

Consequences of helium production from the radioactive decay of tritium on the properties of palladium tritide

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Tritium is an element of considerable interest in the nuclear industry. Since it is radioactive, it needs to be stored in a safe but easily recoverable manner. It is an isotope of H, and hence some of the techniques used for hydrogen storage can be employed, the safest being its storage in the form of a tritide. However, in contrast to the case of hydrogen, tritium decays into ^3He and thus modifies the properties of the tritide. The recoil energy of ^3He in this decay process is very small, ~ 1.03 eV, and not enough for atomic displacements to occur. We show in this paper, on the basis of our electronic structure calculations, that in the case of PdT, the ^3He produced from the radioactive decay of tritium, although not soluble in the tritide, can be easily retained, in a metastable state, in surprisingly large quantities at the octahedral interstitial sites where it is born. This can explain the expansion of the lattice parameter, the lowering of the plateau pressure, and the fragility of the tritide observed experimentally. We also find that the lowering of the plateau pressure is not entirely due to the lattice expansion as usually assumed and that electronic interactions also play a role.

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Tritium is an element of considerable interest and has important technological applications, especially in the nuclear industry. However, the radioactive nature of tritium imposes many conditions on its handling and storage which are in addition to those required for the storage of its sister isotope H. It has been recognized for a long time that the best way to store H is in the form of a hydride, which has the advantage of safety, easy recovery, and also much larger quantities of H can be stored per unit volume than in its liquid form. It is therefore quite natural to propose the storage of T in the form of a tritide, and the metals such as Pd, Ti, Zr, Er, and U and the intermetallic alloys such as LaNi_5 , ZrCo , etc., are commonly used for this purpose. The case of tritium storage, however, differs from the one of hydrogen storage in that, unlike hydrogen, T decays into ^3He with a half-life of 12.3 years,¹ through the decay process $T \rightarrow ^3\text{He} + \beta^- + \nu^-$, where β^- is an electron which is emitted with 18.582 keV of energy, and ν^- is an antineutrino. The recoil energy¹ of ^3He in this decay process is quite small, ~ 1.03 eV, and is insufficient to cause any damage to the lattice.

The presence of ^3He in the matrix considerably modifies the properties of the tritide. First, there is the volume expansion;¹⁻³ second, the plateau pressure isotherms are modified and there is a lowering of the plateau pressure;⁴ and finally the tritide becomes more fragile as it ages.⁷ An understanding of these property changes depends clearly on the knowledge of the location of ^3He in the matrix, and this has been a matter of considerable debate in the literature.¹⁻¹¹ Since helium is inert and insoluble in metals and known to cluster in the form of bubbles,¹² one naturally expects a similar behavior in a tritide. However, there are important differences between ^3He in a tritide and He in metals. In metals, He is not present naturally, but is introduced through He^+ -ion implantation. The defects, including vacancies, are

thus created in this process, and the implanted He can be easily trapped at the vacancies which can then act as nucleating centers for bubble formation. In a tritide, on the other hand, ^3He is naturally produced in the matrix in the decay process and no defects are created. One would thus expect ^3He to stay trapped at the appropriate interstitial sites in the matrix and hence no bubble formation to occur. It is known^{1,10-14} that, in contrast to He^+ -ion implantation in metals, surprisingly large quantities of ^3He can be introduced inside the tritide through this decay process, called the *tritium trick*, which are not possible by any other means. It is also known^{1-3,10-15} that all the ^3He produced is retained in the tritide and there is almost no or very little ^3He release from the tritide until a certain critical concentration of ^3He in the lattice is attained, after which ^3He starts to be released. This release is not gradual and is often termed rapid or accelerated release to distinguish it from the very slow release that occurs in some tritides from fractured surfaces and grain boundaries^{2,16} at low ^3He concentrations. The concentration of ^3He in the tritide is usually defined in terms of a parameter R , which is the ratio of the total number of helium atoms to the total number of metal atoms in the lattice—namely, $R = ^3\text{He}/\text{metal}$ —and accelerated ^3He release occurs only when R exceeds a critical value R_C . The value of R_C depends upon the tritide, but generally lies¹³⁻¹⁶ between 0.25 and 0.4, and apparently does not depend upon the concentration of T, but only on the ^3He concentration. For PdT, a value as large as 0.5 has been reported after several years of aging.^{13,14}

