A meta-stable polymorph of the hydrogen isotopes solidified near the triple-point

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Hydrogen (H_2), deuterium (D_2), and the $0.25D_2$-0.5DT-$0.25T_2$ isotopic mixture of deuterium and tritium (D-T) each form a meta-stable solid state below their respective triple-point temperatures. The meta-stable solid is observed to nucleate and grow from inside of a 5 - 10 μm inner diameter borosilicate glass tube when the liquid hydrogens are slowly cooled through their respective triple point temperatures. These meta-stable solids have their triple-point temperature 15-43 mK below the stable hexagonal close-packed (hcp) crystal of the same composition, a different growth habit, and recrystallizes to the hcp phase. This meta-stable solid may be a crystal with unknown structure or, less likely, hcp with stacking faults and other defects.

Hydrogen and its isotopes are known to crystallize in the hexagonal close-packed (hcp) structure when cooled from the liquid through the triple point [1]. However, other structures are found with other solidification conditions. The structure is face-centered cubic (fcc) when deposited at less than 4 K directly from the vapor, when the $J = 1$ rotational population is high (due to orientational ordering of the molecules), or under pressure [1]. One study claimed that H_2 and D_2 would form an fcc structure when grown from the liquid on a cube-textured gold foil [2]. A mixture of hcp and fcc was observed when depositing J = 0 D_2 and H_2 onto a MgF_2 substrate at temperatures of 0.2 - 0.3 T_{TP}, where T_{TP} is the triple-point temperature [3]. However, the fcc converted to hcp when the sample was warmed. Disordered solids have also been observed for gases condensed into confined geometries such as Vycor glass[4, 5] and cylindrical pores [6].

The Van der Waals bonded rare gas solids (except He) form the fcc phase. A meta-stable hcp phase was reported for polycrystalline argon [7]. Small clusters have been shown to form an icosahedral structure that transforms to fcc with increasing cluster size, [8, 9] with stacking faults responsible for the transformation[10, 11].

We have observed the hydrogen isotopes to solidify into a meta-stable solid state in our many of our inertial confinement fusion (ICF) target assemblies. Although diffraction data is not yet available, there are four key observations that suggest a meta-stable solid phase. The first is that the triple-point temperature of the meta-stable phase is lower than the stable hcp phase by 40 mK, 22 mK, and 16 mK for H_2, D_2, and D-T respectively. The second observation is a sudden recrystallization that produces many visible grain boundaries and defects on time scales of 10 seconds to minutes. Third, nucleation and growth of the hcp phase occurs at the expense of the already present meta-stable phase. Finally, crystallographic growth shape anisotropy typical of the hcp phase is missing in the meta-stable solid. A determination of the nature of the meta-stable phase has not yet been made. The likely candidates are that it is a defect rich hcp structure, e.g. the hcp/fcc mixture full of stacking faults (SF) and twins, or more likely a regular polymorph with unknown structure.

The ICF target assembly consists of a 2 mm OD spherical ablator shell, composed of either beryllium or plastic, approximately 40 - 150 μm wall thickness. A 5 - 10 μm diameter hole is laser drilled into the shell and a fill-tube is attached to first evacuate then admit the hydrogen gas sample to the shell [12–14]. Figure 1 shows the section of the shell with the fill-tube attachment. The fill-tube is made of borosilicate glass, with one end epoxied into the shell and the other into a larger diameter polyimide-coated fused-silica glass. The shell and fill-tube are suspended by polyimide films inside of a 5.5 mm diameter, 10 mm long cylindrical aluminum hohlraum. The assembly is placed inside a cryostat and cooled to 14-20 K. Then the hydrogen gas is admitted to the shell where it condenses as liquid under its own vapor pressure. Characterization is performed using x-ray phase contrast enhanced imaging along one axis[16**?**], and interferometry and back-lit optical microscopy[17] along the perpendicular axis, both in the horizontal plane. Heaters above and below the capsule on the hohlraum allows a temperature gradient if needed.

