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DIFFRACTION OF X-RAYS BY POLYCRYSTALLINE SAMPLES OF HYDROGEN ISOTOPES

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Comparison of the interference patterns obtained in the scattering of x-rays by polycrystalline samples of hydrogen isotopes indicates the existence of isotopic polymorphism. The structural difference between hydrogen and deuterium and the structural proximity of the latter to tritium give evidence that the polymorphism is connected not with dissimilarity of energy spectra but with difference of atomic weights. The observed structural differences of the hydrogen isotopes are in accord with the hydrogen-deuterium state diagram.[1] The parametric data cited in this work as characterizing the structures of the hydrogen isotopes (tritium and deuterium have a tetragonal lattice with $c/a = 1.73$ and $a = 3.3$ and 3.35 A, respectively; hydrogen has either a hexagonal lattice with $c/a = 1.73$ and $a = 3.7$ A or a tetragonal lattice with $c/a = 0.82$ and $a = 4.5$ A), although in accord with density data and with the results of x-ray investigations of isotope mixtures, still need improvement of precision by methods permitting the production of more complete interference patterns.

As previously[1] reported, the scattering of x-rays by polycrystalline samples of hydrogen, deuterium, and their mixtures yields diffraction patterns differing from each other, depending upon the isotopic composition of the samples. The dissimilarity of the diffraction patterns secured with hydrogen and deuterium permitted the supposition that they had different crystalline structures. This difference in crystalline structure may be due both to inequality of the atomic weights and the disparity of the energy spectra of their molecules. To elucidate the relative influence of these factors, it appeared interesting to obtain the diffraction pattern of the scattering of x-rays by samples of the third hydrogen isotope — tritium, which is closer to deuterium in atomic weight, but closer to hydrogen in energy spectrum because, like hydrogen, it has a half-integral spin.

Tritium samples were obtained and x-rayed in the apparatus schematically shown in Fig. 1. The construction of the apparatus takes into account not only the fact that the radioactive tritium irradiates the x-ray film even during brief contact with it, but also that the decay product of tritium is helium, the entrance of which, together with the investigated gas, into the apparatus and consequently into the evacuated space of the helium Dewar flask occasions deterioration of the vacuum and rapid boil-off of the helium. In order to preclude its contact with gaseous helium, the x-ray film was placed outside the Plexiglas chamber 4, used to seal the apparatus. In this chamber a narrow groove is machined out, leaving a wall with a thickness of 0.3 mm. Such a wall freely transmits x-rays but completely absorbs the slow electrons emitted in the decay of tritium.

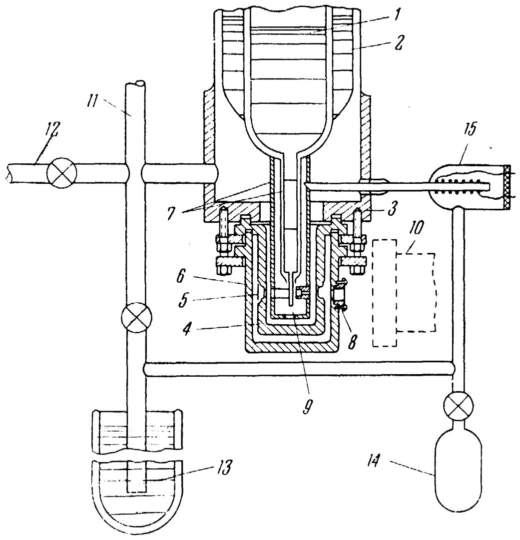

FIG. 1. Cryostat for x-ray photographs of samples of solid hydrogen isotopes: 1) metallic Dewar helium flask, 2) metallic Dewar nitrogen flask, 3) flange with fastening to seal the apparatus, 4) plexiglas chamber sealed to the apparatus, 5) x-ray film, 6) thick-walled safety chamber of plexiglas, 7) shields at nitrogen temperature, 8) beryllium window for admitting x-rays into the chamber, 9) copper capillary cooled from within by liquid helium (serves as the base for condensing samples of solid hydrogen isotopes from the gaseous phase), 10) sharp-focussing x-ray tube, 11) pipe branch to manometer tubes, 12) pipe branch to pump, 13) pipe cooled by liquid helium (serves for removing tritium present in the apparatus after it has warmed up), 14) flask containing tritium, 15) palladium filter.

