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Simultaneous determination of X-ray Debye temperature and Grüneisen constant for actinide dioxides: PuO_2 and ThO_2

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Abstract

The lattice vibrations of PuO_2 and ThO_2 were examined between room temperature and 1274 K using a high temperature X-ray diffractometer. The temperature factors for the metal atom, B_{Pu} and B_{Th} in the dioxides were evaluated by the Rietveld analysis. Debye temperature was calculated using the temperature factor. It was confirmed that the Debye temperature decreased with increasing temperature. From the temperature dependence of the Debye temperature, the Grüneisen constants were evaluated to be 1.62 for PuO_2 and 1.51 for ThO_2. The Debye temperatures modified for the thermal expansion of PuO_2 and ThO_2 were 429 and 463 K, respectively. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Debye model plays a vital role in the comprehension of thermal properties of a solid phase which relate to lattice vibration. It is known that physical parameters such as thermal expansion [1,2], specific heat [3,4] etc., are well described using the Debye temperature, Θ_D. Recently, Yamashita et al. [5] reported that the specific heat, C_p, for UO_2 could be estimated from the data on thermal expansion, compressibility and Grüneisen constant, γ. Usually, accurate measurement for such properties needs great amount of the sample. Thus, when a gram-order amount of the sample cannot be handled easily, which is the case of the actinide compounds, the method seems to have a great advantage, since the data on thermal expansion by X-ray diffractometry can be obtained with minute quantity of the sample. Thus far, there are a few data on Θ_D and γ for actinide dioxides [6–9] measured through different method. However, as is pointed out by Salter [10], the Debye temperatures obtained from different physical properties sometimes do not agree. Then, we planned to study these parameters systematically for a series of the actinide dioxides by X-ray diffraction method. The results on UO_2 and NpO_2 were reported in earlier papers [11,12]. In this work, the X-ray diffraction intensity measurements on PuO_2 and ThO_2 were carried out at high temperature. The X-ray diffraction profiles were examined by the Rietveld method. In the evaluation of the Debye temperature using high temperature data, the thermal expansion or anharmonic lattice vibration must be taken into account. Ordinarily, the effect is compensated by the Paskin's modification [13]. In the correction, the value of γ which is calculated from other properties (atomic volume, specific heat, the volume coefficient of thermal expansion and compressibility) is required. However, in case of actinide dioxides, no reliable information on γ value is available. Therefore, we conducted simultaneous evaluation of these parameters, which has been applied for NpO_2 [12]. The obtained Debye temperatures were discussed from a viewpoint of the relationship between the Debye temperature and the thermal expansion in a series of actinide dioxides.

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2. Experimental procedures

ThO_2 was prepared through an oxalate precipitation. The impurity of the sample was measured by the chemical analysis. The main impurity included in ThO_2 was C (880 ppm). In addition, impurities (Ag, Al, B, Ca, Cd, Cl, Co, Cu, Fe, Mg, Mn, Mo, N, Si, Sn, and V) were also present in total amount less than 150 ppm. PuO_2 sample was purified by the ion-exchange method to eliminate Am-241 and other impurities (Al, Ca, C, Cr, Fe, Ni, N, Si, Cl and F). The nominal value for the total impurities amount, except for Am, was 305 ppm. The pulverized specimens, PuO_2 and ThO_2, were heated at 1273 K for 5 h in air before the measurement. The X-ray diffraction measurement was carried out in air.

A high-temperature horizontal X-ray diffractometer apparatus with high temperature Pt-heater attachment (Ultima, RIGAKU) installed in a glovebox was used in the diffraction study. A reflection intensity of β-filtered Cu-Kα radiation was measured with a Na(Tl) scintillation counter. The slit width was 0.5° for both divergence and scatter ones. The sample was loaded on a platinum plate with a thin hole for a pair of thermocouples. The sample temperature was controlled within ±2 K during the measurement. Before the intensity measurement, the sample temperature was checked by comparing the lattice parameter of ThO_2 and its thermal expansion data [14].

Prior to the measurement at each temperature, the geometrical arrangement of the diffractometer was adjusted to cancel the deviation of the optical alignment caused by the thermal expansion of the sample holder. The intensity data of each diffraction peak were obtained by a fixed time method for the period of 1.5 s at each angle of 0.01°, while the diffraction data for Rietveld analysis were obtained by the same method with the step width of 0.05°.

