclusion regarding the structure of hydrogen and deuterium was based, however, upon the analysis of x-ray diffraction patterns having an extremely small number of lines, and those only at small angles. The sparseness of the interference patterns was due to the rapid fall in the intensity of the x-ray interferences with increasing scattering angle, characteristic of diffraction by light elements. The lines in the x-ray patterns for solid hydrogen could not be indexed uniquely, and as a result of their analysis this isotope could be assigned, with equal probability, either a hexagonal (with axis ratio $c/a = 1.73$) or a tetragonal (with axis ratio $c/a = 0.82$) structure. The structure of deuterium was determined to be tetragonal (with axis ratio $c/a = 1.73$).

With the object of securing more complete information on the crystalline structures of hydrogen and deuterium, a neutron diffraction study of these isotopes was undertaken. The coherent scattering amplitude for neutrons does not depend upon the angle of scattering. This led to the expectation that neutron diffraction patterns could be obtained for the hydrogen isotopes which would have a greater number of interferences at large angles than the x-ray patterns. Such neutron diffraction patterns could be accurately indexed, and a more certain solution could be found to the problem of the crystalline structure of hydrogen and deuterium.

EXPERIMENTAL METHOD

The investigation was carried out using the apparatus previously described.[2,3] The absence of any need for a magnetic field allowed a modification to be introduced in the construction of the cryostat: the outer jacket and screen (both of copper) were removed to a distance of 100 mm from the central container holding the object under study. In addition, the copper container was replaced by one made from a titanium-zirconium alloy (32 atomic percent zirconium), clamped with an indium gasket to the bottom of the reservoir containing the cooling agent. These changes made it possible to avoid completely the effects of coherent scattering of the neutrons by the jacket and screen (through collimation) and also by the container (since a titanium-zirconium alloy containing 32% zirconium does not yield coherent scattering).

Liquid hydrogen was employed as the cooling agent, being pumped on with a forevacuum pump.

The samples had a temperature of 11 - 12° K, as determined from the vapor pressure at their surfaces. One filling of the cryostat with the coolant liquids (nitrogen and hydrogen) sufficed for more than 24 hours of operation.

Under the conditions of crystallization prevailing in the experiment, the hydrogen and deuterium samples took the form of aggregates of coarse crystals. The orientation of these crystals varied in an uncontrollable fashion from sample to sample; in all probability, they did not remain constant even in a given sample over the duration of a run, due to the intensive recrystallization and self-diffusion processes taking place at the temperatures of the experiment. The following measures were taken to reduce the effect of the coarse crystalline structure of the samples:

1. The sample was made to oscillate, together with the entire cryostat, through 120°, at a period such that an integral number of oscillations took place during a single measurement.
2. The neutron diffraction patterns obtained on different days from separate samples, under varying experimental conditions (i.e., statistics, collimation, etc.), were averaged, with these differing conditions taken into consideration.

These measures, however, could not insure the provision of unique data on the intensities of the interference maxima, which would have permitted determination of the orientations of the molecules in the unit cell. The neutron diffraction patterns yielded information only on the absence or presence of the maxima, and on their positions.

RESULTS

A. Deuterium. Figure 1 presents some of the neutron diffraction patterns obtained for deuterium samples having an ortho-molecule concentration equal to or somewhat smaller than the equilibrium value for room temperature. As noted above, the relative intensities of reflections having the same indices vary among the diffraction patterns obtained from different samples. The positions of the reflections, however, can be established with a sufficient degree of precision, especially if through a particular choice of the cryostat position it is possible to find one peak of such intensity as to correspond to reflection from a monocrystal oriented at the Bragg angle. Indexing, using the Hull-Davey curves, and appropriate elementary calculations permitted establishment of the fact that the crystalline lattice of deuterium belongs to the tetragonal system. The dimensions of the unit cell are a = 3.38 A and c = 5.60 A (c/a = 1.66). Positions of the maxima as computed from these parameters are indicated in Fig. 1 by the small arrows. The slight deviations of some of the maxima from their calculated positions may be explained by the fact that the monocrystals giving rise to the corresponding reflections are displaced relative to one another within the container, the diameter of which is 10 mm. The incoherent scattering background for deuterium (after subtracting out the instrumental background) is essentially zero.