We thus have a unique situation for ^3He in the tritides. The experimental evidence in favor of ^3He accumulation in the form of bubbles comes essentially from transmission electron microscopy (TEM) observations¹⁷ on thin films of tritides and from the interpretation of the nuclear magnetic resonance (NMR) line shapes.⁸ Bubbles of ~ 10 – 20 Å in

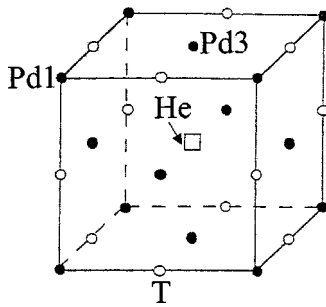


FIG. 1. Simple cubic unit cell of $\text{PdT}_{0.75}\text{He}_{0.25}$ which shows the different sites.

diameter have been observed by TEM. However, it should be noted that the thin films used in TEM experiments can be strained during charging by tritium or the thinning of the bulk tritide sample, which could favor bubble formation in the region investigated by TEM experiments. NMR line shape data has also been interpreted¹¹ as evidence of bubble formation. Kass¹⁸ has presented evidence for ^3He trapping at interstitial sites by desorption experiments. He finds a single trap with an activation energy of ~ 0.74 eV in an aged tritide while two traps with activation energies of ~ 0.65 and 2.70 eV are found in He^- -ion-implanted tritide. The difference of the two activation energies, ~ 2 eV, is roughly the ^3He -vacancy binding energy. This would indicate that vacancies are not created in a naturally aging tritide, unlike the case of ion implantation.

Experimentally, only very limited information¹⁹ can be obtained concerning the location of ^3He since it is trapped in the bulk of the tritide. Nevertheless, it is extremely important to know where precisely ^3He resides in the lattice, especially when large quantities are concerned. For large ^3He concentrations in the lattice it seems reasonable to assume that some of it will agglomerate in the form of platelets or bubbles, but for very large concentrations it is not clear that all the ^3He can be in the form of bubbles since in this case bubbles of very large diameters will be required.¹⁵ Due to the inert nature of ^3He , it is also not at all obvious that ^3He can be retained at the interstitial sites, especially in large quantities. This has motivated the present work in which we have investigated the question of ^3He retention at the octahedral interstitial sites in PdT by performing *ab initio* electronic structure calculations^{20,21} using the linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA). The so-called combined correction terms were also included to account for the overlapping of the muffin-tin spheres. We have chosen the case of PdT since Pd is considered⁶ to be a very good matrix for T storage.

We describe here the results for the case where 25% of T has decayed into ^3He . This represents a very large quantity of ^3He in the tritide and transforms it into a ternary compound $\text{PdT}_{0.75}\text{He}_{0.25}$. Although PdT crystallizes in an NaCl-type face-centered-cubic (fcc) type structure, we do not choose the fcc primitive cell in this work, but a simple cubic unit cell which has a volume 4 times the one of the primitive cell and contains four molecules of PdT. This is shown in Fig. 1. The Pd atoms in this simple cubic cell are located at the corners of the cube and the centers of the faces, and the