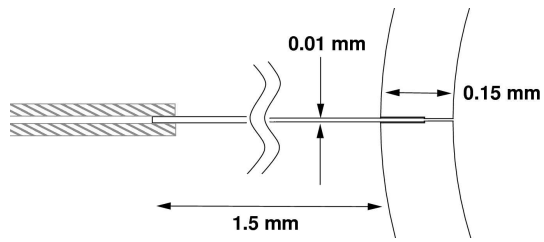

FIG. 1: Detail of the shell and fill-tube assembly showing the section of the spherical ablator shell 0.15 mm thick with the fill-tube. The borosilicate fill-tube is 0.010 mm in diameter where it enters the shell, tapering up to 0.020 mm where it is inserted into the larger diameter polyimide-coated silica-glass tube.

The meta-stable state was first observed with the D-T mixture that is taken from a palladium storage system. The isotopic composition of the D-T mixture is nominally $25\%D_2$-50%DT-$25\%T_2$, but is not measured at the time of use. The above experiments were repeated using D_2 in the same shell that had previously been used with D-T experiment. Then a new shell assembly was built and measurements were made using H_2 and D_2 before D-T to verify that the observations were not due to radiation damage from β-decay of tritium. The H_2 and D_2 were research purity, with 99.9999% purity of the H_2 and 99.5% purity of D_2, with 0.5% HD being the dominant impurity in the D_2 gas. The meta-stable phase was

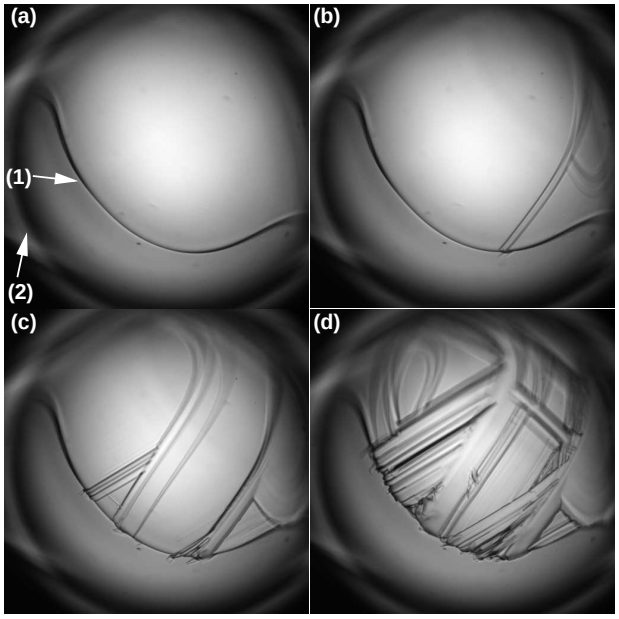

FIG. 2: Back-lit visible light images taken during recrystallization of D_2. The meta-stable solid is at the top of the images, with the arrow in (a) pointing to the solid-vapor interface. The meta-stable solid was solidified from the liquid over 7 hours at T^*_{TP} - 1.5 mK, and is constant for the four images. Images are taken (b) 11 s, (c) 56 s, and (d) 120 s after (a) and show the conversion of the featureless meta-stable solid to the stable hcp phase.

