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TEXTURE IN LAYERS OF HYDROGEN ISOTOPES CONDENSED ON A COOLED SUBSTRATE

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A comparison of the x-ray photographs obtained from specimens of the hydrogen isotopes condensed in one case inside a beryllium tube, and in the other case on the surface of a copper rod, shows that the latter specimens have a texture which is not the same for protium layers as it is for deuterium. The existence of the texture requires previous structure data to be reevaluated. This reevaluation leads to the conclusion that both isotopes have a hexagonal structure with somewhat differing axial ratios c/a.

1. INTRODUCTION

It has been established, during x-ray structure studies on layers of the hydrogen isotopes condensed on a cylindrical capillary tube cooled from within by liquid helium, that different diffraction pictures are obtained from protium and deuterium.[1] Two diffraction lines are present in x-ray photographs of the former and only one in x-ray photographs of the latter. Despite the extremely poor diffraction photographs, a fact related to the characteristics of x-ray scattering from light elements, an attempt was made to decipher them. It was assumed that the layers were isotropic, and that the absence of certain lines at small angles was related to the extinction rules of the corresponding structures.[2]

However, the absence of diffraction lines could also be caused by the existence of texture. In order to clarify the question of the texture in layers of the hydrogen isotopes, the method of obtaining the specimens was changed. Instead of condensation on the side surface of a cold cylinder,[2] the specimens were condensed inside a beryllium tube of inside diameter 0.8 mm (wall thickness 0.4 mm). The cryostat in which this was carried out is shown in Fig. 1. The beryllium tube 1 is soldered at one end to a copper rod 2, cooled by liquid helium with the aid of a thick copper rope 4, and at the other end to a German silver capillary 3 which is led out from the cryostat. This capillary admits the gas which is condensed on the end of the copper cylinder and on the walls of the beryllium tube. Despite the fact that helium and nitrogen screens 5 and 6, with entrance and exit windows for the x-rays, were provided around the specimen, the temperature of the condensed layer (measured by the vapor pressures over it) was approximately 1°K above the temperature of the helium bath, and the specimens crystallized in the form of coarse-grained layers which gave a small number of reflections on the x-ray photograph. The specimen in the cryostat could be oscillated within angle limits ± 300°.

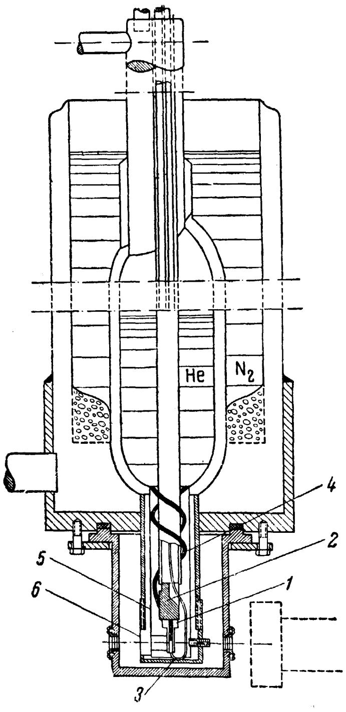

FIG. 1. Cryostat for x-ray photography of specimens of the hydrogen isotopes condensed in a beryllium tube.

2. RESULTS

1. Protium. The x-ray photographs from specimens of protium condensed inside the beryllium tube showed clearly reflections lying on three lines (see Fig. 2). For photographs in copper radiation these lines were seen at angles the sines of which were 0.235, 0.250, and 0.265; they are well identified as the (100), (002), and (101) lines of a hexagonal lattice with axial ratio c/a = 1.63 (c = 6.16 Å and a = 3.78 Å). The presence of only two lines on x-ray photographs taken from a layer of hydrogen condensed on the side surface of a cylinder[2] can, apparently, be explained by the disappearance (or extreme weakening) of the middle line.