T atoms occupy the octahedral sites in the cube. Clearly, the decay of T into ^3He occurs at random sites in the structure, but we assume, for the sake of simplicity, an ordered arrangement in which the ^3He atom is placed at the center of the cube while the centers of the faces remain occupied by the T atoms. This results in a nearest neighbor He-He separation of a , where a is the lattice parameter of the cubic lattice. The wave functions of an He atom are very compact due to its filled-shell configuration so that any significant direct He-He interaction can be excluded. We therefore expect our calculations, although performed for an ordered arrangement of He atoms, to be representative of an actual disordered arrangement. Due to the presence of the He atom at the center of the cube, all Pd atoms are no longer identical and instead fall into two groups. The nearest neighbors of the He atom are the six Pd atoms at the centers of the faces of the cube at a distance of $a/2$, and these are the most affected by the presence of He. These are denoted as Pd₃ since there are three of these atoms per cubic cell. The Pd atoms situated at the corners of the cube and denoted as Pd₁, since there is only one atom of this type per cubic cell, are much farther away at a distance of $0.86a$ and are much less affected by the presence of He. In addition, a Pd₁ atom retains its nearest-neighbor local environment since it still has six T atoms at a distance of $a/2$, while a Pd₃ atom, in contrast, has only four T atoms and two He atoms at this distance.

Our total energy calculations yield a value of the lattice parameter a for PdT of 4.2141 Å both in this simple cubic geometry and with the NaCl type of lattice. This is roughly 3% larger than the experimental value of 4.09 Å. This is the usual discrepancy that one finds in the local density approximation (LDA). A calculation was also performed for PdHe which corresponds to the hypothetical case in which all of the tritium in the tritide decays into ^3He . The total energy decreases continuously as the lattice expands, but no minimum in the total energy versus lattice parameter curve was found. This calculation confirms the fact that no PdHe compound actually exists. On the other hand, in contrast to the case of PdHe, a clear minimum in the total energy versus lattice parameter curve was obtained for $\text{PdT}_{0.75}\text{He}_{0.25}$ at a value of $a = 4.2989$ Å. The existence of a minimum for $\text{PdT}_{0.75}\text{He}_{0.25}$ and none for PdHe shows that only a certain quantity of ^3He can be retained at the octahedral interstitial sites in the lattice, and once a critical concentration of ^3He has been attained, any further ^3He generated in the lattice can no longer be retained due to the inherent lattice instability. The lattice parameter due to ^3He is larger by $\sim 2\%$ than the value obtained for pure PdT and amounts to a volume expansion of ~ 4.6 Å.³ This value of volume expansion is in good agreement with the generally accepted value in the literature.²² Put in another way, for every atomic percent of ^3He produced in the lattice this amounts to a lattice expansion of $\sim 0.08\%$ or a volume expansion of $\sim 0.24\%$, assuming a linear relationship between the ^3He production and the lattice expansion. This stability of ^3He at the octahedral interstitial sites should not be construed as ^3He forming a compound or solid solution with Pd for this concentration. In reality, it is trapped at these sites in a metastable state due to a relatively large energy barrier for migration.^{2,23} Our calcu-

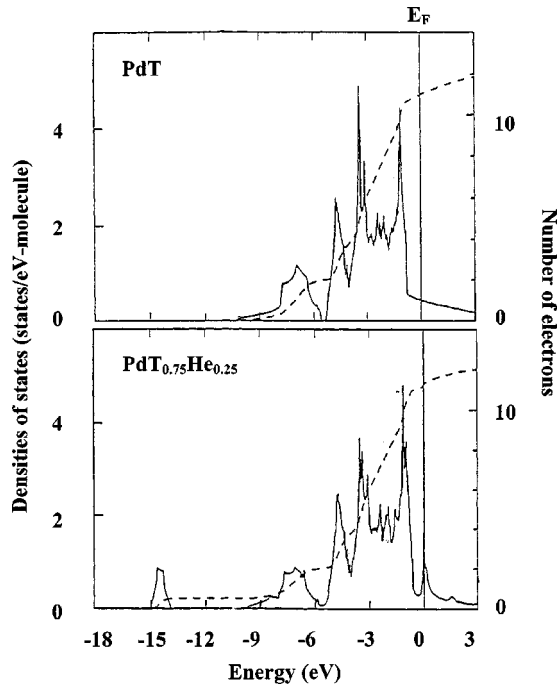


FIG. 2. Total densities of states as a function of energy for PdT (upper panel) and PdT_{0.75}He_{0.25} (lower panel) calculated at the equilibrium lattice parameter of PdT. All energies are with respect to the Fermi energy E_F taken as the origin. The dotted line in both panels shows the number of electrons.

