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To cite this article: K R Lund et al 2013 J. Phys.: Conf. Ser. 443 012021

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# Vacancy Formation Enthalpy in Polycrystalline Depleted Uranium

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Abstract. Positron Annihilation Spectroscopy was performed as a function of temperature and beam energy on polycrystalline depleted uranium (DU) foil. Samples were run with varying heat profiles all starting at room temperature. While collecting Doppler-Broadening data, the temperature of the sample was cycled several times. The first heat cycle shows an increasing Sparameter near temperatures of 400K to 500K much lower than the first phase transition of 941K indicating increasing vacancies possibly due to oxygen diffusion from the bulk to the surface. Vacancy formation enthalpies were calculated fitting a model to the data to be  $1.6\pm$ 0.16 eV. Results are compared to previous work [3,4].

#### **1. Introduction**

Positron Annihilation Spectroscopy (PAS) can be used to determine vacancy formation enthalpies in metals [1]. Using Doppler-Broadening of the Annihilation Radiation (DBAR), one is able to observe changes in the line shape parameter, also known as the S-parameter, to calculate vacancy concentrations [2]. Uranium has three phases between temperatures of 300K to its melting point of 1407K [3-5].  $\alpha$ -U from ambient temperatures to 941K is orthorhombic,  $\beta$ -U from 941 to 1048K is a complex tetragonal, and  $\gamma$ -U from 1048K to its melting point is BCC.

Matter et al [3] and Kögel et al [4] used PAS to report phase transition formation enthalpies using bulk PAS measurements, however their results are conflicting with one another. Both Matter and Kögel annealed large polycrystalline uranium samples; 8mm diameter 15mm long cylinder for Reference 3, and 13mm diameter 6.5mm long cylinder for Reference 4 to remove stresses, strains, and impurities such as oxygen. It is possible that not all of the oxygen was removed from their samples; this could be the cause of the lower enthalpies that were reported..

Senanayake *et al* [6] used high-resolution X-ray photoelectron spectroscopy to study the formation of defects created by argon sputtering in  $UO_2$ . They report a decrease in the oxygen and uranium binding energy, along with an increase in the rate of oxygen diffusion from the bulk to the surface, at temperatures greater than 400K.

This experiment uses a variable energy PAS technique in an attempt to understand the significant discrepancy of the previously reported results for formation enthalpies from the  $\alpha$  to the  $\gamma$ phase. The effects of oxygen migration from the bulk to the surface are found to be important to understand the difference in the reported results.

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### 2. Procedure

2.1. Doppler Broadening of the Annihilation Radiation. For temperature dependent DBAR measurements, the positron energy was set to 66keV, corresponding to a mean positron implantation depth of  $\approx$ 1.7µm into the bulk of the DU. This value was obtained using [1] <z>400E^1.6/  $\rho$ , where  $\rho$  is the density in g/cm<sup>3</sup> and E is the energy of the positron beam, <z> is given in Å.

The formation enthalpy was calculated using the temperature dependant scans and the equations [2],

$$C_{\nu} = C_{\nu}^{0} \exp\left(\frac{-H_{\nu}^{J}}{k_{b}T}\right) \tag{1}$$

and,

$$K = \mu C_{\nu} = \lambda_b \frac{S - S_b}{S_{\nu} - S}$$
<sup>(2)</sup>

Here  $C_v^{0}$  is the pre-exponential factor containing the entropy of formation, K is the trapping rate,  $\mu$  is the specific trapping coefficient,  $C_v$  is the concentration of vacancy defects,  $\lambda_b$  is the bulk annihilation rate, S is the line shape parameter (from here on referred to as the S-parameter),  $S_b$  is the S-parameter for the bulk,  $S_v$  is the S-parameter for vacancies,  $H_v^{f}$  is the vacancy formation enthalpy, and  $k_b$  is Boltzmann's constant. Combining equations 1 and 2, and solving for the S-parameter as a function of temperature we obtain,

$$S(T) = \frac{S_b(T) + S_v \xi \exp(\frac{-H_v^f}{k_b T})}{1 + \xi \exp(\frac{-H_v^f}{k_b T})}, \qquad S_b(T) = S_b(300K) + \Delta S(T - 300K)$$
(3)

where,  $\xi = C_v^0 \mu \lambda_b^{-1}$ . By measuring  $S_v$  and  $S_b$  from the data and assigning  $\xi$  and  $H_v^{f}$  as fitting variables, Equation 3 was used to fit the temperature dependent data.

2.2. Sample Preparation. Depleted uranium foil 150µm thick was purchased from International Bio-Analytical Industries, with isotopic and elemental purities greater than 99.8%. A 4cm<sup>2</sup> rectangle was cut. It was mounted to a HeatWave Labs molybdenum body ultra high vacuum substrate-heating element, with tantalum wire to hold it in place. Tantalum and titanium foil was placed around the sample and used as heat shielding. K-type thermocouples were spot welded onto the sample and heater. Ta wire provided additional tension to securely hold them down.