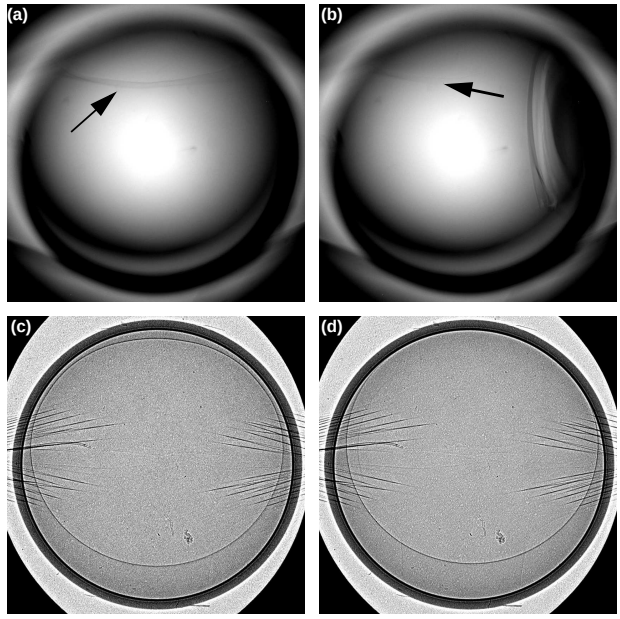

FIG. 3: Visible (top) and x-ray images (bottom) of D-T just before and after recrystallization. Image (a) is 34 s before the recrystallization event, (b) 26 s after. Image (c) is taken 10 s before recrystallization, (d) 120 s after recrystallization. In (a) and (c) the meta-stable solid phase is located at the top of the image, with the arrow in (a) pointing to the interface between the meta-stable solid and liquid. In (b) and (d) the stable solid phase is growing from the side of the shell at the expense of the meta-stable phase. The arrow in (b) point in the direction of the retreating meta-stable phase. X-ray images are orthogonal to the visible images. The fill tube enters from the left side in all images.

observed with both H_2 and D_2.

The procedure to generate the meta-stable solid is as follows. Solid initially in the shell is melted by raising the temperature 2 - 50 mK above the hcp phase triple-point temperature, T^I_{TP}. Solidification inside the shell typically begins at the fill-tube and propagates into the shell when $T^I_{TP} > T > T^I_{TP} - 50$ mK, with the under-cooling decreasing with increasing isotope mass. In some cases, the hcp c-plane emerges typically parallel, but sometimes normal to the fill-tube axis[18]. However, the meta-stable phase can emerge from the fill-tube instead, appearing much more often within the 5 - 10 μm inner diameter borosilicate fill-tubes than the previous 30-40 μm fused silica (SiO_2) fill-tubes.

Figure 2 shows the optical microscope images of the D_2 meta-stable solid and its recrystallization. In these images gravity is down, the supporting polyimide films are visible out-of-focus at the top and bottom of the shell, and the fill-tube enters from the left side of the image at the center plane of the shell. The microscope is focused on the side of the shell closest to the camera. The temperature was held 1.5 mK below T^*_{TP} for 7 hours. The 1×10^{-3} cc liquid solidified in 4-5 hours and the solid slowly migrated due to the vertical thermal gradient over the next 2-3 hours. Figure 2(a) is taken just before the recrystallization begins. The solid–vapor interface is indicated by the arrow (1), with the solid in the upper portion of the shell. Figures 2(b)-(d) were taken with the temperature held constant at 11 s, 56 s, and 120 s after (a), respectively. Increasing numbers of grain boundaries replace the featureless solid of (a) as the recrystallization occurs. Few changes to the solid are visible after $\approx$ 600 s.

Figure 3 shows visible (top) and x-ray (bottom) images just before and after the recrystallization of D-T from the meta-stable to stable phase. Panels (a) and (c) show the meta-stable phase near the top of the shell. As in Fig. 2, the meta-stable solid emerged from the fill-tube. The temperature was then increased by 3 mK and held constant to keep the solid volume approximately constant. The solid migrated from the center-plane to the colder top of the shell. Panels (a) and (c) were taken about 1 hour after the meta-stable solid emerged from the fill-tube. The x-ray image shows that the surface tension draws the liquid up the side of the shell into contact with the solid phase. It also shows that the meta-stable phase is up to 60 μm thick at the very top of the shell and 700 - 1000 μm in lateral extent. Panels (b) and (d) show the corresponding images just after recrystallization. The optical image shows the disappearance of the meta-stable phase at the top of the shell and the appearance of the stable hcp phase on the right side of the image. Panels (a) and (b) are 60 s apart. The x-ray image in panel (d) shows that the meta-stable solid is gone within 120 s of the start of recrystallization. The fill-tube, partially masked by straight lines due to wrinkles of the polyimide support films, is visible in (c) and (d) entering from

the left and stopping just short of the center of the shell.

