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Modelling thermal conductivity and self-irradiation effects in mixed oxide fuels

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Abstract

The present paper describes a physical model for thermal conductivity of actinide oxides. The model is based on the Debye–Einstein theory of thermal energy of ionic dielectrics, on the Klemens–Callaway's approach for the heat conductance modelling and on correlations between thermoelastic properties of solids. Some results of calculations and a comparison between the calculated and measured values of the thermal conductivity of UO_2, UO_2–Gd_2O_3 and also of ThO_2, AmO_2, Am_2O_3 and Cm_2O_3, for which a limited data-set is available in the open literature, are reported. Moreover, self-irradiation effects in AmO_2, Am_2O_3, $(Am,U)O_{2-x}$, $(Am,Np,U)O_{2-x}$ and Cm_2O_3 were analysed with the developed model.

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1. Introduction

In order to reduce the amount of transuranium elements (TRU) produced in the uranium-based fuels during their operation in the nuclear power plants, various strategies of TRU burning and different types of TRU-targets are being considered at present. Among these candidates, the oxide mixtures, including inert matrix and thoria-based fuels, are rather promising. The design and interpretation of irradiation experiments needed to test the applicability of these oxide compounds are based on fuel performance codes, which require information on thermo-physical and thermo-mechanical properties of the materials of interest. However, literature data on the properties of actinide oxides show a wide spread even for pure materials (except UO_2). For most of the oxide mixtures of interest they are still missing, therefore sound physical models could be used at this stage for their estimation.

Thermal conductivity is a key property of nuclear fuel, since it determines the temperature level and distribution which strongly affect the creep rate and fission gas release. In many cases, the complex physical approach and the similarity principle allow to deduce the missing data, basing on those for the well-known materials. In many practical cases related to nuclear fuel operation conditions, the temperature dependence of the lattice thermal conductivity of the actinide oxides is often presented by a widely used hyperbolic function [1]. From the theoretical point of view this empirical approach is a rather drastic simplification which can lead to errors when irradiation effects are considered.

The main objective of this paper is to develop an approach which will allow assessing the thermal conductivity of homogeneous compounds of actinide oxides. Basing on this approach, a model for the thermal conductivity of ThO_2, UO_2, TRU (including: PuO_2, NpO_2, AmO_{2-x}, CmO_{2-x}, Am_2O_3 and Cm_2O_3) and their mixtures was developed and presented. The model for the lattice thermal conductivity is based on the Debye–Einstein theory of ionic dielectrics and on the Klemens–Callaway approach to heat conduction problem [2–4].

In the next part of this paper, a general theoretical approach for modelling the thermal conductivity of the isotropic dielectric solids is presented. Models for phonon scattering mechanisms are considered in the third part. The fourth part describes the model parameters, and the fifth gives the comparison of the model predictions with a limited experimental data-set available in

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the open literature for oxides of interest and their mixtures. Self-irradiation effects in AmO_{2-x}, $(Am,U)O_{2-x}$, $(Am,Np,U)O_{2-x}$, Am_2O_3 and Cm_2O_3 due to alpha-decay of some isotopes of americium and curium are analysed in the sixth part. Finally, the conclusions about the model capabilities and some perspectives are outlined.

2. Theoretical approach

It is well-known that thermal conductivity of the actinide oxides, such as UO_2, is mostly determined by the lattice thermal conductance, usually described as the phonon mechanism. Other mechanisms (charge carriers, photons, vacancies) give only few percents contribution at sufficiently high temperatures. In order to evaluate correctly the lattice thermal conductivity, three type of interactions should be considered: the phonon scattering by the static defects (always resistive because of quantum nature of phonons as quasi-particles), the non-resistive phonon–phonon interactions (N-processes), and the resistive phonon–phonon interactions (U-processes).

It was shown by Callaway that the scattering for N-processes, which redistribute phonons and make all phonons 'aware' of the particular resistive scattering mechanisms, have to be taken into account, although N-processes themselves can not cause directly the thermal resistance of the lattice. Without consideration of N-processes in physically based models the conductivity of lattice should be underestimated and additional correction terms to the Debye lattice conductivity is required to complete formal consideration. Without correction for N-processes any model even being successive in verification predictions should be regarded as estimation model with limited applicability to the cases where they can be neglected.