The sample was placed in the positron beam line at Washington State University under a vacuum of  $10^{-8}$  Torr, and analyzed with energy and temperature dependent Doppler-Broadening of the Annihilation Radiation (DBAR). The temperature of heating element was varied by using an AC HeatWave Labs control box (see Table 1). While the temperature was cycling, an HPGe detector with resolution of  $\approx 1.34$ keV at 511keV collected the annihilation radiation spectrum. Total counts for each spectrum was greater than  $2 \times 10^6$ , and had total peak counts greater than  $3 \times 10^5$ . These spectra were

Table 1. Heating History				
Cycle #	Highest	Measured	Measured	
	Temperature	Rate up	Rate Down	
	(K)	(K/min)	(K/min)	
1	550	8.8	-3.8	
2	1000	1.5	-23.2	
3	1000	14.4	-4.9	
4	1150	2.7	-33.2	
5	1100	2.7	-2.8	
6	1150	2.7	-12.3	
7	1100	1.9	-1.8	
8	1150	3.2	-2.7	
9	1100	2.4	-13.7	
10	1270	2.7	-8.0	
11 <sup>†</sup>	1270	3.0	-2.6	

<sup>†</sup>Data reported in Figure 1 and 2.

compiled to show the temperature dependence of the S-parameter. The low momentum S-parameter limits were set to 510.3 and 511.7keV while the high momentum W-parameter limits were set symmetrically about the 511 peak to 513.4 to 514.4 and 506.0 to 508.6keV. These settings produce an average bulk S value (beam energy between 20 and 70keV) of 0.5009±0.0007 for Si(100).

#### 3. Results and Discussion

Figure 1 shows the fit of Equation 3 over data of a sample after being annealed at 1200K. There is a linear dependence between the S-parameter and temperature from 300 to 800K because of thermal expansion or a change due to a positron-electron wave function overlap. The data from this region were fit linearly to find  $S_b(T) = [(1.4\pm0.1)\times10^{-5}]T + (0.433\pm0.006)$ . If we assume a linear dependence with temperature for S<sub>v</sub>, we find  $S_v(T) = [(1.4\pm0.5)\times10^{-5}]T + (0.441\pm0.006)$ .

These relations were inserted into Equation 3 for  $S_b$ and  $S_v$  to find  $H_v^{f} = 1.6\pm0.2$  eV and  $\xi/10^{+7}=8.3\pm17$ . This  $H_v^{f}$  is greater than previously reported  $\gamma$ -phase values that were obtained using other PAS techniques (see Table 2). If, however,  $S_v$  was set to a constant, 0.459 or 0.464, the enthalpy ranged from 2.14 eV to 1.03 eV respectively.



**Figure 1.** S vs. T data and fit to Equation 3. Vertical lines indicate the phase transition temperatures.

<b>Table 2.</b> Formation Enthalpy Summar
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Source	H <sub>v</sub> <sup>f</sup> (eV)	$\Delta H_v^{f}(eV)$
This Work	1.6	0.2
Ref 3	1.2	0.3
Ref 4 <sup>a</sup>	0.3	

<sup>a</sup> Error not reported



**Figure 2.** S vs. W plot corresponding to the data in Figure 1 showing a single defect type in the three phases.

Figure 2 shows the S vs. W plot for the same data in Figure 1. The lower temperatures are on the bottom right of the graph and the higher temperatures are displayed on the upper left corner. Two data points closest to the transition temperatures are marked with arrows and the corresponding phases are labelled. The data in Figure two fall on one of two lines, first for data ranging from 300 to 700K and then for data where T>700K. Because of the single slope from 700K and above, we see that there is only one defect type [7] as seen by these measurements spanning the three phase transitions.

It is important to note the differences between this work and Reference 3 and 4. First, this work used a variable energy beam of positrons where as the previous work placed the positron source in contact with the samples. Second, the depleted uranium sample used here is much smaller than those used in the earlier work. The last major difference between this work and that done before is that in the previous work, both publications report discontinuous jumps in the S data at or near the phase transition temperature. In this work those discontinuities are not observed. This is possibly due to the differences in sample preparation.

Figure 3 shows three heat cycles of a sample while the energy was set to 66 keV. The sample's surface was consisting of an oxide layer  $(U_3O_8 \text{ and } UO_2)[8]$ . After heating past 800K, the samples

turned from black to a metallic grey color. Heating the sample creates vacancies observed by an increase in the S-parameter until equilibrium is achieved. Because the S-parameter is related to the materials vacancy concentration [1] and the primary mechanism for oxygen diffusion at these temperatures is vacancy diffusion, the results in Figure 3 are interpreted as oxygen desorbing through the uranium and leaving vacancies in its stead. The increase in the S-parameter near 450K is in close agreement with the findings on oxygen out-diffusion reported by Senanyake [6]. These vacancies were noticeably reduced when heated past the first phase transition of 941K (see Figure 4).





**Figure 3.** S vs. T (K) plot showing an asreceived sample heated and cooled at 1 degree K per minute for three heat cycles.

**Figure 4.** S vs. E plot showing the depth profile changes after different heat treatments.

### 4. Conclusion

PAS has been used to calculate a formation enthalpy of  $1.6\pm0.16$  eV for polycrystalline depleted uranium. Oxygen desorption from the bulk to the surface was observed near temperatures of 450K. After annealing, vacancies were removed and a single defect type was consistent with our data in all three phases of the uranium sample.

Future work could be used to investigate the effects oxygen has on the formation enthalpy. Different sample preparations, such as acid etching and annealing, will be compared to the as-received samples. A 2-detector coincidence measurement could be used to identify impurity-vacancy complexes. Investigation of uranium alloys and single crystals would be of considerable interest to analyze in the same fashion.

### Acknowledgments

We would like to acknowledge Idaho National Laboratory for funding under contract number 00014002, as well as Narendra Parmar and Ryan Stewart for their discussions and help in the lab.

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