3. Calculation of the Debye temperature and Grüneisen constant

Details of the analytical method were described in the previous paper [12]. The relationship between Θ_D and temperature factor of each component, B_M and B_O is given as

$$\frac{1}{3}(m_M B_M + 2m_O B_O) = \frac{6hT}{k\Theta_D^2}\left(\phi(x) + \frac{x}{4}\right), \tag{1}$$

where the symbols m_M and m_O in Eq. (1) are the masses of metal and O atoms; $\phi(x)$ is the Debye function with $x = \Theta_D/T$ [8], which can be successfully approximated by a quadratic equation as follows [12]:

$$\phi(x) + \frac{x}{4} = 2.585 \times 10^{-2}\frac{\Theta_D^2}{T^2} + 2.175 \times 10^{-3}\frac{\Theta_D}{T} + 9.995 \times 10^{-1}. \tag{2}$$

In the calculation, the value of B_O was fixed to that for the O atom of UO_2 [15]. The reasonableness of this approximation will be discussed in the following chapter.

It should be noted that there is one additional point in the calculation of the Debye temperature by Eqs. (1) and (2). In the Debye–Waller theory, it is assumed that crystal volume does not depend on the temperature. However, actually, as the pressure is constant during the measurement, the volume varies as a result of thermal expansion. Consequently, if Θ_D is plotted as a function of the temperature, a curve with negative curvature is obtained in the temperature ranges in which the contribution of the anharmonic vibration cannot be neglected. In order to get a true parameter without the effect of the dilation, some correction must be applied to the collected data or a series of the analysis.

The modification of the theory has been discussed by Paskin [13], who showed that the absolute temperature in Eqs. (1) and (2) had to be replaced by the reduced temperature T' expressed as

$$T' = T\left(\frac{V_T}{V_{T_O}}\right)^{2\gamma}, \tag{3}$$

where V_T and V_{T_O} are the volumes of the lattice at the temperature of T and T_O, respectively. The value of γ is usually given by the thermal parameters such as specific heat, compressibility and thermal expansion coefficient [8,13,16]. However, these parameters for actinide dioxides are not well known. Then, we tried to determine both of Θ_D and γ simultaneously. The method is based on the presupposition that the reduction of the Debye temperature with increasing temperature is attributable only to the effect of the thermal expansion, which is the same premise as the Paskin's modification [13].

From Eqs. (1)–(3), the value of Θ_D at each temperature can be calculated as a function of γ. Then we determined the most suitable value of γ by which the reduction of the Debye temperature can be compensated successfully [12]. Using the γ value evaluated here, we calculated the true value of Θ_D.

4. Results and discussion

4.1. Contribution of O atom to diffraction intensity

The diffraction data for each reflection peak were first analyzed by the method described by Buerger [17]. The integrated intensity, *I*, of the diffraction peak is given as

$$I = KL_{\mathrm{P}}P|F|^2_{hkl}, \tag{4}$$

where K is a constant, L_{P} the Lorentz-Polarization factor, P a multiplicity, and F is the modulus of the structure factor. L_{p} and F are denoted as a function of the Bragg angle. In Eq. (4), if the difference of the atomic scattering factor between the metal atom and O atom can be neglected, the structure factor term is written as

$$|F|^2_{hkl} = \left|\sum f_{\mathrm{a}}\right|^2 \mathrm{e}^{-2M(T)}, \tag{5}$$

where f is the atomic scattering factor, $M(T)$ is expressed with overall temperature factor, B, as

$$M(T) = B\frac{\sin^2\theta}{\lambda^2}. \tag{6}$$

From Eqs. (4)–(6), the corrected structure factor, F_{corr}, is defined as follows:

$$|F_{\mathrm{corr}}|^2 = \frac{I}{L_{\mathrm{P}}P} = K\left|\sum f_{\mathrm{a}}\right|^2 \mathrm{e}^{-2B(\sin^2\theta/\lambda^2)}. \tag{7}$$