To prevent the possible escape of tritium into the atmosphere in the event of rupture of the thin plexiglass, a second thick-walled enclosure 6 is provided, with a beryllium window 8 for the passage of the x-rays.

The helium was separated from the gas entering into the apparatus by a palladium filter, 15. The gas fed into the apparatus was condensed on a copper capillary, 9, cooled by liquid helium from within.

The apparatus for x-ray photography of hydrogen and deuterium differs from that described above by having a valve with a fine adjustment in place of the palladium filter; the x-ray film is not situated outside the plexiglass chamber, but located within it, thus eliminating the need for an internal chamber with a thin wall.

It should be noted that we did not succeed in eliminating all the fog from the tritium x-ray pictures. Apparently, it is due to the x-rays produced when β-electrons are slowed down in the sample substance. The intensity of this radiation amounts to $\sim 10^{-5}$ of the original beam intensity from the x-ray tube and is, of course, sufficient to produce considerable fogging of the x-ray film in a 2 or 3 hour exposure. The tritium vaporized after the helium Dewar flask has warmed up is collected in a tube, 13, which is cooled by liquid helium.

An x-ray pattern of a polycrystalline tritium sample is shown in Fig. 2. From a comparison with patterns of hydrogen and deuterium (Fig. 3) it is evident that in interference pattern character tritium is closer to deuterium than to hydrogen.

The character of the diffraction patterns obtained for hydrogen isotopes requires some supplementary remarks. As already pointed out in a previous communication,[1] the peculiarities of the method employed to obtain the samples (a transparent layer of condensed gas on a copper rod which is not transparent to x-rays) occasion the appearance of extraneous lines on the pattern, the causes of which are clear from Fig. 4. The use of lead screen 7 eliminates both of the extraneous lines 6 and 6′, while lead screen 8 removes one of the extraneous lines 6 and one of the principal lines 5′. The patterns shown in Figs. 2, 3a, and 3b were taken in Fe K_α radiation with a manganese filter. Patterns a and b in Fig. 3 were taken with screen 7 and do not have the extraneous lines; Fig. 2 was taken with screen 8 and shows one principal line and one extraneous one (marked by dashes). Pattern c in Fig. 3 was taken without screens and it displays all the principal and supplementary lines.*

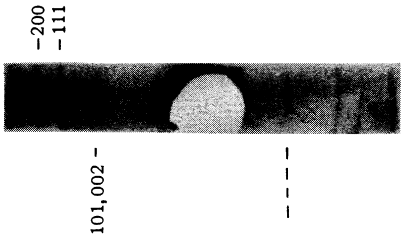

FIG. 2. X-ray pattern of tritium. Lines 200 and 111 are the standard copper lines from the capillary; 101 and 002 are the tritium lines. The extraneous line of type 6′ (see Fig. 4) is indicated by the dashes.

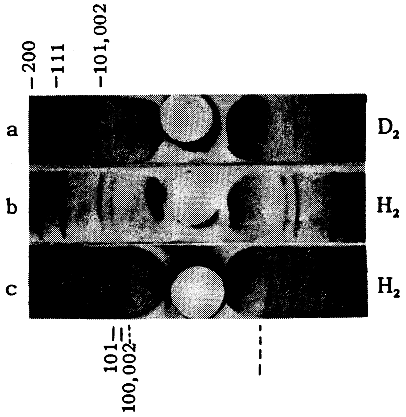

FIG. 3. X-ray pattern of deuterium and hydrogen. 200 and 111 are the copper lines; 101 and 002 are the deuterium lines; 101, 100 and 002 are the hydrogen lines (the indicated indices are for hexagonal lattice). The dashes point to the extraneous lines in the hydrogen x-ray pattern, taken without lead screens.