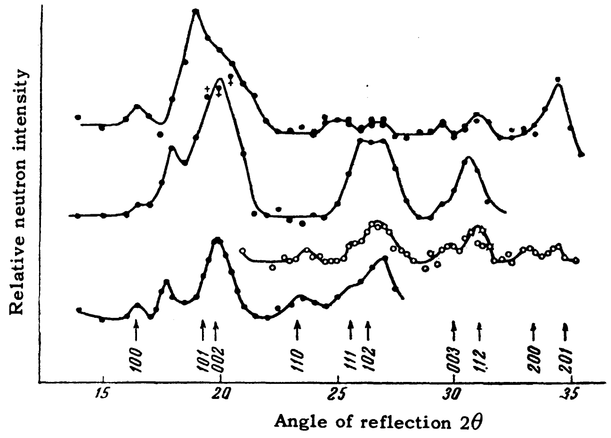

FIG. 1. Neutron diffraction patterns for deuterium at T ~ 12°K (upper curve obtained by averaging four neutron patterns taken without oscillation of the sample).

B. Hydrogen. The investigation of hydrogen by neutron diffraction is greatly hampered by the

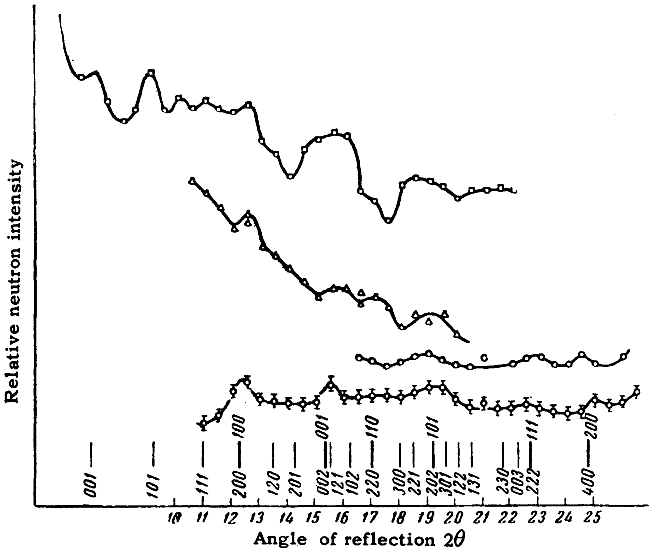

FIG. 2. Neutron diffraction patterns for hydrogen at T ~ 12°K (two lower patterns obtained with the aid of the flat container; upper pattern with the ordinary cylindrical container; second from the top, obtained with a cylindrical container empty at the center).

presence of strong incoherent spin scattering of the neutrons. In order to reduce the level of the background associated with the incoherent scattering, containers were employed which provided sample thicknesses not exceeding that of a 50%-attenuating layer (3 - 4 mm). A flat copper container, as well as a double-walled cylinder, empty within, were used in place of the ordinary cylindrical container. The use of the copper container was rendered feasible by the fact that the hydrogen lines are produced at smaller angles than the first line from copper.