For a hexagonal lattice the absence on the x-ray photographs of the line (002) can, in such a method of photography, signify the presence of texture with the plane (002) perpendicular to the surface of the substrate. In fact, from the schematic diagram of Fig. 3a it is clear that reflection from the plane (002) can occur with such a texture near the equatorial plane of the x-ray film only due to scattering of x-rays at crystals situated either in the shadow of the opaque cylinder (region A), or in such a position that this cylinder screens the diffracted beams (region B). In Fig. 3b the pole figures of the (002) plane are given first for the part of the layer directed along the radius of the specimen perpendicular to the x-ray beam (direction S_0), and second for the regions which are in a reflecting position, i.e., rotated relative to the first by an angle $90° + \theta$ clockwise or by an angle $90° - \theta$ anticlockwise.

By a similar construction of pole figures for the planes (100) and (101) with the texture specified it can be shown that reflections from these planes will always be present on the x-ray film.

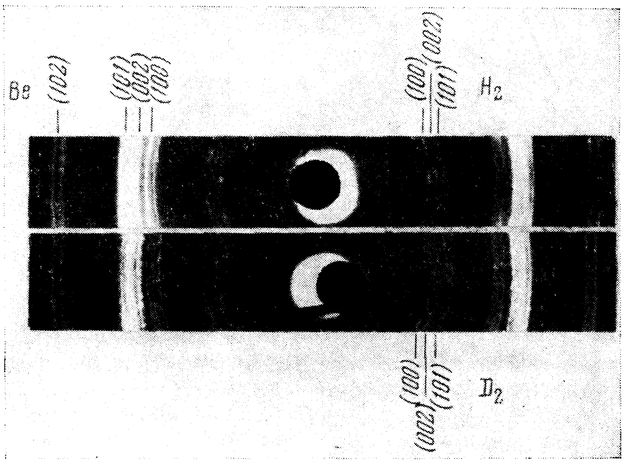

FIG. 2. X-ray photographs from specimens of the hydrogen isotopes condensed in a beryllium tube.

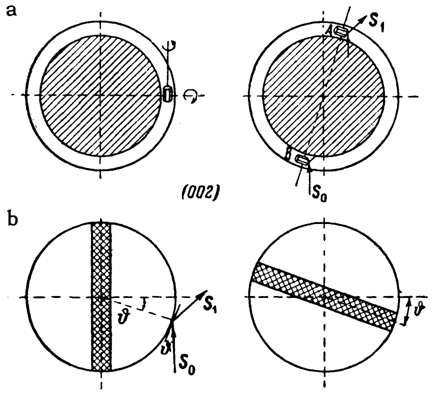

FIG. 3. Pole figures for the (002) plane: a—for the portion of the condensed layer lying along the specimen radius perpendicular to the x-ray beam; b—for the portions of the layer which are in the reflecting position for this line.

The absence of texture effects in x-ray photography on specimens of solid protium condensed inside the beryllium tube is due to the fact that the condensation occurs on the bottom of the copper cylinder and on the walls of the beryllium capillary which are perpendicular to it. This causes a wide range of crystallite orientations to be present in the specimen. In addition there is in this case no screening copper cylinder, so that all portions of the specimen are of equal weight, and this increases the probability of obtaining on the x-ray film a complete diffraction pattern as one would from an isotropic polycrystalline specimen.

2. Deuterium. The x-ray photographs of deuterium taken in the cryostat shown in Fig. 1 contain, just as in the case of protium, a larger number of lines than the x-ray photographs of layers condensed on the side surface of a cylinder coaxial with the x-ray film. On x-ray photographs taken in copper K_α radiation, diffraction lines were present at angles the sines of which were 0.251, 0.261, and 0.283 (the first two of these are resolved with difficulty). These lines can be identified as the (100), (002), and (101) lines of a hexagonal lattice with axial ratio c/a = 1.67 (a = 3.54 Å, c = 5.91 Å). In that case the single line present on x-ray photographs taken from layers deposited on the side surface of a cold cylinder is the (002) line. Thus, in distinction from protium layers, deuterium has a texture which, under the methods specified for obtaining these specimens and their x-ray photographs, causes the (002) line not to disappear, but, on the contrary, to remain alone on the x-ray photographs. It is easy to show that a texture with a preferential orientation of the (002) plane parallel to the substrate is such a texture.

