

Correlating Atomic Structure and Material Properties in Erbium Tritide

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Motivation—The well-known justifications for storing H in the form of metal hydrides remain valid for storage of deuterium (D) and tritium (T). As such, tritides and deuterides of Sc, Pd, Ti, Zr, and Er are commonly used in the nuclear industry as storage media. Here at Sandia ErT_2 is used to make targets in neutron generators. To ensure proper functionality in this application, it is critical that we understand the transient behavior of the material. A complicating factor is the short half-life (12.3 years) of T, which results in the substantial build-up of impurity He. This is concerning because, as an inert impurity, He is detrimental to the physical integrity of the host tritide and when released from the solid can be catastrophic to component functionality. In addition, O can be introduced during processing, creating unknown changes in material properties. Our goal is to develop a science-based understanding of this material and facilitate a predictive response to production and design needs.

Accomplishment—We have used first-principles density functional (DFT) calculations to study the structure of ErT_2 and atomic processes within the solid. The ideal ditritide has the CaF_2 crystal structure where Er sits at FCC lattice sites, T fills all of the tetrahedral positions, and the octahedral sites remain empty (Fig 1). This is known as the β -phase, and is stable for a small range (± 0.1) of T/Er ratio centered at 2. Our calculations reveal that T prefers the tetrahedral, rather than octahedral, site by 0.75 eV. However, once the tetrahedral sites are filled, additional T loaded into the sample is forced into octahedral positions. Continued loading will eventually drive a phase change, but even small amounts of overloading

have significant effects. For example, we found that the mechanism (and barrier) for T migration depends on the T/Er ratio. Moreover, the mechanism involves concerted motion of both tetrahedral and octahedral T.

Experimental examination of ErT_2 thin-films indicates significant concentrations of O within the crystal. It is also observed that O-rich inclusions form during annealing. We find that O is most stable in the tetrahedral site, displacing T into the octahedral site and in doing so, O effectively increases the amount of overloaded (octahedral) T, changing the stability of the β -phase and modifying the behavior of He. In agreement with observations, we predict that O will become mobile at 200 °C, and similar to T, the mechanism is one of concerted diffusion. Once O becomes mobile, oxide inclusions will nucleate.

It is known from aging studies, that He forms bubbles within the tritide that will eventually out-gas. However, the mechanisms for bubble formation and growth are not understood. We predict that He prefers to reside in the large empty octahedral sites where the electron density is low, and will diffuse just above room temperature (Fig 2). We are currently studying the formation of He clusters, the mechanism of bubble formation, and how impurities and octahedral T affect these processes.

Significance—Our DFT calculations add significant insight to the sparse literature on this material. Building on the fundamentals, we are moving toward a science-based understanding of how T, He, and O behave during processing and throughout the service life of the product.

Sponsor for various phases of this work include: Nuclear Weapons

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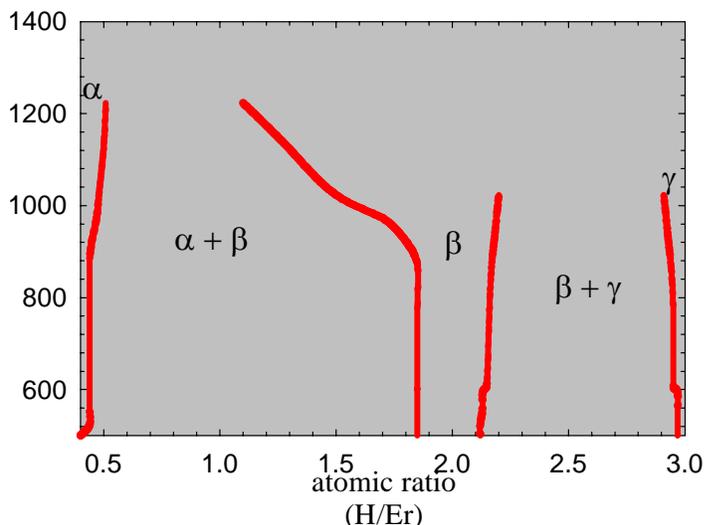
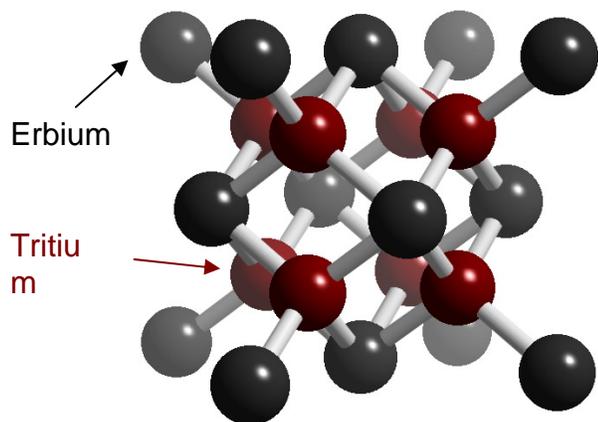


Figure 1. Left: Crystal structure of β -phase ErT_2 showing ideal occupation of tetrahedral sites by tritium. The octahedral site, in the center of the unit cell, is nominally empty. Right: The phase diagram of ErT_x .

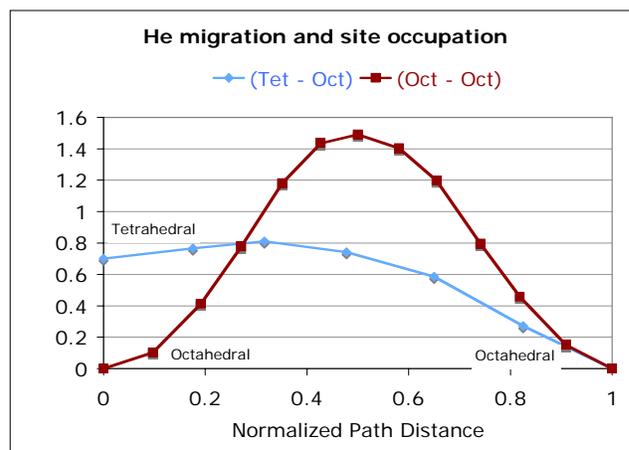
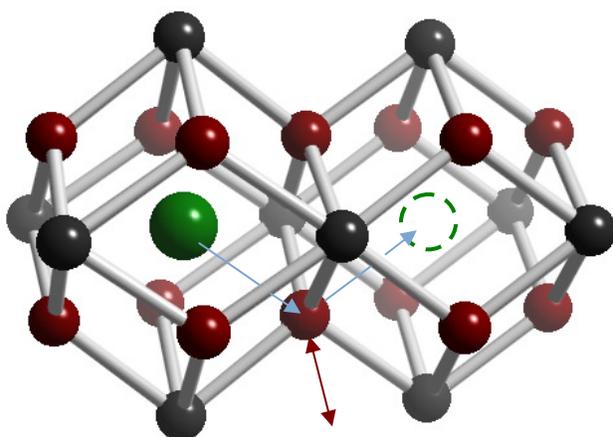


Figure 2. Left: Octahedral occupation of helium (green) and the minimum energy migration path for motion between octahedral sites. The blue arrows represent motion of the helium atom. The red arrow illustrates the temporary displacement of tritium while helium moves through the tetrahedral site into another octahedral position. Right: Data from nudged elastic band DFT calculations showing the relative energy of tetrahedral vs. octahedral site occupation as well as the barriers for two unique diffusion mechanisms. The blue line represents the rate-limiting barrier for the tetrahedral-octahedral mechanism shown left. The red line represents a direct octahedral-octahedral jump.