Thermal Expansion of Solid Uranium Dioxide

Summary and Recommended Equations

The recommended equations for the thermal expansion of solid uranium dioxide are from the 1988 assessment by D. G. Martin [1], which included the high temperature neutron diffraction data of Hutchings [2] that were not available to previous assessments [3,4]. Martin compared data from lattice parameter measurements and macroscopic length changes from 15 references [2, 5-18], made corrections to macroscopic thermal expansion measurements that exhibited a zero error, and excluded data that did not agree with the common consensus. Martin fit the remaining data to two cubic polynomials. Refitting the data fit by Martin plus new data by Momin et al. [19] and the data of Christensen [11], which was not included in the fit by Martin, gave equations that differed little from those of Martin. Thus, the equations of Martin are recommended. The recommended equations for the linear thermal expansion of solid UO_2 are:

for 273 K $\leq$ T $\leq$ 923 K,

$$L = L_{273}\,(9.9734\text{x}10^{-1} + 9.802\text{x}10^{-6}T - 2.705\text{x}10^{-10}T^2 + 4.391\text{x}10^{-13}T^3); \qquad \textbf{(1)}$$

for 923 K $\leq$ T $\leq$ 3120 K,

$$L = L_{273}\,(9.9672\text{x}10^{-1} + 1.179\text{x}10^{-5}T - 2.429\text{x}10^{-9}T^2 + 1.219\text{x}10^{-12}T^3) \qquad \textbf{(2)}$$

where L and L_{273} are the lengths at temperatures T(K) and 273 K, respectively. The fractional change in the linear thermal expansion of UO_2, $\Delta L/L_{273} = (L - L_{273})/L_{273}$, expressed as a percent, is shown in Figure 1 with the recommended uncertainties, the data fit by Martin and new data by Momin et al. [19]. Recommended values for the fractional change in linear thermal expansion, $\Delta L/L_{273}$, are tabulated in Table 1. Values for the fractional change in volumetric thermal expansion of UO_2, $\Delta V/V_{273}$, are given in Table 2.

From assessment of the available data on hyperstoichiometric uranium dioxide (UO_{2+x}), Martin recommends using these equations for the linear thermal expansion of UO_{2+x} for x in the ranges 0 to 0.13 and 0.23 to 0.25.

The recommended equations for the instantaneous linear thermal expansion coefficients, $\alpha_P(l)$, are cubic polynomial approximations[1] to the exact partial differentials

$$\alpha_P(l) = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \qquad \mathbf{(3)}$$

of Eqs.(1) and (2). These approximations do not differ by more than 0.6% from the exact differentials over the given temperature range. Martin recommends:

for 273 K $\leq$ T $\leq$ 923 K,

$$\alpha_P(l) = 9.828\text{x}10^{-6} - 6.930\text{x}10^{-10}T + 1.330\text{x}10^{-12}T^2 - 1.757\text{x}10^{-17}T^3; \qquad \mathbf{(4)}$$

for 923 K $\leq$ T $\leq$ 3120 K,

$$\alpha_P(l) = 1.1833\text{x}10^{-5} - 5.013\text{x}10^{-9}T + 3.756\text{x}10^{-12}T^2 - 6.125\text{x}10^{-17}T^3; \qquad \mathbf{(5)}$$

where $\alpha_P(l)$ is the coefficient of thermal expansion in K^{-1}. Recommended values of the instantaneous linear thermal expansion coefficient of UO_2 are shown in Figure 2, and tabulated as a function of temperature in Table 1. Dotted lines in Figure 2 represent the recommended uncertainties, which are larger than those suggested by Martin. Values for the instantaneous volumetric thermal expansion coefficient, the thermodynamic quantity, $\alpha_{P,}$ are given in Table 2. Equations relating the linear and volumetric thermal expansion coefficients and fractional changes in length, volume, and density with temperature are given in the appendix entitled **Density and Thermal Expansion Relations**.

Uncertainties

From 293 through 535 K, the recommended uncertainty in the fractional linear expansion (L/L_{273} -1) is $\pm$ 2.6 x 10^{-4}, which is the uncertainty given by Martin. In terms of the percent of the linear expansion, $\Delta L/L_{273}$, this constant uncertainty decreases from 105% at 298 K to 10% at 535K. The percent uncertainty is 10% from 600 to 1000 K and 7% from 1400 to 3120 K with a linear percent decrease from 535 to 600 K and from 1000 to 1400 K. Above 535 K, larger uncertainties are recommended than those given by Martin so that most of the new data by Momin et al.[19] and some of the high-temperature data of Baldcock [17] and Christensen [11] fall between the recommended values and the uncertainty limits.