lations show indeed that the energy in this configuration of ^3He is ~ 0.8 eV higher than the sum of the energies of PdT_{0.75} and He_{0.25} separately. This confirms the fact that, as in metals, ^3He is indeed not soluble in the tritide, but is present at these octahedral interstitial sites due to the fact that it was produced there in a natural manner. Of course, our calculations concern only pure PdT without any defects. The calculations were also performed for a case with the ^3He in a vacancy at a Pd₁ site. We found that ^3He was trapped in the vacancy with a binding energy of ~ 1 eV. This value was obtained by comparing the total energy of the system with a vacancy at the Pd₁ site to the system with the He at the Pd₁ site and a vacancy at the original He site. These results, in conjunction with the dissociation energy from the vacancy of ~ 2 eV obtained by Kass,¹⁸ imply a migration energy of He of ~ 1 eV and are consistent with the observed low diffusivity.²

The lowering of the plateau pressure, meaning an increased stability of the tritide, in the presence of ^3He , has usually been attributed to be due to the volume expansion³ due to ^3He . As we show below, this assumption is not really correct. For this purpose, we show in Fig. 2 the total densities of electronic states (DOS) for PdT and PdT_{0.75}He_{0.25}, both calculated at the equilibrium lattice parameter of PdT. In this way, no effect due to volume expansion by ^3He is included and a comparison of the two curves thus allows us to separate the effect of the electronic interactions alone. In Fig. 3 are shown the total DOS and the partial DOS (PDOS) decomposed at various atomic sites for PdT_{0.75}He_{0.25} calculated at its equilibrium lattice parameter. In PdT, the states

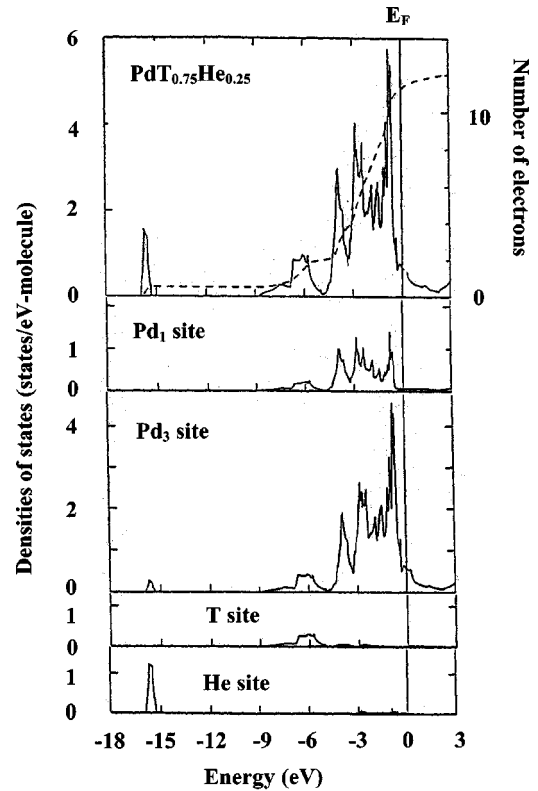


FIG. 3. Total densities of states as a function of energy for PdT_{0.75}He_{0.25} (upper panel) calculated at its equilibrium lattice parameter. The lower panels show the partial densities of states decomposed at various atomic sites as indicated. All energies are with respect to the Fermi energy E_F taken as the origin. Notice an upward shift in the states at the Pd₃ site relative to the Pd₁ site and the appearance of new states in the vicinity of the Fermi level.

