JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. II

Neutron Diffraction Study of the Crystal Structure of Solid Hydrogen and Deuterium

R. P. OZEROV, V. S. COGAN, G. S. ZHDANOV
AND G. B. LAZAREV

Karpov Institute of Physical Chemistry, Moscow
Institute of Technical Physics, Charcow, U.S.S.R.

A neutron diffraction analysis at 12°K confirms the structure of deuterium determined by X-ray method and the tetragonal version of the structure of hydrogen. It was found that the neutron diffraction pattern for hydrogen as well as deuterium shows much more diffraction peaks than those in X-ray pattern. This is due to the appearance of the reflections at angles which are larger than these which the intensity of X-ray diffraction (which sharply drops off with the scattering angle) vanishes and to the appearance of the reflections with odd sum of indices which are forbidden for body-centered structures consisting of identical particles. The latter fact can be understood if one assumes that ortho- and paramolecules are arranged in an orderly manner in the lattice and possess different coherent scattering amplitudes for neutrons.

The forms and sizes of unit cells and the intermolecular distances are given.

The investigation of the crystal structure of solid hydrogen and deuterium is of great interest from different points of view. Hydrogen is one of the several chemical elements which crystal structures remained unknown because of Keesem's incorrect data in 1930[1]. Thus this investigation is of great importance for crystallography. We first meet the existence of new phenomena in the case of hydrogen and deuterium: isotopic morphotropy and probably spin morphotropy. While the hydrogen molecule has already been treated theoretically in detail, the intermoleclar interaction in gas and especially in solid state has not yet been studied enough. Neutron-proton interaction was considered both theoretically and experimentally but mainly for inelastic scattering; the coherent scattering of thermal neutrons by hydrogen molecules has not yet been studied.

These are the reasons why the investigation of the crystal structures of solid hydrogen and deuterium was undertaken.

The choice of the neutron diffraction method instead of and in addition to X-ray method[2] was based on the facts that the neutron coherent scattering amplitudes for hydrogen and deuterium atoms, are of the same magnitude as those of other atoms and that they are independent of the scattering angle.

The neutron diffraction equipment employed has been described earlier in the literature[3),4] and at the Cambridge Congress, 1960. A cryostat of the usual design with the sample holder made up of Ti-Zr alloy was employed. Liquid hydrogen under pumping was used as a cooling agent (10~11°K). The concentrations of para and ortho molecules in the sample investigated were not controlled during the first stage of experiment and we suppose them to be equimolar.

The scattering curves were obtained point by point. There were some difficulties which prevented us from getting precise and reproducible results. First, the grain size of the solid hydrogen which was obtained by condensation and solidification of the gas was very large. That is why we were obliged to oscillate the cryostat around the vertical axis. This action, however, was only partly eliminating the large grain size effect. Second, the reactor operates continuously for only about 12~15 hours. So, we had to deal with different samples every day. Third, since the diameter of the sample holder is 10 mm, the change of the large grain size sample led to some displacement of scattering maxima. The effect of these factors was reduced by taking average of many curves.

Because of these unfavourable factors only the positions of maxima (but not their intensities) were measured from the neutron diffraction patterns. These averaged patterns are shown in Fig. 1 and 2 (in which the angle scale is very much drawn out).

Deuterium: The neutron diffraction patterns were indexed by use of the Hull's diagrams. It was established that solid deuterium possesses a body-centered tetragonal unit cell with the ratio *c* to *a* equal to 1.66.

Hydrogen: The neutron diffraction patterns of solid hydrogen were vaguely pronounced because of the very high level of incoherent scattering. It was very difficult to estimate this level theoretically in relation to the coherent maxima because of the large grain size of samples. But it is obvious that solid hydrogen is not isomorphous with solid deuterium. Hydrogen has also a body-centered teteragonal unit cell but the ratio *c* to *a* is less than unity—namely 0.81.