The uncertainties in the instantaneous linear thermal expansion, $\alpha_P(l)$, are: $\pm$ 0.11 x 10^{-6}, $\pm$ 0.22 x 10^{-6}, and $\pm$ 1.1 x 10^{-6} for the temperature ranges 293 - 1273 K, 1273 - 2273 K, and 2273 - 2929 K, respectively.

Discussion of Recommended Equations for UO_2

Martin [1] reviewed and compared UO_2 thermal expansion data from macroscopic length changes [5-13], neutron diffraction [2, 18], and X-ray diffraction measurements [17] except for the recent X-ray diffraction results by Momin et al.[19]. In his thorough data assessment, Martin examined the macroscopic expansion data for possible zero errors and made corrections to the data of Lambertson and Hanwerk [6], the data of Brett and Russell [9], and the data of Murray and Thackery [10]. He found good agreement between the data from macroscopic length changes and lattice parameter measurements so that these data could be combined in the final analysis. The good agreement between data from macroscopic measurements by Conway et al. and the lattice parameter measurements of Hutchings [2] led Martin to conclude that at least up to 2523 K, the contribution to the macroscopic expansion due to Schottky defects is negligible. In formulating equations to represent the linear thermal expansion of UO_2, Martin excluded data that did not agree with the common consensus. Data excluded by Martin are: data of Bell et al.[5], data of Christensen [11], data of Halden et al.[12], data above 1871 K from measurements by Baldock et al.[17], and data from 1118 to 1200 K from measurements by Hoch and Momin [15].

The analysis of Martin [1] has been re-examined because it excluded the data of Christensen [11], which are still being used in determining density equations [20] and because the recent data of Momin et al.[19] fall outside the errors given by Martin. A weighted least squares minimization procedure has been used to fit the thermal expansion data that were fit by Martin, the data of Christensen [11], and the data of Momin et al.[19]. The weights used for the data fit by Martin and the data of Momin et al. are the inverse of the squares of the standard deviations from the equations recommended by Martin. The deviation of the data of Christensen near 1700 K from the common data was used to weight the data of Christensen. The least squares fit to these data gave equations that differed from those given by Martin by less than 1%. Thus, the equations given by Martin are consistent with this larger data set and are therefore recommended. This larger set of data has been included in Figure 1, which shows the recommended equations of Martin, expressed as the percent change in length relative to the length at 273 K, ie. ($\Delta L/L_{273}$, %).

Percent deviations of the data from the recommended equations of Martin are shown in Figure 3. Percent deviations in Figure 3 are defined as:

$$Deviation(\%) = \frac{\dfrac{\Delta L(Data)}{L} - \dfrac{\Delta L(Martin)}{L}}{\dfrac{\Delta L(Martin)}{L}} \cdot 100\% \qquad \textbf{(6)}$$

The recommended uncertainties are included in Figure 3 for comparison with the deviations of Martin's equations from the analyzed data. Figure 3 shows that most of the data fall within the uncertainty limits. However, the data of Christensen [11] show considerable scatter with significant numbers of deviations greater than the uncertainty. Figure 3 shows that the data of Momin et al.[19], based on X-ray diffraction measurements, are consistently lower than the recommended values. Deviations of the data of Momin et al. calculated from Eq. (6) range from -24% at 298 K to -0.5% at 1600 K. Momin et al. report 0.5469 nm for the lattice parameter of UO_2 at room temperature, which is slightly lower than the 0.54704 nm at 293 K obtained by Gronvold [16] and the 0.5470 nm at 293 K obtained by Hutchings [2]. Thus, the results reported by Momin et al. appear to be low relative to other data as well as compared to the recommendation of Martin.

Comparison of UO_2 Recommendation with Previous Recommendations

The 1981 recommendation of Fink, Chasanov, and Leibowitz [3] and the recommendation of MATPRO [4] were based on an analysis by Olsen [4], which used the data of Conway et al.[13] from 1263 to 2535 K and that of Christensen [11] from 1473 to 3073 K. Although the data of Christensen showed much scatter, they were the only data available in 1981 above 2535 K. The current version of MATPRO [20] gives an equation that is a function of stoichiometry from analysis of data in references [6, 8, 9, 11, 13-17]. This set of data is the same as that included in the final analysis by Martin except the MATPRO analysis included the data of Christensen but did not include the data of Hutchings. The recent data of Hutchings [2] are in much better agreement with that of Conway et al. than the data of Christensen and show that the data of Christensen are not reliable. Figure 4 compares $\Delta L/L_{273}$ from data of Hutchingson, Conway, and Christensen with the recommended equations of Martin, the 1981 recommendation of Fink et al.[3] and the MATPRO values [20]. Differences are significant at high temperatures where the fits are based on different sets of data. From 2800 through 3120, deviations of the equation of Fink et al. from the recommended one increase from 3% to 6.5%. These deviations are greater than the uncertainties given by Martin but are within the 7% uncertainty that is recommended. Deviations of the

MATPRO values from those of Martin increase from 7% at 2400 K to 22% at 3100 K.