Fig. 1 shows typical plots of $\ln(|F_{\mathrm{corr}}|^2/|\sum f_{\mathrm{a}}|^2)$ versus $\sin^2\theta/\lambda^2$ at several temperatures. In the case of CaF_2-type oxide, the reflections from the crystal are grouped into two classes. One is due to the metal and O atoms, the other is caused only by the metal atom. As can be seen in the figure, all data points lay on a straight line in spite of the significant difference in the Debye–Waller factor between the metal and O atoms. It means that the contribution of the O atom to the integrated intensity is considerably small compared with that of actinide atom. This is attributable to a small atomic scattering factor of O atom. Meanwhile, the result also implies that it is difficult to refine the temperature factor of O atom in Rietveld analysis just the same as the case for NpO_2 [12].

4.2. Temperature factor

Temperature factors for Pu and Th atoms, B_{Pu} and B_{Th}, obtained using the Rietveld analysis code 'RIETAN97b' [18] are plotted in Fig. 2, together with the reported values for Np atom in NpO_2, B_{Np} [12] and O atom in UO_2 [8]. It is difficult to compare these two parameters directly since the B value obtained in this method includes an error derived from the evaluation method of the diffraction intensity, such as the treatment of the background data.

In the Rietveld refinement, the temperature factor for O atom in PuO_2 and ThO_2 was fixed to that for O atom in UO_2. The assumption is considered to be pertinent as described in Section 4.1. In all cases, the discrepancy index calculated in the final refinement was less than 4%, which means that the analysis was successfully done.

The temperature factors, B_{Pu} and B_{Th}, increase with increasing temperature almost linearly below 800 K. However, the data points deviate from the linearity in higher temperature region. This result suggests that the contribution of the anharmonic lattice vibration is not so remarkable at low temperature.

The value of B_{Pu} at each temperature is nearly coincident with B_{Np} for NpO_2 [12], which implies that the values of Θ_{D}, for PuO_2 and NpO_2, are almost comparable. Whereas, the B_{Th} value obtained in this study was slightly smaller than B_{Pu} and B_{Np} ones. In addition, our result for B_{Th} is smaller than those reported by Willis [8]. Though we recalculated the value of B_{Th} using the value

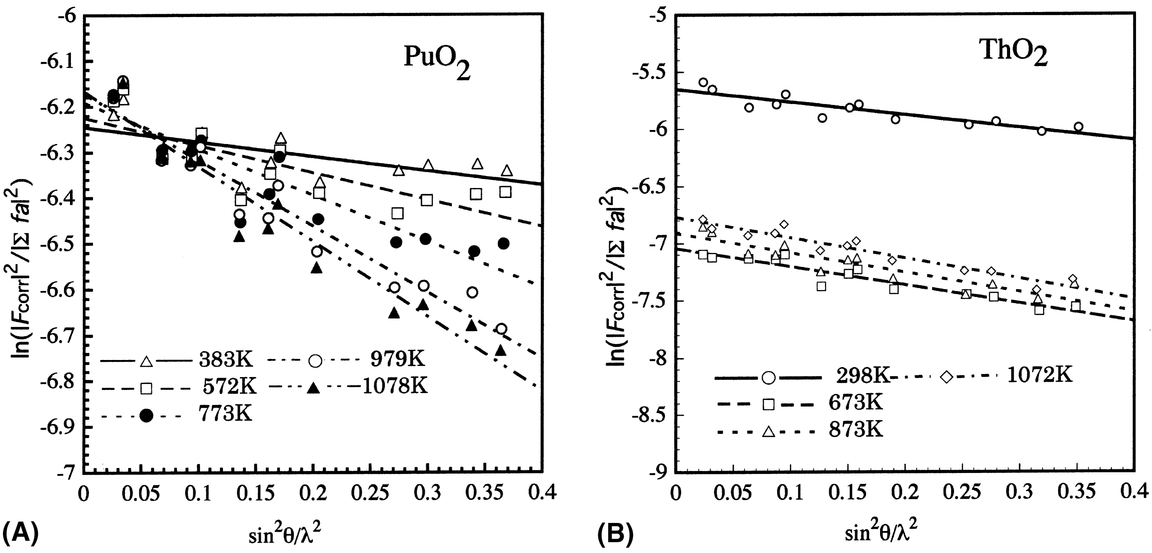

Fig. 1. Typical plot of $\ln(|F_{\mathrm{corr}}|^2/|\sum f_{\mathrm{a}}|^2)$ versus $\sin^2\theta/\lambda^2$.