Callaway, by solving the Boltzmann equation for phonon distribution function in presence of temperature gradient, has produced the expression for the conductivity, which is most widely used and, probably, is the most successive for the interpretation of the experimental results and for evaluation of the lattice thermal conductivity in a wide temperature range in presence of nanometric lattice imperfections. In original formulation of the Callaway's theory the total lattice thermal conductivity is written as a sum of two terms ($\lambda_{\text{Callaway}} = k_1 + k_2$) with the definitions as follows [3]:

$$k_1 = \frac{k}{2\pi^2 \bar{c}_s}\left(\frac{k}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \tau_C \frac{x^4 e^x \, dx}{(e^x - 1)^2}, \tag{1}$$

$$k_2 = \frac{k}{2\pi^2 \bar{c}_s}\left(\frac{k}{\hbar}\right)^3 T^3 \frac{\left\{\int_0^{\theta_D/T} (\tau_C/\tau_N)\cdot x^4 e^x (e^x - 1)^{-2} \, dx\right\}^2}{\int_0^{\theta_D/T} (\tau_C/\tau_N \tau_R)\cdot x^4 e^x (e^x - 1)^{-2} \, dx}, \tag{2}$$

where k is Boltzmann's constant, $\hbar$ is Planck's constant, $\bar{c}_S$ is the mean phonon velocity (or sound velocity); θ_D is the characteristic Debye temperature; T is the absolute temperature; $x = \hbar\omega/kT$; ω is the phonon frequency; τ_N denotes the time of phonons relaxing to the displaced distribution corresponding to a non-zero heat flow, and τ_R is the total relaxation time for phonons relaxing with the resistive processes to the equilibrium Planck distribution. The combined relaxation time is given by $\tau_C^{-1} = \tau_R^{-1} + \tau_N^{-1}$. In the Callaway theory the relaxation time τ_R includes the effect of Umklapp processes according to the addition of relaxation rates, i.e.

$$\frac{1}{\tau_R} = \frac{1}{\tau_U} + \frac{1}{\tau_{R_1}} + \frac{1}{\tau_{R_2}} + \cdots \tag{3}$$

when there are several types of resistive scattering processes acting simultaneously (Umklapp scattering, isotopic scattering, boundary scattering, etc.), i.e. the all corresponding scattering mechanisms are assumed to be independent and additive.

The term k_2 is not only a correction term to k_1 but is essential to counteract the effect of N-processes as if they were entirely resistive. Consequently, in general case k_2 is a non-negligible part of Callaway's theory. The magnitude of k_2 is essentially controlled by the concentration of lattice imperfections (point defects, mass-different isotopes). However, in case of temperatures high enough when phonon free path is short compared with the average size of grains in polycrystalline solids and characteristic free path due to N-process, then the resistive scattering dominates ($\tau_N \gg \tau_R \Rightarrow k_2 \ll k_1$) and only k_1 becomes important.

For materials of our interest (actinide oxides) it is not correct to ignore a priory the contribution of k_2, but it may be expected that at actual fuel operation temperatures and under conditions of continuous production of fission products and fission-induced disordering of lattice, the first Callaway's term k_1 will solely dominate over the second term k_2. Although it was shown by Berman [4] that Callaway term k_2 (generally regarded as a correction term) can be the major term at temperatures close to the characteristic Debye temperature and determines the maximum of lattice thermal conductivity.

At temperatures close or higher than the characteristic Debye temperature the Callaway's lattice conductivity can be re-written in the form [5]:

$$\lambda_{\text{Callaway}} = \frac{k}{6\pi^2 \bar{c}_s}\left(\frac{k}{\hbar}\right)^3 \theta_D^3 \left\{ \langle \tau_C \rangle_{\text{DOS}} + \frac{\langle \tau_C/\tau_N \rangle_{\text{DOS}}^2}{\langle \tau_C/\tau_N \tau_R \rangle_{\text{DOS}}} \right\}, \tag{4}$$

where averaging of time probabilities is taken with the Debye function of density of states (DOS approximation), $g(\omega) = 3\omega^2/\omega_D^3$, i.e.

$$\langle f\rangle \equiv \langle f\rangle_{\mathrm{DOS}} \equiv \int_0^1 f(y)3y^2\,\mathrm{d}y. \tag{5}$$