The recommended instantaneous linear thermal expansion coefficient given by Martin [1] is compared in Figure 5 with the 1981 recommended values[3]. Deviations between these instantaneous linear thermal expansion coefficients are even greater than the deviations between the fractional changes in linear thermal expansion ($\Delta L/L_{273}$) because the linear instantaneous thermal expansion coefficient is the temperature derivative of the linear thermal expansion.

Discussion of Hyperstoichiometric Uranium Dioxide (UO_{2+x})

Martin has examined the X-ray lattice parameter measurements of UO_{2+x} of Gronvold [16] for O/M ratios of 2.00, 2.10, 2.25, and 2.60; of Roth et al.[21] for O/M ratios of 2.08, and 2.24; of Fergusson et al.[22] for O/M = 2.235; and the macroscopic expansion studies on UO_{2+x} by Murray and Thackery [10] for O/M=2.00 and 2.13 and those by Leblanc and Andriessen [7] for O/M=2.00, 2.10, and 2.21. He made a zero error correction to the data of Murray and Thackery. He excluded the data of Gronvold with an O/M ratio of 2.60 on the basis that these data relate to an orthorhombic (U_3O_8) structure not a fluorite structure. From comparison of the remaining data to his equations for the thermal expansion of $UO_{2.00}$, Martin concluded that the thermal expansion of UO_{2+x} is the same as that of $UO_{2.00}$ for x values of 0-0.13 and 0.235-0.25 up to 1520 K. Figure 6, which compares some of the UO_{2+x} data with Martin's recommended percent change in the linear thermal expansion of $UO_{2.00}$, shows that Martin's conclusion is justified. The data for UO_{2+x} are very close to the recommendation for $UO_{2.00}$ with deviations and scatter similar to that for the $UO_{2.00}$ thermal expansion data. Because no data for UO_{2+x} exists above 1520 K, Martin speculates that his conclusion for thermal expansion at lower temperatures may be extended to the melting point.

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Table 1. Recommended Linear Thermal Expansion of UO_2

T, K	$\Delta L/L$, %	$\alpha_p(l) \times 10^{6}$, K^{-1}
273	0.000	9.74
298	0.025	9.74
300	0.027	9.74
400	0.125	9.76
500	0.223	9.81
600	0.322	9.89
700	0.422	9.99
800	0.523	10.12
900	0.626	10.27
1000	0.730	10.51
1100	0.837	10.78
1200	0.948	11.12
1300	1.062	11.53
1400	1.181	12.01
1500	1.305	12.56
1600	1.436	13.18
1700	1.573	13.86
1800	1.718	14.62
1900	1.871	15.45
2000	2.034	16.34
2100	2.206	17.30
2200	2.388	18.33
2273	2.528	19.12
2273	2.528	19.12
2300	2.582	19.43
2400	2.788	20.59
2500	3.006	21.82
2600	3.238	23.11
2670	3.409	24.06
2670	3.409	24.06
2700	3.484	24.47
2800	3.745	25.90
2900	4.021	27.39
3000	4.314	28.94
3100	4.624	30.56
3120	4.688	30.89

Table 2 Recommended Volumetric Thermal Expansion of UO_2

T, K	ΔV/V, %	α_p x 10 ^{6}, K^{-1}
298	0.075	29.22
300	0.080	29.22
400	0.374	29.29
500	0.670	29.44
600	0.969	29.66
700	1.271	29.97
800	1.578	30.35
900	1.891	30.81
1000	2.206	31.54
1100	2.533	32.35
1200	2.870	33.36
1300	3.220	34.59
1400	3.585	36.03
1500	3.968	37.67
1600	4.370	39.53
1700	4.794	41.59
1800	5.243	43.87
1900	5.720	46.34
2000	6.226	49.02
2100	6.764	51.91
2200	7.337	54.99
2273	7.779	57.37
2273	7.779	57.37
2300	7.947	58.28
2400	8.598	61.77
2500	9.292	65.46
2600	10.032	69.34
2670	10.578	72.18
2670	10.578	72.18
2700	10.820	73.42
2800	11.660	77.70
2900	12.556	82.17
3000	13.509	86.83
3100	14.524	91.69
3120	14.734	92.68