of B_O for ThO_2 reported by Willis, the result was almost the same as the data plotted in Fig. 2. The reason for this is that the reflection related to O atom does not contribute significantly to the integrated intensity of the X-ray diffraction. As is known, the diffraction intensity largely depends not only on the precise optical alignment but also on the purity of the sample. It is difficult to discuss the difference in the absolute value of the data. Thus, we will discuss the validity of our value from the relationship between the linear thermal expansion and Θ_D in Section 4.4.

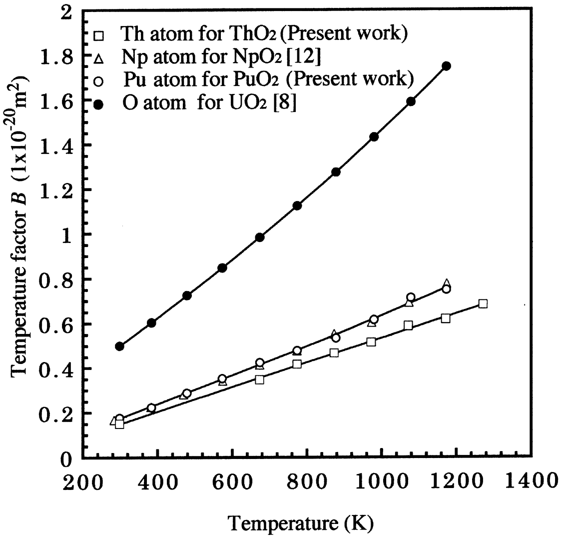

Fig. 2. Temperature dependence of overall temperature factor.

4.3. X-ray Debye temperature and Grüneisen constant

Fig. 3 shows the temperature dependence of Θ_D for PuO_2 and ThO_2 calculated from temperature factors given in Fig. 2 without the correction for the thermal expansion. In both cases, the value of Θ_D gradually declines with elevating temperature. The inclination is remarkable especially in high temperature region. The reduction of Θ_D suggests that as the contribution of the anharmony to the lattice vibration cannot be neglected, some kind of the modification is necessary in this point. Almost the same phenomenon has been observed for another actinide dioxide, NpO_2 [12].

Fig. 4 shows the temperature dependence of Θ_D uncorrected and corrected by Paskin's modification with the several values of $\gamma (\gamma = 0, 1, 2, 3)$. The solid lines show the results without correction for the thermal expansion. The slopes of these lines are given as a function of γ in Fig. 5. The figure indicates that the value of the slope increases almost linearly with increasing γ value. From the figure, it was found that the slope of the fitting line becomes zero when the γ value equals 1.62 for PuO_2 and 1.51 for ThO_2.

The final values of Θ_D for PuO_2 and ThO_2 calculated with each γ value are shown against the temperature in Fig. 6. The temperature dependence of Θ_D in the figure is almost negligible, which means that the contribution of anharmonic vibration is well corrected. The error arisen from the incorrectness in the estimated value of B_O is also shown by open triangle. Here, the estimated error in B_O was ±15%, which was slightly larger than the average difference between B_O in UO_2 and that in ThO_2. The values of Θ_D obtained finally were 429 K for PuO_2