Figures 2 and 3 show two examples where the meta-stable D_2 and D-T solids can be held neither growing nor shrinking 22 and 16.5 mK below T^I_{TP}, respectively. Increasing the temperature by 0.5 mK results in the meta-stable solid completely melting. Once all the solid is melted in the shell, the temperature needs to be reduced back to T^I_{TP} - 20 mK to T^I_{TP} - 23 mK to re-initiate the meta-stable solid growth from the fill-tube. In contrast, once the recrystallization event occurs it is necessary to raise the temperature to T^I_{TP} to completely melt the solid in the shell. Table I shows the difference between the hcp and meta-stable solid triple-point temperatures, ΔT_{TP}, for H_2, D_2, and D-T. The J = 1 concentration is calculated based on the self-conversion rates[19] for the H_2 and D_2 samples, which were held at or below T^I_{TP} for extended times. The range in J = 1 concentration is set by using the conversion time for liquid and solid samples. The D-T converts to a low J = 1 concentration quickly, with an 8-10 hour time constant, due to the radioactive decay[19]. Only a weak dependence is observed with the J = 1 concentration.

TABLE I: Triple-point temperature difference between the meta-stable phase and the hcp phase. The J=1 concentrations are estimated based on conversion rates and known time the solid is at or below its melting temperature.

Isotope	J = 1 (%)	ΔT_{TP} (mK)
H_2	75	42.0 ± 2.0
H_2	32-38	37.5 ± 0.7
D_2	33	21.0 ± 1.0
D_2	12-18	22.2 ± 0.5
D-T	< 2	16.5 ± 1.0
D-T	2-30	22.0 ± 1.0

The meta-stable phase was identified in a search of our previous experimental images for one shell with a 40 μm fill-tube suspended vertically in a spherical cavity. The meta-stable phase appeared with a frequency of less than 10% of the nucleation attempts for that shell. Additional experiments were carried out with H_2 and D_2 using an older style shell and fill-tube assembly, consisting of a 30 - 40 μm diameter fused-silica glass fill-tubes with plastic shells [15, 18, 20–23]. The meta-stable phase was not observed with the fill-tube either horizontal or vertical with the larger silica glass fill-tubes, in contrast to the observation with the borosilicate 5 μm tubes. Furthermore, the meta-stable phase appears in Be shells with the small-diameter fill-tubes, based on indirect x-ray images and the under-cooling necessary for solid to appear.

We do not yet have diffraction tools to characterize the structure of the meta-stable sold. Thus we will use the available data to analyze if the meta-stable solid is either a new hydrogen polymorph with unknown structure or a heavily defected hcp phase containing stacking faults (SF), twins, dislocations, and/or grain boundaries. The amorphous solid is not considered here because it exists at T $\lesssim$ 0.5 T_{TP}[24].

The upper limit to the defect density may be estimated as follows. We assume the total energy of the defects is responsible for the difference of the chemical potential $\Delta\mu$ of the meta-stable solid over the stable hcp phase. This $\Delta\mu$ value determines the shifts ΔT and ΔP of the temperature and pressure of the triple point between the meta-stable solid relative to that of the hcp solid phase (S) with the same liquid (L) and vapor (C):

$$\Delta T = (\omega_V - \omega_S)\,\Delta\mu/D, \Delta P = (s_V - s_L)\,\Delta\mu/D,$$
$$D \equiv (s_V - s_S)(\omega_L - \omega_S) - (s_L - s_S)(\omega_V - \omega_S)\,. \quad (1)$$

Here ω and s are the molecular volumes and entropies of the phases indicated by the subscripts. For D-T, ω_V = 1.33×10^{-20}cm^3, ω_L = 3.75 $\times10^{-23}$cm^3, ω_S = 3.30×10^{-23} cm^3, $s_V - s_S$ = 1.33×10^{-15} erg/K, $s_L - s_S$ = 1.83×10^{-16} erg/K [19]. Then $\Delta\mu$ = 3.01×10^{-18} erg, ΔP = 142 Pa (compared to the D-T saturated vapor pressure of 20080 Pa).