below ~ -5 eV result from bonding Pd d -T s interactions, while those above ~ -5 eV and in the vicinity of the Fermi level, E_F , are mainly of Pd d character. The replacement of T by ^3He results essentially in three modifications in the electronic structure. First, a new structure of very narrow width ~ 1 eV appears at ~ 15 eV below E_F . This is primarily of ^3He s character with an extremely small admixture of ^3He with the nearest-neighbor Pd₃ states. Second, new states appear in the vicinity of E_F that were absent in PdT. The appearance of these states is highly unexpected if one assumes that ^3He is acting simply as an inert atom expanding the lattice, but playing no role in the electronic structure. These are in fact the Pd₃ states that have been pushed upwards by the interaction of ^3He with Pd₃ atoms, as seen in Fig. 3 by a comparison of the states at Pd₃ and Pd₁ sites. This indicates a strong repulsive character of ^3He in the matrix. Third, there is a depletion of states from the Pd d -T s bonding band due to the absence of 25% T atoms in the tritide. But it is important to note from Fig. 2 that this depletion occurs preferentially from the higher-lying electronic states. The net result of such a preferential depletion is to enhance the cohesion of the remaining T atoms in the matrix relative to PdT. This increases the relative stability of the tritide, thus lowering the plateau pressure. As stated above, the lattice expansion due to ^3He has not been included in Fig. 2 and thus this contri-

bution to the lowering of the plateau pressure arises purely from the modifications in the electronic structure caused by ^3He and is not at all related to the lattice expansion. This is in contrast to the usual assumption in the literature³ that the lowering of the plateau pressure of tritium occurs purely due to the volume expansion caused by ^3He . Our calculations yield a value of ~ 0.13 eV per tritium atom for this increase in the stability of the tritide due to this purely chemical effect. The lowering of the energy of $\text{PdT}_{0.75}\text{He}_{0.25}$ due to the lattice expansion of $\sim 2\%$ is much lower and amounts only to ~ 0.05 eV per tritium atom. We thus obtain a total value of ~ 0.18 eV per tritium atom for the relative stability of the tritide, of which only $\sim 28\%$ is contributed by volume expansion.

A comparison of Figs. 2 and 3 shows that the DOS at the Pd_1 site, which are the next nearest neighbors of ^3He atoms, remain practically unchanged from those in PdT, reflecting the compact nature of the ^3He wave functions. On the other hand, the states at the Pd_3 sites, which are the closest to the ^3He atoms, are substantially affected and have been pushed towards higher energies. Such a shift signals a loss of cohesion of the Pd atoms at these sites. From a detailed analysis of the DOS, the value of decohesion at these sites can be estimated, and we obtain a value of ~ 0.94 eV per Pd atom. This is to be compared to the cohesive energy of ~ 3.7 eV per Pd atom in Pd metal. This large decrease in the value of the cohesion of Pd atoms closest to the ^3He atom clearly weakens considerably the metal-metal bonds and renders the matrix fragile, in the decohesion model of fragilization, at these large concentrations of ^3He in the matrix. This decrease

in the ductility of the tritide due to helium production has been observed experimentally.⁷ We should also mention that the tritides containing ^3He have large dislocation densities, and this also plays a role in the fragility of the tritides.

In conclusion, our calculations have shown that the ^3He produced in PdT from the radioactive decay of T into ^3He is insoluble in the tritide, but it can be trapped at the octahedral interstitial sites, in a metastable state, at a surprisingly large He/Pd ratio R of at least 0.25. For a value of R between 0.25 and 1.0 the underlying lattice configuration eventually becomes unstable as more and more helium accumulates. We find that, in contrast to the usual assumption in the literature, only $\sim 28\%$ of the lowering in the plateau pressure can be attributed to the volume expansion due to ^3He and a majority of it is caused by the electronic interactions, essentially the preferential removal of the higher-lying Pd d -T s states. We have also shown that the presence of ^3He has an extremely detrimental effect on the cohesion of the closest Pd atoms, which renders the tritide fragile. We have not investigated the question of bubble formation, but it is quite reasonable to consider that some ^3He will be also be trapped in the form of bubbles, and this contribution should be included in a more complete analysis, but we believe that our results may have important implications in the development of new procedures for storing and removing tritium.

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