Figure 1 Recommended UO_2 Linear Thermal Expansion

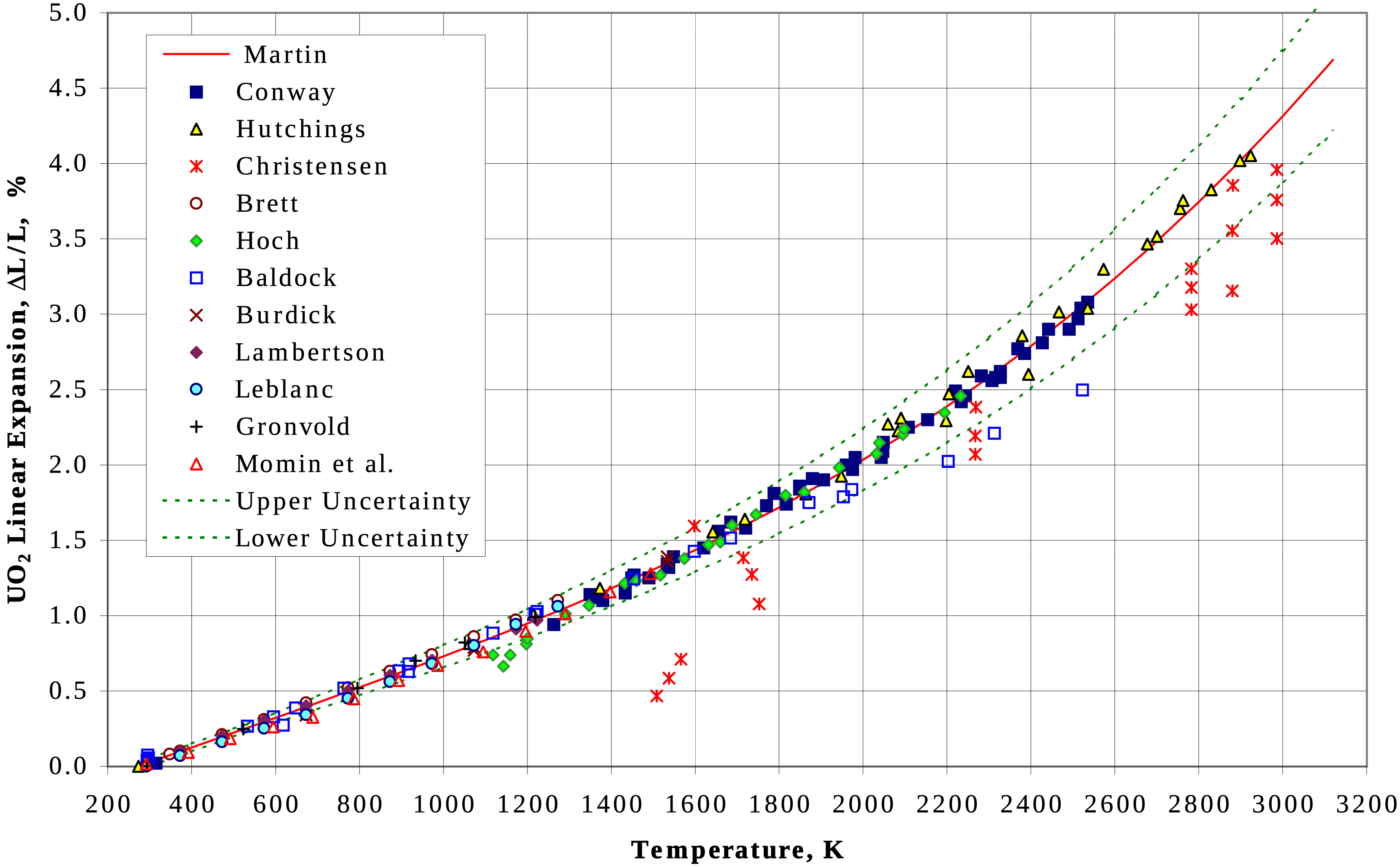

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Figure 2 UO_2 Instantaneous Linear Thermal Expansion Coefficient