The elastic strain that would raise the hcp chemical potential by $\Delta\mu$ is $\epsilon \approx (2\Delta\mu/E\omega_S)^{1/2} \approx 6\times10^{-3}$, using the Young's modulus E = 5×10^9 erg/cm^3[25]. The residual strain storing the same energy $\Delta\mu$ would be generated by $\approx 2\times10^{12}$ dislocations/cm^2, or by SF with the average distance of $\approx$ 200 lattice spacings in between. The former number comes from the assumption that the SF energy is proportional to the evaporation enthalpy over the area $\omega^{2/3}$ per one molecule at an interface. That scaling works for the measured SF energy in Al, Ag, Cu, Ni, Pt[26] with the proportionality factor 7.2 $\times10^{-3}$ and estimates the SF energy in D-T to be 0.18 erg/cm^2. In our earlier experiments the hcp D-T layer was also grown near the triple point in the shell and was then cooled down by 1.5 K[18]. In those experiments, the difference in the D-T and shell thermal expansion coefficient led to the thermoplastic strain 2×10^{-3}, comparable with the above calculated strain of 6×10^{-3} equivalent to the energy $\Delta\mu$. In the previous experiments, the thermoplastic strain relaxed, forming optically visible grain boundary grooves in about one minute and continuing to evolve over approximately one hour. On the contrary, the meta-stable solid remained fully homogeneous for up to 48 hours of annealing near the triple-point, and also down to 0.25 K below the triple-point temperature. This behavior makes it unlikely that the dislocation network is responsible for the meta-stable solid.

The SF are much less mobile than dislocations so that the SF structures should be more stable to annealing. Formation of the SF may also lead to the hcp/fcc mixing[27]. However, no morphological features develop in the meta-stable solid neither during annealing nor when it migrates along the shell wall due to an applied thermal gradient. During the latter process, the meta-stable solid moves along the shell wall from a warmer to a cooler area at the speed of $\approx 10^{-5}$ - 10^{-6} cm/s by sublimation and recondensation, termed beta-layering[28, 29] for D-T. There is no crystallographic anisotropy on the smooth or wavy border of the meta-stable solid. That behavior excludes the reproduction of stacking fault sequence during growth by deposition of lattice layers generated by screw dis-

locations on a singular face, like in SiC growing layer by layer from the vapor. The lack of noticeable stress in hydrogens slowly growing near the melting temperature eliminates the similar replication of SFs in the material bulk by the Frank-Reed dislocation sources. Nearly parallel SFs crossing the growth front should merge with one another at the growth front (due to the Gibb-Thomson effect), thus decreasing the SF density and ΔT_{TP}. However, experiments show no dependence of ΔT_{TP} on the growth rate or history in general. The SF and twin formation occurs at high supersaturations in small particles but not in large samples[10]. Table I shows that ΔT_{TP} decreases when the isotope mass increases. That sequence is opposite to the triple-point temperature sequence, evaporation enthalpies, and thus SF energies. The same data in Table I above suggest a moderate effect of the J = 1 concentration on the meta-stable solid.

The facts and arguments discussed above suggest that the meta-stable solid is more likely a hydrogen polymorph rather than a defect rich hcp phase. Determination of the solid structure of the polymorph requires diffraction studies. Here we may only speculate that the close packing requirement might result in fcc, icosahedrons, or polygons with higher coordination, or even quasi-crystalline features in the structure.

The meta-stable solid seems to be a surface induced phase. The nucleation requires super-cooling of only 3 - 20 mK relative to T^*_{TP}, if initiated after melting the previous solid by T^I_{TP} + (1 - 50) mK. If the temperature is taken higher, typically T^I_{TP} + (100 - 500) mK, then the liquid often reaches super-coolings of 0.5 - 1.5 K before nucleation occurs. This well known effect[27] suggests that nucleation occurs on the subsurface crystalline islands not completely disordered by melting. The borosilicate glass fill-tube with the 5-10 μm inner diameter most often generates the meta-stable solid. Therefore, it is seems likely that the geometry plays a role in determining if the meta-stable or hcp solid grows. Additional experimental data is necessary to determine the mechanism that generates the meta-stable solid. We may speculate the meta-stable solid to be responsible for the triple-point dewetting.

In summary, a meta-stable polymorph of solid H_2, D_2, and D-T in equilibrium with both vapor and liquid at 16 - 43 mK below the respective hcp triple point has been observed. The solid does not change after annealing. When the regular hcp phase appears it grows at the expense of the meta-stable solid. The new solid has isotropic growth rate; it may grow and recrystallize preserving its properties. The unknown solid might be either a real polymorph with unknown structure, or, less likely, an hcp/fcc mixture with high density of stacking faults and twins entangled with other defects.

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