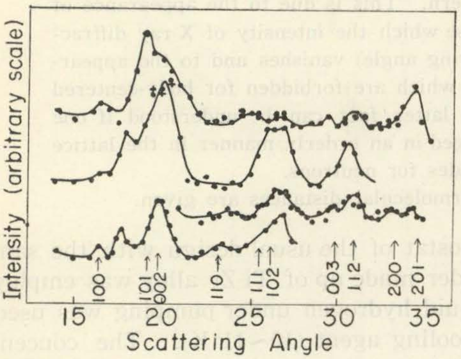

Fig. 1.

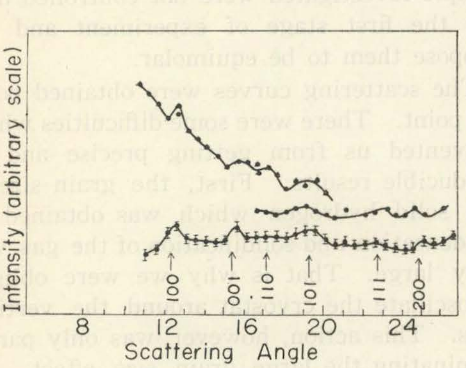

Fig. 2.

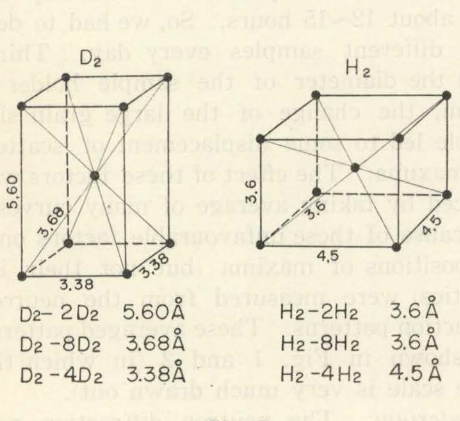

Fig. 3.

Quite unexpectedly, maxima with an odd sum of the Miller indices appear on the patterns. This indicates that para and ortho molecules possess different coherent scattering amplitudes and are arranged in an ordered manner in the unit cell.

In the Fig. 3 the forms and sizes of unit cells of solid deuterium and hydrogen are given. The lack of knowledge of the intensities of maxima did not allow us to determine the orientation of the molecules in the cells. Each molecule has 14 neighbours on 3 coordination spheres.

In spite of the difference of the structures the shortest intermolecular distances in solid hydrogen and deuterium are of the same length. The molecular radius of hydrogen and deuterium was determined as 1.7~1.8Å. The minimum approach of 2 protons of different molecules is 2.6~2.8Å, in comparison with 2.6Å in organic compounds.

The absence of isomorphisms in solid hydrogen and deuterium was called isotope morphotropy. In a different sence this phenomenon takes place in solid helium: He^3 has two polymorphic modifications α and β, but He^4 has only one form. We suppose that pure ortho and pure para hydrogen (just as deuterium) may possess different structures. The difference in the symmetries of para and orthoparticles is the reason for this supposition: the paramolecules having a quantum number $l=0$, do not rotate and hence possess the form of dumbells, on the other hand the orthomolecules having $l=1$ are in rotation and possess the form of spheres. There is no reason to suppose them to be isomorphous. This phenomenon has been called spin morphotropy. But we have to note that the comparatively large intermolecular distances may obscure this effect.

References

1 Keesem, 1930 (see reference 2)).
2 V. S. Cogan, B. G. Lazarev and R. Ph. Bulatova: J. Exp. Ther. Phys. **37** (1959) 678.
3 R. P. Ozerov, S. V. Kiselev, I. R. Karpovitch, V. I. Gomankov and A. A. Loshmanov: Krystallographija **5** (1960) 317.
4 V. S. Cogan, R. P. Ozerov, B. G. Lazarev and G. S. Zhdanov: Ibid, **5** (1960) 319.