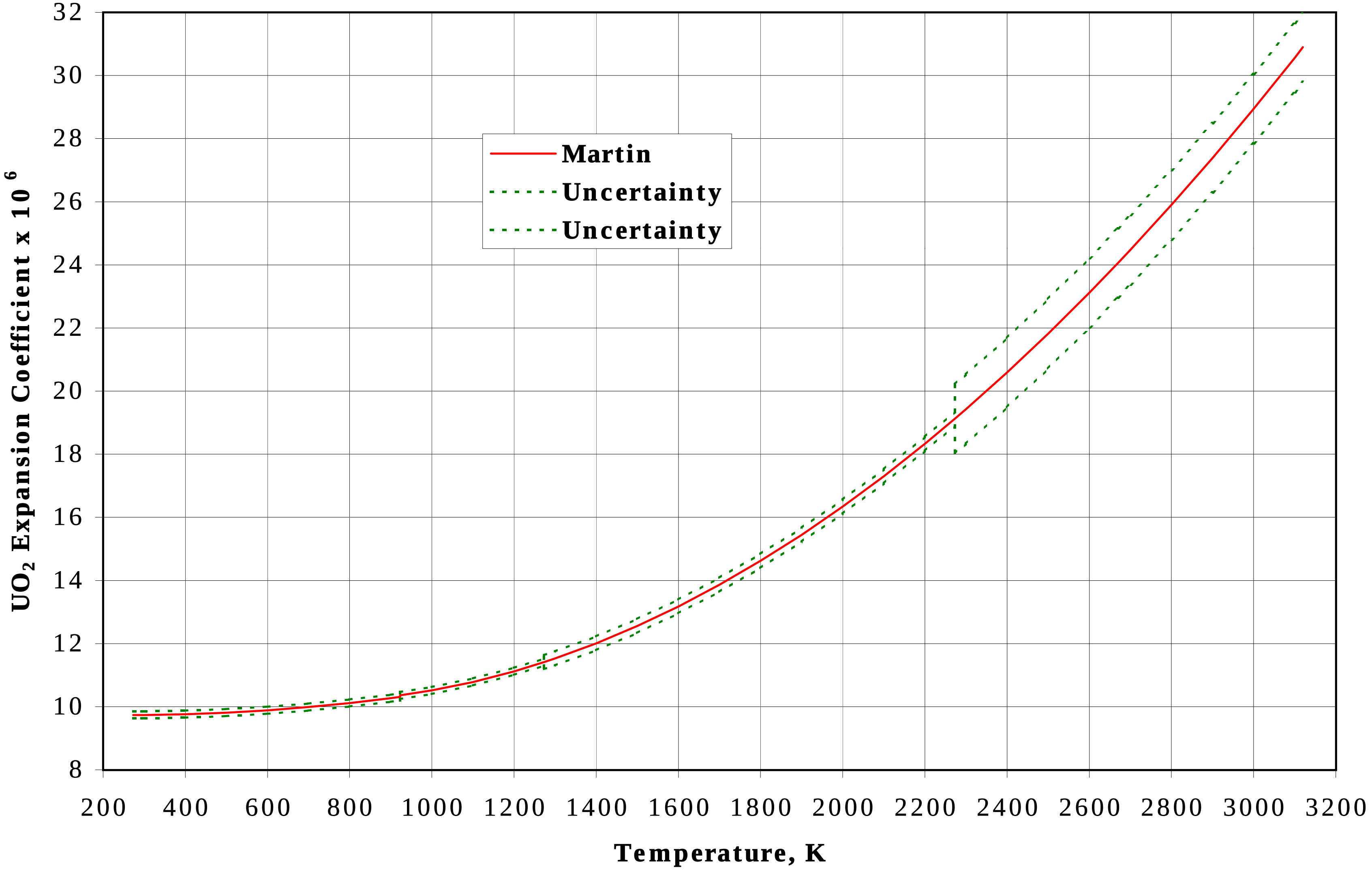

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Figure 3 Deviations of UO_2 Thermal Expansion Data from Recommendation