A few typical neutron diffraction patterns for hydrogen (a mixture of ortho- and para-molecules having nearly the equilibrium distribution for room temperature) are presented in Fig. 2. The coherent scattering maxima in these patterns are only weakly evident above the incoherent scattering background; however, analysis of a large number of the diffraction patterns (more than 20) permitted determination of the positions of the maxima with adequate precision. Indexing, with the aid of the Hull-Davey curves, and subsequent computation permitted assignment of the hydrogen structure to the tetragonal system. The unit-cell dimensions are $a = 4.5\,A$, $c = 3.6\,A$ ($c/a = 0.81$). The positions of the interference maxima corresponding to this structure are indicated in Fig. 2 by the heavy lines; the indices of these maxima are written in above the corresponding lines. In a few cases (see, for example, the upper neutron diffraction pattern in Fig. 2) still other maxima are visible, in addition to those already pointed out, some of them at extremely small angles (these are indicated in Fig. 2 by the narrow lines). Indexing of the neutron diffraction patterns showing this interference system (the corresponding indices are written in below the lines) and subsequent computation again yields a tetragonal lattice, having the same ratio of axes, but with doubled parameters ($a \approx 9\,A$, $c \approx 7\,A$).

DISCUSSION OF THE RESULTS

The neutron diffraction study has confirmed the structure of deuterium and the tetragonal variant of the hydrogen structure,* as determined by x-ray diffraction methods.[1] The small discrepancy in the axis ratios for the tetragonal deuterium lattice determined from the x-ray data and from the neutron structural analysis is perhaps to be attributed to the difference in the temperatures at which these investigations were carried out (4.2 and 12° K, respectively). However, the agreement of the results from the x-ray and neutron structural analyses is confined to the symmetry, the parameters, and the axis ratio of the unit cell. In the x-ray diffraction patterns only those reflections having even index sums were present as is characteristic for body-centered structures. In the neutron diffraction patterns, in addition to further maxima with even sums of indices, appearing at relatively large angles, lines are also present which have odd index sums; this corresponds to a primitive unit cell rather than the body-centered one inferred from the x-ray structural analysis data. This discrepancy might be explained in the following manner:

1. The amplitudes for coherent scattering of neutrons by the ortho- and para-molecules in hydrogen and deuterium are unequal.
2. The distribution of the ortho- and para-molecules within the lattice is not purely statistical. In this event the lines having odd sums of indices could be regarded as coming from the superstructure. With respect to x-rays the ortho- and para-molecules are completely equivalent, and the superstructure has no effect.

Published data on the properties of hydrogen and deuterium in the ortho- and para-states do not as yet permit a definite answer to the question of the validity of the hypothesis, advanced above, that the interference patterns observed in neutron diffraction by these isotopes are to be attributed to an ordered arrangement of ortho- and para-molecules in their lattices.

The ortho- and para-molecules of one and the same isotope are so similar in all their properties that until fairly recently it was thought that they constitute ideal mixtures. Vapor pressure data,[6] however, have shown that, for hydrogen as well as deuterium, the ortho - para mixtures fail to obey Raoult's law for ideal solutions. Through the use of Clapeyron's equation it has been established that the latent heat of vaporization and the internal energy in the liquid and solid phases are quadratic, rather than linear, functions of the composition. This suggests a difference in the mutual energies of the various types of molecular pairs, and the possibility, in principle, of an energetic advantage in the ordering of the ortho- and para-molecules in the hydrogen and deuterium lattices. Further, this hypothetical ordering is not contradicted by the data on the specific heats of ortho - para hydrogen mixtures (a departure, beginning at 12° K, of the temperature dependence of the mixture spe-

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*This variant is also confirmed by measurements of the specific heat and the nuclear magnetic moment, as is shown in a theoretical paper by Dukhin[4] and in the experiments of Galkin and Matyash.[5]

cific heats from the analogous curve for pure parahydrogen[7]), nor by the results of a study of nuclear magnetic resonance in solid hydrogen (a rapid broadening of the resonance line, from 0.1 oersted at 12°K to ~ 8 oersteds at 10°K and below, which implies a sharp change in the rates of the diffusion processes within this temperature interval[8]).

A direct experimental test of the validity of the hypothesis concerning the existence of a superstructure in the lattices of solid ortho - para mixtures of hydrogen and deuterium would, it appears, be provided by the investigation of mixtures of controlled composition, ranging down to pure parahydrogen and ortho-deuterium.

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