Relaxation time functions $\tau_i(\omega)$ may be expressed in terms of corresponding macroscopic cross-sections Σ_i reverse values of which represent the relaxation length of scattering processes to be considered:

$$\tau_i = \frac{\Lambda_i}{\bar{c}_{\mathrm{S}}} = \frac{1}{\bar{c}_{\mathrm{S}}\Sigma_{(i)}} = \frac{\Lambda_0}{\bar{c}_{\mathrm{S}}}\frac{1}{\Lambda_0\Sigma_{(i)}} = \frac{\Lambda_0}{\bar{c}_{\mathrm{S}}}\frac{1}{S_{(i)}}, \tag{6}$$

where Λ_i represents the relaxation length of processes, $\Sigma_i = \sigma_i n_i$ is the macroscopic cross-section of point defects randomly distributed in lattice with concentration n_i and scattering phonons with microscopic cross-section σ_i, and $S_{(i)} = \Lambda_0\Sigma_{(i)}$ is the dimensionless scattering strength (to be defined with respect to a particular mechanism of phonon scattering). As earlier the assumption is held that resistive scattering rates are additive, so that

$$\Lambda_{\mathrm{R}} \equiv \Lambda_0 \cdot \left(S_{\mathrm{U}} + \sum_{\text{defects}} S_{(i)}\right)^{-1} + \frac{1}{2}\Lambda_0 \equiv \Lambda_0(S_{\mathrm{R}}^{-1} + 1/2), \tag{7}$$

where term $(1/2)\Lambda_0$, half the limiting phonon wavelength, is to be included to avoid the non-physical case where the mean free path (calculated as reduced value of corresponding macroscopic cross-sections of scattering processes) becomes short compared to the interplanar spacing; $S_{\mathrm{U}} = \tau_{\mathrm{U}}^{-1}\Lambda_0/\bar{c}_{\mathrm{S}}$ is the strength function of U-processes.

The true two-term Callaway expression takes the classical Debye form ($\lambda_{\mathrm{Debye}} = k_1$, assuming also that $k_2 \ll k_1$) if normal processes are ignored ($\tau_{\mathrm{C}} = \tau_{\mathrm{R}}$) or $\tau_{\mathrm{N}} \gg \tau_{\mathrm{R}}$ (then again $\tau_{\mathrm{C}} \approx \tau_{\mathrm{R}}$).

In terms of macroscopic scattering strength functions and DOS approximation the true Callaway equation (4) takes the following form, which is adequate for Debye model in high-temperature region [5]:

$$\lambda = K_{\mathrm{Class}}\left\{\frac{1}{2} + \left\langle\frac{1}{S_{\mathrm{R}} + S_{\mathrm{N}}}\right\rangle + \frac{\left\langle\frac{S_{\mathrm{N}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle^2}{\left\langle\frac{S_{\mathrm{N}}\cdot S_{\mathrm{R}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle}\right\} \tag{8}$$

with the following equivalent definitions for the classical Debye limit of the lattice thermal conductivity:

$$K_{\mathrm{Class}} \equiv \frac{k\Lambda_0\theta_{\mathrm{D}}^3}{6\pi^2\bar{c}_{\mathrm{S}}^2}\left(\frac{k}{\hbar}\right)^3 = \frac{2}{3}\left(\frac{k}{\hbar}\right)\frac{k\theta_{\mathrm{D}}}{\Lambda_0} = \frac{4\pi}{3}\frac{k\bar{c}_{\mathrm{S}}}{\Lambda_0^2}, \tag{9}$$

where Λ_0 is the limiting value of the phonon free path, and the characteristic Debye temperature and the average velocity of phonons (sound velocity, $\bar{c}_{\mathrm{S}}$) are linearly correlated:

$$\theta_{\mathrm{D}} = \frac{2\pi}{\Lambda_0}\left(\frac{\hbar}{k}\right)\bar{c}_{\mathrm{S}}. \tag{10}$$

To be applicable for the whole temperature range, this formula should be corrected with porosity correction function, F_P, and with the Debye function $D(\theta_{\mathrm{D}}/T)$ taking into account the heat capacity temperature dependence:

$$\lambda = D(\theta_{\mathrm{D}}/T)F_P K_{\mathrm{Class}}\left\{\frac{1}{2} + \left\langle\frac{1}{S_{\mathrm{R}} + S_{\mathrm{N}}}\right\rangle + \frac{\left\langle\frac{S_{\mathrm{N}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle^2}{\left\langle\frac{S_{\mathrm{N}}\cdot S_{\mathrm{R}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle}\right\}. \tag{11}$$

Eq. (11) is 'exact' in the Debye model and applicable for all temperatures. In the Callaway theory this equation is approximate, while Eqs. (1) and (2) are exact, however, it does not appear possible to evaluate the basic integrals analytically. DOS approximation allows to solves this problem.