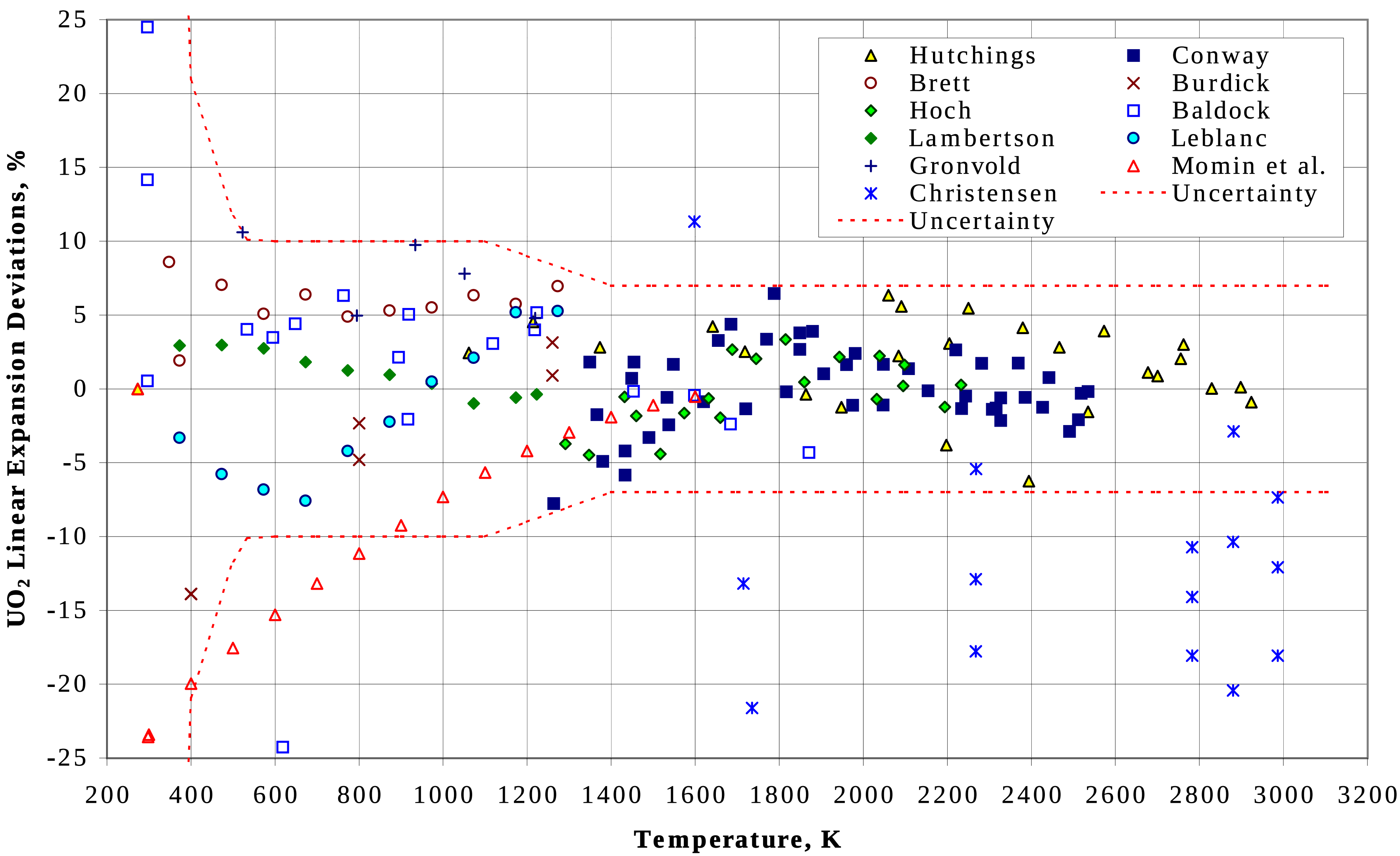

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Figure 4 Comparison of Recommended UO_2 Thermal Expansion with Previous Recommendations and Data of Christensen, Conway, and Hutchings