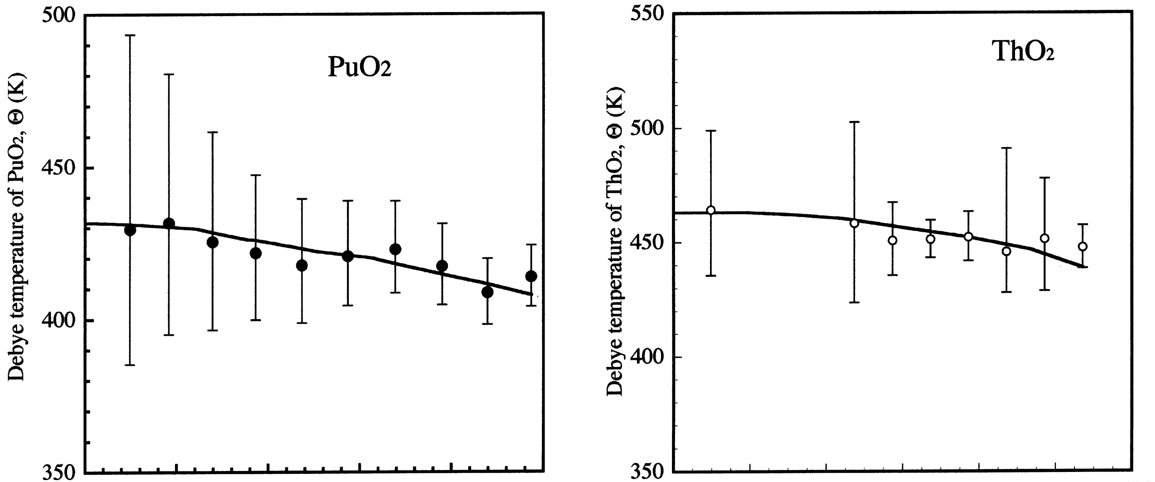

Fig. 3. Temperature dependence of Debye temperature, Θ_D, calculated without Paskin's correction for the thermal expansion (Grüneisen constant $\gamma = 0$).

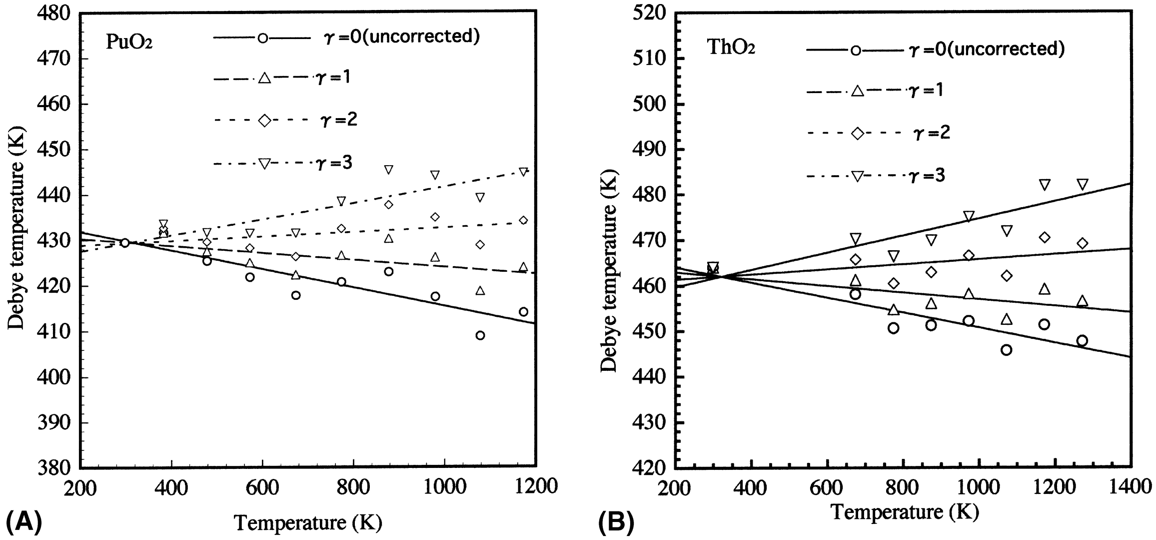

Fig. 4. Variation of the temperature dependence of Θ_D with changing Grüneisen constant, γ.