It is well-known due to R.E. Peierls (see [6]) that N-processes cannot themselves lead to a finite thermal conductivity. Consequently, it can not be legitimate just to add the reciprocal relaxation time for the normal processes (or strength function S_{N}) to those which do not conserve the crystal momentum. Certainly it can be shown, that at high temperatures the strength function of N-processes, S_{N}, shall be eliminated in Umklapp term of Eq. (11):

$$\lambda = D(\theta_{\mathrm{D}}/T)F_P K_{\mathrm{Class}}\left\{\frac{1}{2} + \left\langle\frac{1}{S_{\mathrm{R}}}\right\rangle + \frac{\left\langle\frac{S_{\mathrm{N}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle^2}{\left\langle\frac{S_{\mathrm{N}}\cdot S_{\mathrm{R}}}{S_{\mathrm{R}}+S_{\mathrm{N}}}\right\rangle}\right\}. \tag{12}$$

For any type of lattice defects, the partial scattering strengths are certain power functions of frequency ($S_{\mathrm{R}}^{(i)} \propto \omega^{m_{(i)}}$) where the power of frequency dependence (m) may take values from 0 (grain boundaries) to 4 (point defects). With any combination of frequency terms in the resistive scattering strength functions, the DOS averages can be obtained with elementary functions and will lead to finite thermal conductivity in the whole temperature range.

For completion of theoretical consideration, the expressions for the scattering strength functions have to be given.

3. Scattering mechanisms and scattering strength functions

In case of actinide oxides, there are several types of resistive processes to be first considered: (i) U processes with relaxation time τ_{U}; (ii) scattering by random distribution of different isotopes with relaxation time τ_{I}; (iii) scattering by point defects (vacancies, interstitials) or mass irregularities; (iv) scattering by line imperfections, typically for in-pile conditions this is track network caused by fission fragments. The scattering of phonons by lattice irregularities considered as a scattering of sound waves can be calculated from first principles based on Landau theory of elastic theory of compressible mediums [7,8]. The detailed considerations have been made in our previous paper [5]. They present the relaxation time of the normal processes τ_N as follows:

$$\begin{aligned}\tau_N^{-1} &= D(\theta_D/T)\frac{\omega}{2\pi}\frac{c_T}{c_L} \\ &= D(\theta_D/T)\frac{\omega}{2\pi}\left(\frac{1-2v}{2(1-v)}\right)^{1/2} = \frac{\bar{c}_S}{\Lambda_0}S_N,\end{aligned} \tag{13}$$

where c_L and c_T represent the propagation of sound waves of the longitudinal and transverse modes, respectively, and the ratio c_T/c_L is expressed via adiabatic Poisson coefficient, v.

Umklapp phonon–phonon interaction involves at least the three phonons where one of them has to be the low-frequency longitudinal phonon and others are the thermal phonons [3,6]. Since Umklapp phonon–phonon interaction tends to restore the equilibrium Planck distribution disturbed by N-processes, a certain amount of mechanical work has to be done in transition from the given non-equilibrium state to the Planck state corresponding to the thermodynamic equilibrium. This work can be done on the account of dissipation of energy associated with the low-frequency longitudinal phonons, since thermal phonons have already reached the Debye limit for possible frequencies in the Umklapp interactions. Both, in the Debye and Callaway models, phonons are synonymic to sound waves. In terms of the sound waves, the relaxation time for the Umklapp processes (τ_U) is to be equal the characteristic time of attenuation of the amplitude in the low-frequency longitudinal sound wave interacting with the thermal phonons. The total energy of the sound wave per unit volume of solid is $\bar{E} = \rho \cdot \bar{c}_S^2/2$, where ρ is density of solid. The rate of mechanical energy dissipation ($\dot{E}_{\text{mech}}$) in the sound waves in an approximation of solid with the isotropic medium is [8]: $\dot{E}_{\text{mech}} = -(\lambda_{\text{U-phonons}}/T) \times \int (\vec{\nabla} T)^2 \, \mathrm{d}V$, where $\lambda_{\text{U-phonons}}$ is the thermal conductivity coefficient caused by thermal phonons, and $\vec{\nabla} T$ is the deviation of the temperature in the sound wave (adiabatic conditions) from its equilibrium value. This gives for the plane low-frequency waves:

$$\dot{E}_{\text{mech}} = -\frac{\omega^2 V_{\text{solid}} K_{\text{Class}}}{2}\left(\frac{1}{c_V} - \frac{1}{c_P}\right), \tag{14}$$

where c_V and c_P are the heat capacities per unit mass at constant volume and constant pressure respectively.