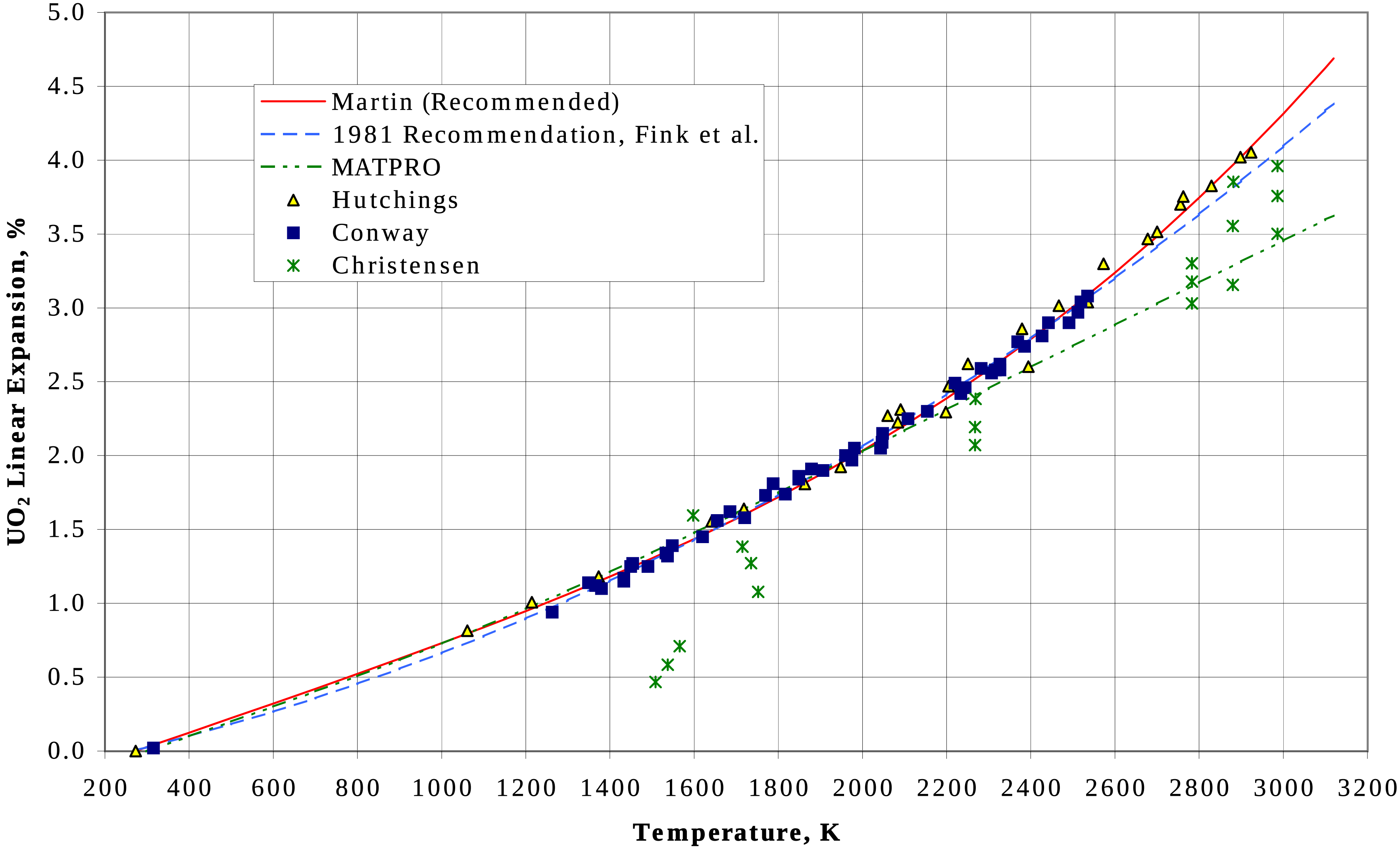

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Figure 5 Comparison of Recommended UO_2 Linear Thermal Expansion Coefficient of Martin with Previous Recommendation