3. Other isotopes of hydrogen. X-ray photo-

graphs from a third isotope of hydrogen, deuterohydrogen, obtained in the apparatus with the beryllium capillary, were similar to the x-ray photographs of deuterium. It was also possible to identify the diffraction lines as the (100), (002), and (101) lines of a hexagonal lattice with axial ratio $c/a = 1.66$ ($a = 3.68\,\text{Å}$, $c = 6.06\,\text{Å}$). A calculation based on the x-ray photographs of tritium previously obtained[2], and containing only one line, gives values of the parameters $a = 3.47\,\text{Å}$, $c = 5.80\,\text{Å}$ ($c/a = 1.67$) if we attribute to this line the indices (002) of a hexagonal cell.

3. DISCUSSION OF RESULTS AND CONCLUSIONS

A. The difference in the diffraction patterns obtained when x rays are scattered from layers of the hydrogen isotopes condensed on the side surface of a cold cylinder can be explained consistently by the presence of texture in such layers and by its difference for protium and deuterium. This isotope effect in the type of texture can be compared with the temperature variation, well known in the literature,[3] in the type of texture in layers of the hexagonal metals deposited from the vapor phase. Thus, for example, at a substrate temperature above $\sim 0.7\,T_M$ (T_M is the melting temperature of the corresponding metal), zinc and cadmium crystallize with a preferential orientation of the (002) plane perpendicular to the substrate (as in protium at 4.2°K), and for a substrate temperature below $0.7\,T_M$ they crystallize with a preferential orientation of this plane parallel to the substrate (as for deuterium at 4.2°K).

For protium and deuterium, which have different melting temperatures and sharply differing equilibrium vapor pressures at a given temperature, a substrate at a temperature of 4.2°K has different effective temperatures. It is effectively colder for deuterium than for protium. It is possible that the isotope effect in the texture type for the hydrogen isotopes should, in fact, be explained by this temperature variation of texture.

B. The evaluation of the x-ray photographs of the hydrogen isotopes with account of the preferred orientation effect leads to the conclusion that all hydrogen isotopes crystallize at helium temperature in a hexagonal lattice. Consequently, the conclusion contained in previous work[2] about the presence in hydrogen of the phenomenon of isotopic polymorphism, which was based on the interpretation of the x-ray photographs under the assumption that the specimens were isotropic, apparently requires reconsideration. One can speak, not of polymorphism, but of an isomorphic transition in the lattice of the hydrogen isotopes when molecules of protium are replaced by molecules of its heavier isotopes. In this transition the axial ratio of the hexagonal lattice jumps from $c/a = 1.63$ for protium to $c/a = 1.66-1.67$ for all its heavier isotopes. It is characteristic that this change is principally brought about by the change of the parameter a (for example, in the transition from protium to deuterium it changes by 6.5%, whilst the parameter c changes only by 4%). This is easily explained by the fact that the a axis lies in the (001) plane of maximum density. In this plane there are the minimum intermolecular distances and, correspondingly, the greatest bond strengths f between molecules. The change of energy of the zero-point vibrations in a lattice when their mass is changed is, in fact, a maximum for those frequencies which correspond to vibrations in the plane with greatest bond strengths, since $\Delta E \sim h\Delta\nu = \sqrt{f}\,\Delta m/2m^{3/2}$. It is obvious that in this particular plane should be observed the maximum isotope effect in the value of the lattice parameter.

Apparently the inadequate resolving power of the neutron diffraction patterns obtained from solid protium and deuterium[4] caused the maxima present in them to be assigned indices that could be fitted in the diffraction patterns of the structures proposed on the basis of x-ray evaluation under the assumption that the specimens were isotropic. Taking into account the uncertainty in the position of the diffraction maxima, due to the large specimen volume and to the possibility that crystals capable of reflecting a given line can be located in different parts of this volume, it is possible to fit these maxima, with the same degree of precision, in the diffraction pattern of a hexagonal lattice.

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