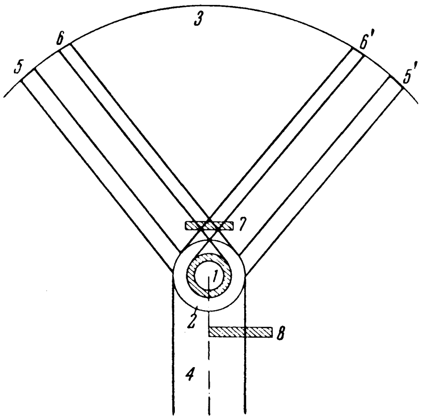

FIG. 4. Diagram of the arrangement for getting diffraction pictures from a layer of gas condensed on the copper capillary and transparent to x-rays. 1) copper capillary, 2) layer of condensed gas, 3) x-ray film, 4) primary beam, 5 and 5′) principal refracted rays, 6 and 6′) supplementary (extraneous) refracted rays, 7) lead screen to eliminate both extraneous rays, 8) lead screen to eliminate one extraneous ray (6) and one principal ray (5′).

In previous work on the structure of hydrogen[2,3] and deuterium,[3] the extraneous lines were not sifted

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*The distance between the principal and supplementary lines is somewhat greater than would result from the diagram in Fig. 4, since the latter does not take into account the dispersion of the primary beam.

Isotope:	Hydrogen		Deuterium	Tritium
Possible syngony and space group	Tetragonal C_4^5	Hexagonal D_{6n}^4	Tetragonal C_4^5	Tetragonal C_4^5
Number of molecules per unit cell	2	6	2	2
Absence of lines at small angles	001, 100	001	001, 100	001, 100
Lines present in the pattern	110 and 101	100, 002 and 101	101, 002	101, 002
$\sin\vartheta$*	0.298 and 0.335	0.298 and 0.335	0.330	0.335
c/a	0.82	1.73	1.73	1.73
c, A	3.75	6.49	5.86	5.78
c^{**}_{extrap}, A	3,68	6.42	5.79	5.71
a_{extrap}, A	4.5	3.7	3.35	3.3
Density at 4.2° K, g/cm^3	0.09	0.089	0.205	0.324
Data in literature on density at 4.2° K	0.089 [4]		0.205 [4	0.27[5]***

*Corrected for the diameter of the copper capillary and the thickness of the layer of condensed gas. The effective diameter of the cassette was determined for each pattern on the basis of the copper lines.

**The value of c_{extrap} for deuterium was obtained by extrapolating the graph in Fig. 5. Hydrogen and tritium were photographed only in Fe radiation. The same extrapolation law was adopted for them as for deuterium.

***Density value cited for 20.6°K. If the variation of this density with temperature is taken to be the same as for deuterium,[4] extrapolation to 4.2°K gives a value of 0.32 g/cm^3, which is in good agreement with the value secured from the x-ray data.

out, so that, naturally, the conclusions contained in these reports with regard to the structure of hydrogen and deuterium must be reconsidered.

After removal of the extraneous lines, there remain two lines on each of the hydrogen patterns and one line on each of the deuterium patterns. These lines are seen at small angles, since with increasing angle the intensity of the diffraction is sharply diminished on account of the angular dependence of the atomic and thermal factors. The small number of interference lines on the patterns of the hydrogen isotopes does not permit reliable indexing and the determination of the law of interference extinction, and thus an unambiguous selection of the space groups. However, this might still be attempted with a certain degree of reliability.

Knowing the densities of hydrogen, deuterium,[4] and tritium[5] it can be shown (if consideration is restricted to the simplest cubic, tetragonal, and hexagonal syngonies) that the lines present in the patterns do not represent reflections from the planes with the smallest indices. This immediately permits the establishment of a series of extinctions at the smallest angles and thereby reduces the range of possible space groups. Thus it proves possible to propose one most probable space group for deuterium and tritium, and two for hydrogen between which a final choice could not be made on the basis of the available patterns. The results of the calculations are presented in the table.

In calculating the lattice parameters on the basis of lines not only few in number, but also arrayed at small angles, the following method was employed to render possible extrapolation up to 90°.* Using the same object under identical conditions, x-ray photographs were taken with different radiation sources. The lattice parameters calculated according to the lines in these photographs, located in dependence upon the wavelength at the different respective angles, furnished the set of values needed for executing the extrapolation. Figure 5 shows the extrapolation line for the parameter c of the deuterium lattice, calculated on the basis of the single line 002, taken with four radiation sources.