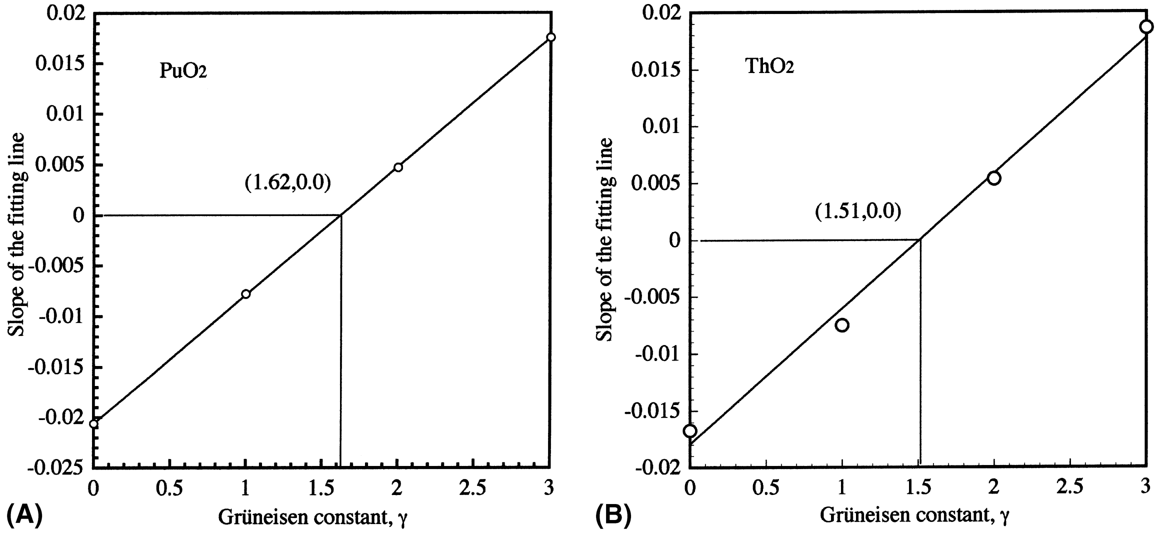

Fig. 5. Determination of Grüneisen constant, γ.

and 463 K for ThO_2, respectively. The estimated error originated in a least-squares fitting was ±4 K.

4.4. Evaluation of the obtained values for γ and Θ_D

The values of γ and Θ_D obtained in this study are summarized in Table 1 with those of the reported ones. All of the Θ_D values listed in the table were evaluated by the diffraction method [7,8,11,12]. The value of γ for ThO_2 obtained in this work is slightly lower than that employed by Willis in his calculation of the Θ_D value [8]. Whereas, γ for PuO_2 is apparently low compared with those used by Roof [7]. Although Roof [7] states that the γ value for PuO_2 is empirically 2.6, no information on the basic parameters is presented in his paper. However, the value is distinctively high compared with that for a series of the actinide dioxides. So far, there is no evidence that indicates the special volume dependence of Θ_D for PuO_2 among actinide dioxides. Thus, at the present time, we consider our result seems to be appropriate. As discussed by Hall [9], the γ value varies with the temperature. In the case of UO_2, the maximum variation in the γ value is about 10% in the temperature ranges from 300 to 1500 K [9]. Thus, it should be noted that the γ value obtained in this study is an average one.