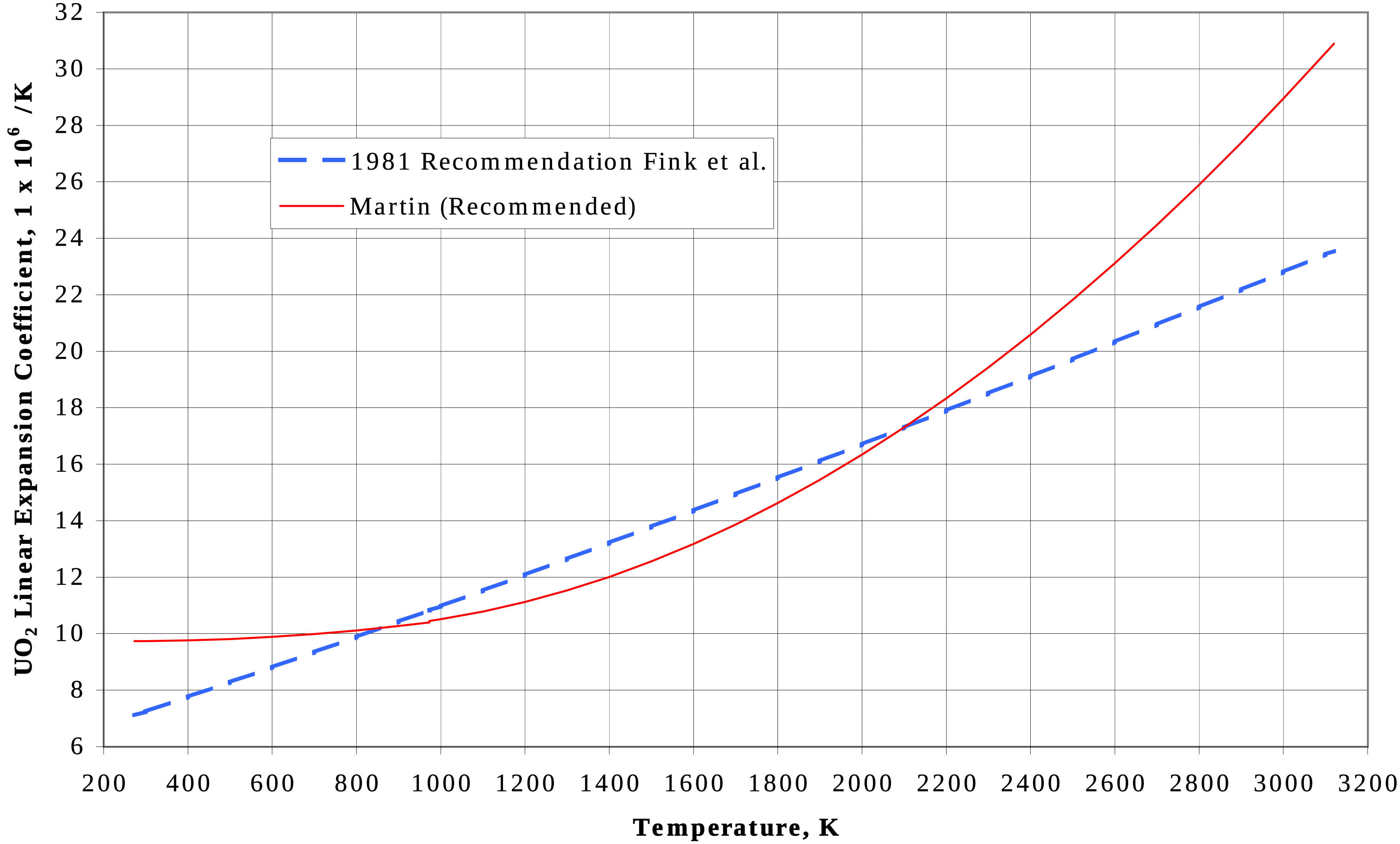

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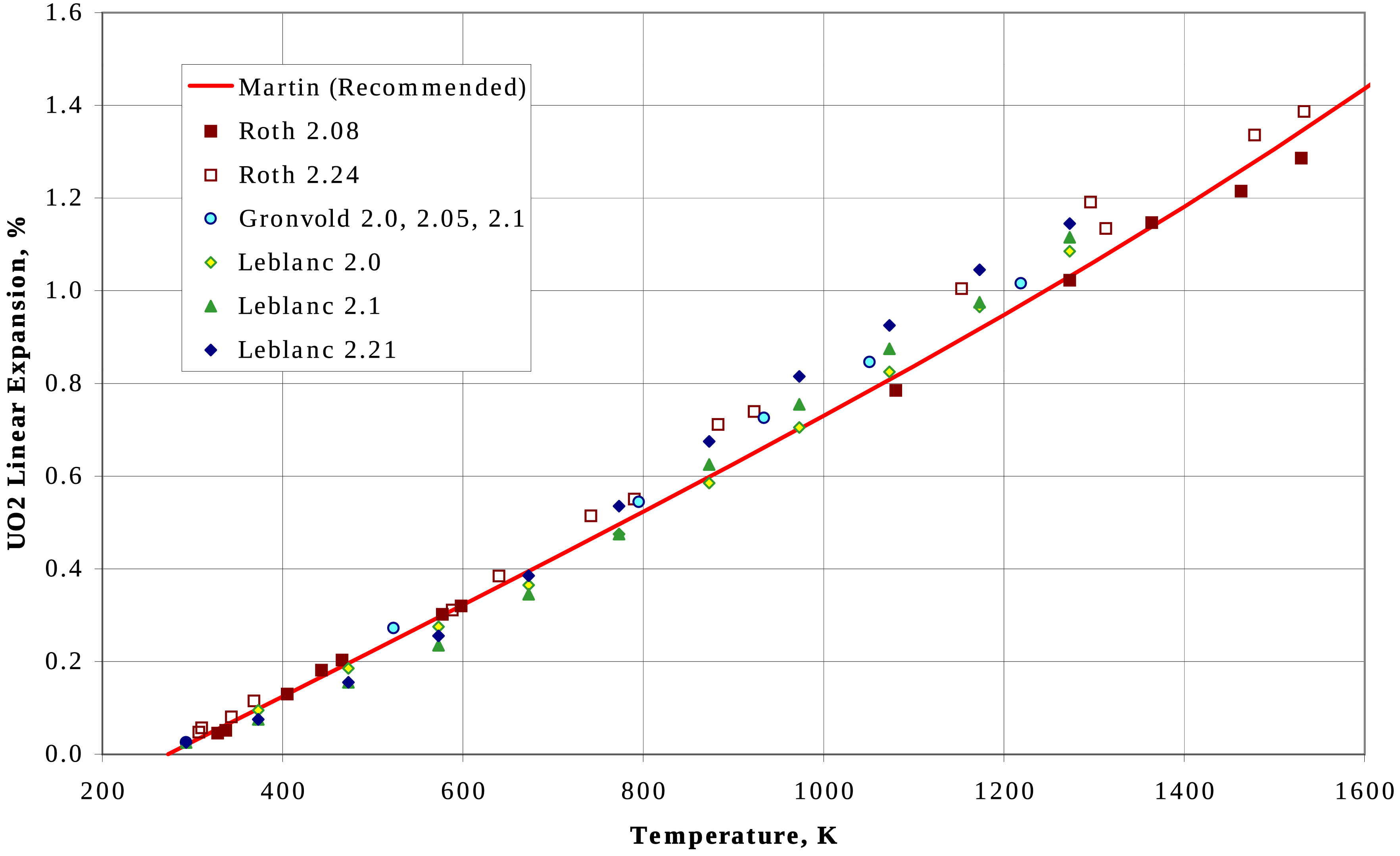
Figure 6 UO_{2+X} Thermal Expansion Data Compared with Recommendation



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