The accuracy of the calculated lattice parameters shown for hydrogen and deuterium in the table, as well as the choice of the space group for deuterium, is corroborated by the results of x-ray structural analysis for samples of hydrogen-deuterium mixtures: in the range of solid solutions an increase in the concentration of deuterium occasions

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*To reduce the relative error in determining the lattice parameters.

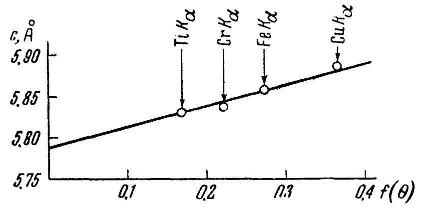

FIG. 5. Extrapolation graph for the parameter c of deuterium (the value of c is determined in accordance with line 002, in patterns taken with each of four radiation sources: Cu K_α, Fe K_α, Cr K_α, Ti K_α). The abscissas represent

$$f(\theta)=\frac{1}{2}\left[\frac{\cos^2\theta}{\sin^2\theta}+\frac{\cos^2\theta}{\theta}\right]$$

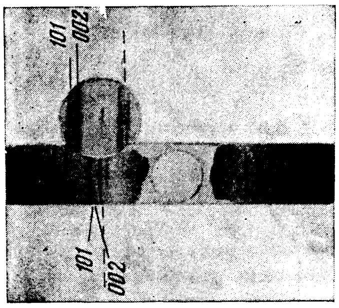

FIG. 6. Enlarged pattern of a hydrogen-deuterium mixture (80% deuterium by volume). 101 and 002 are the lines of a solid solution of hydrogen in deuterium. The dashes point to the extraneous lines of type 6 and 6′ (see Fig. 4).

a decrease of the average volume per molecule, while an increase in the concentration of hydrogen causes a decrease of this volume. This agrees with the tabulated data, from which it is seen that the volume per molecule in the deuterium lattice (~ 33 A^3) is smaller than the value in the hydrogen lattice (~ 38 A^3). At both of the solid-solution limits (15% and 80% deuterium by volume) the mean volume per molecule is ≈ 35 A^3.

Patterns of deuterium samples with large hydrogen admixtures (20% hydrogen by volume) have not one line, like those of pure deuterium, but two closely spaced lines. This corresponds to a change in the ratio of the tetragonal lattice axes up to values at which coincidence of the lines 101 and 002 no longer occurs. A magnified pattern of such a mixture is presented in Fig. 6; it was taken without a filter and without lead screens, so that the lines of Fe K_β and the extraneous lines of type 6 (Fig. 4) are visible in it.

The foregoing data on the structures of the hydrogen isotopes should not be considered definitive until they have been confirmed by some other method permitting the display of a larger number of interferences. The most effective would probably be the neutron diffraction method, which possesses the advantage that its application is not subject to so sharp a decrease of interference intensity with increasing scattering angle. Thus the use of neutron diffraction would in considerable measure remove the difficulty encountered in the observation of interferences in the scattering of x-rays in such light objects as the hydrogen isotopes, and which yields only one or two interference lines at small angles.

However, independently of the results of the experiments which will be undertaken for the more accurate determination of the structures of the hydrogen isotopes, it is already possible, from the character of the interference patterns, to affirm a difference in the structures of hydrogen and deuterium and a close similarity of the structures of deuterium and tritium. The solid-liquid phase diagram for the hydrogen-deuterium system,[1] in which there is no region occupied by a continuous series of solid solutions right up to the melting point, is also in accord with the fact that these isotopes crystallize in lattices of different structure.

The existence of the phenomenon of isotopic polymorphism, observed in the hydrogen isotopes,[3] was recently corroborated by studies of the structure of helium isotopes, in which it was shown that He^3 has a second modification, different in structure from He^4.[6]

The authors express their thanks to M. N. Massalitin for the construction of the cryostats used in this work.

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