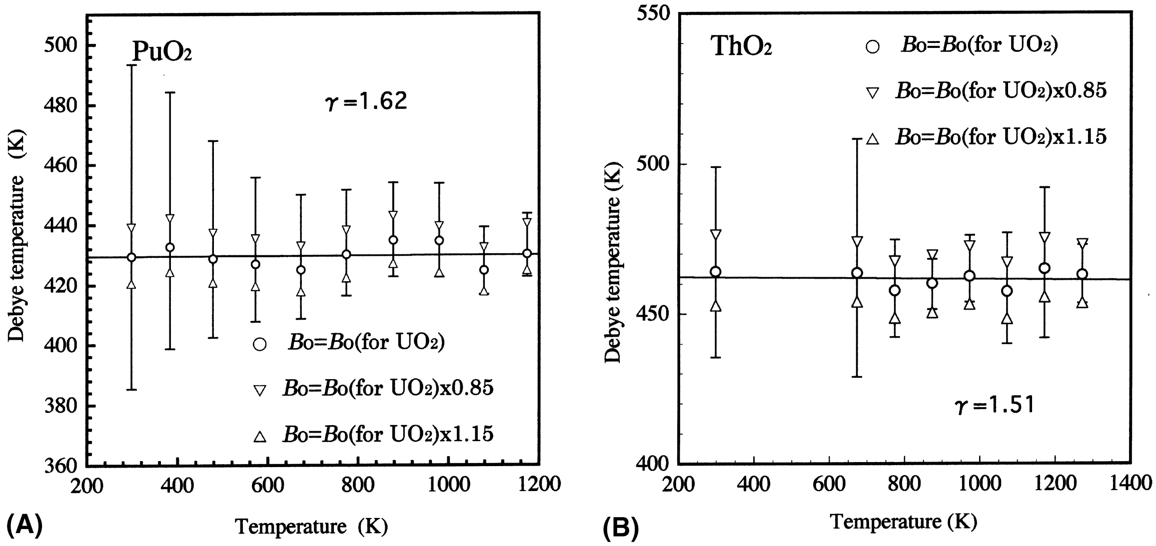

Fig. 6. Debye temperatures of PuO_2 and ThO_2 corrected by Paskin's method.

The obtained value of Θ_D for PuO_2 is almost compatible with that by Roof [7] in spite of the different value for γ. This unexpected consistency is due to the temperature range of the data used in the calculation. As can be seen in Fig. 3, the temperature dependence of Θ_D at low temperature region is almost negligible, which means that the contribution of the anharmonic vibration is not so distinguishable. Thus, the result of the Paskin's modification also does not change depending on the γ value. However, Roof [7] applied the modification to the diffraction data measured at relatively low temperatures. It should be emphasized that the measurement at higher temperature is necessary to determine the γ value.

On the other hand, the present value of Θ_D for ThO_2 is evidently higher than that by Willis [8]. Let us now look at Θ_D for actinide dioxides from a different angle, the relationship between Θ_D and linear thermal expansion (LTE). Ruffa [1,2] extended a model of thermal expansion for insulating materials in terms of the Morse potential at low temperature up to high temperature. According to his theory, LTE is given by two terms as

$$\beta(T) = \beta_1(T) + \beta_2(T), \tag{8}$$

where

$$\beta_1 \propto \frac{C_V}{a r_e D}, \tag{9}$$

$$\beta_2 \propto \frac{T\beta_1}{D}, \tag{10}$$

a, r_e and D in Eqs. (9) and (10) are the inverse width, the nearest neighbor distance and the depth, respectively. Therefore, the value of LTE tends to decrease with increasing the Debye temperature and interatomic forces. Here, as stated by Peng and Grimvall [3], the lattice parameter and interatomic distance for actinide dioxides are almost constant. From the standpoint of Ruffa's consideration, this means that the magnitude of LTE mainly depends on Θ_D value. The values of LTE for actinide dioxides are reported by Yamashita et al. [6]. According to Yamashita et al., the LTE values at room temperature become smaller in the order, $UO_2 > PuO_2 > NpO_2 > ThO_2$. Thus, if we take the suggestions by Ruffa [1,2] and Peng and Grimvall [3], Θ_D for ThO_2 should be larger than that for NpO_2. Peng and Grimvall [3] also discusses the specific heat of ThO_2

Table 1
Debye temperature and Grüneisen constant for actinide dioxides[a]

Material	γ	Θ_D (K)
ThO_2	1.7 [8] 1.51[a]	393 [8] 463[a]
UO_2	1.7 [8] 1.9 [5]	377 [8] 383 [12]
NpO_2	1.97 [12]	435 [12]
PuO_2	2.6 [7] 1.62[a]	415 [7] 429[a]

[a] Present study.

measured at high temperature. Their theoretical treatment gave the Θ_D value as high as 524 K. Although the value of Debye temperature generally depends on the measurement method [10], we cannot disregard their results. Comparing with their value, Θ_D for ThO_2 obtained in this study is considerably low. Nevertheless, our results well explain the order of the magnitude of LTE for a series of actinide oxides.

5. Concluding remarks

The Debye temperatures and Grüneisen constants for PuO_2 and ThO_2 were evaluated from the value of the temperature factor and its temperature dependence. The contribution of the anharmonic vibration to the temperature factor was fairly observed. It was confirmed that the Debye temperature reduced with elevating temperature in analogy with that for NpO_2. The Grüneisen constants derived from the reduction of the Debye temperature were 1.62 for PuO_2 and 1.51 for ThO_2. The Debye temperatures for PuO_2 and ThO_2 obtained finally were 429 and 463 K, respectively. Though the value for ThO_2 was appreciably high compared with previous data, our results well interpret the thermal expansion behavior of the actinide dioxides.

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