The energy of thermal phonons $\hbar\omega_{\text{U-phonons}} \approx \hbar\omega_D$, which means that $\lambda_{\text{U-phonons}} \approx K_{\text{Class}}$, where K_{Class} is the classical Debye limit for the lattice thermal conductivity. The energy in the sound wave caused by interaction with the thermal phonons leads to attenuation of amplitude in plane wave with the distance in the direction of propagation. Absorption coefficient (γ_L) of sound wave energy is defined by the ratio [8]: $\gamma_L = |\dot{E}_{\text{mech}}|/2\bar{c}_S\bar{E}$. Physical meaning of this coefficient is revealed by a decrease of amplitude of the low-frequency wave, which is determined by the factor $e^{-\gamma_U r}$. The reverse value of the absorption coefficient gives the characteristic length of propagation of the low-frequency phonons due to Umklapp phonon–phonon interactions $\Lambda_U \equiv \tau_U/\bar{c}_S = \gamma_U^{-1}$. Then for the relaxation time of Umklapp phonons one can obtain [6]:

$$\tau_U^{-1} = \frac{|\langle \dot{E}_{\text{mech}} \rangle_{(\text{time-average})}|}{2\bar{E}\bar{c}_S^2} = \frac{\omega^2 K_{\text{Class}}}{2\rho\bar{c}_S^2 c_V} \cdot \frac{c_V}{c_P} \cdot \left(\frac{1}{c_V} - \frac{1}{c_P}\right). \tag{15}$$

Taking into account the well-known thermodynamic formula, $c_P/c_V = 1 + \alpha_V\gamma_G T$ (where α_V is the volumetric thermal expansion coefficient and γ_G is Gruneisen's constant), and the simple kinetic theory definition for $K_{\text{Class}} = (1/3)c_V\rho\bar{c}_S\Lambda_0$, the Umklapp relaxation time can be re-written in the form:

$$\tau_U^{-1} = (1/6)\alpha_V\gamma_G T\Lambda_0\bar{c}_S(\omega_D/\bar{c}_S)^2(\omega/\omega_D)^2 \tag{16}$$

which gives the Umklapp relaxation time (τ_U^{-1}) and strength function $S_U = \tau_U^{-1}\Lambda_0/\bar{c}_S$ as a parabolic function of frequency and a linear function of temperature (which is generally assumed for this parameter in the Callaway theory [3,4,7]).

In the Callaway theory the problem of calculating relaxation time functions caused by scattering on point defects of any types (vacancies, interstitials, and isotopic mass irregularities) is reduced to the problem of calculating microscopic cross-sections of phonon-defect interactions, as can be also seen from the definition equation (6). The first quantum mechanical consideration of the problem was given by Klemens [2]. It is essential for Klemens theory that point defects are considered to be isolated, immobile and the size of sphere (which is indeed an atomic volume) associated with defects is short compared to the phonon wavelength. In real solids, however, considering high-temperature thermal conductivity the first two conditions are not satisfied (in particular because of the Dulong–Petit law). The solution of the problem for mobile point defects has been proposed by Landau from perspectives of fluid dynamics [7] and elasticity theory of compressible mediums [8]. According to Landau theory two types of motion should be considered, i.e. translation motion of spheres associated with point defects (3-D oscillatory motions) and radial oscillatory changes of atomic volumes leading to emitting of long waves longitudinal phonons (further converted into transverse phonons). Accounting for translational motion leads to conventional ω^4-frequency dependency of corresponding relaxation times due to Rayleigh scattering of long-wave phonons, while accounting for radial oscillations of spheres associated with point defects leads to resonance scattering with total relaxation time τ_{Defects}, which can be expressed as [5]:

$$\tau_{\text{Defects}}^{-1} = \frac{\bar{c}_{\text{S}}}{\Lambda_0}\left(S_{\text{defects}}^{(\text{L})} + S_{\text{defects}}^{(\text{R})}\right), \tag{17}$$

$$\begin{aligned} S_{\text{defects}}^{(\text{L})} &= \sum_{\text{defects}} S_i^{(\text{L})} \equiv \frac{\Lambda_0}{\upsilon_0}\sum_{\text{defects}} \sigma_i^{(\text{L})} n_i \\ &= \frac{\Lambda_0}{\upsilon_0}\left(\frac{\omega}{\omega_{\text{D}}}\right)^4 \sum_{\text{defects}} \frac{4\pi R_i^2}{3}\left(\frac{\omega_{\text{D}} R_i}{\bar{c}_{\text{S}}}\right)^4 \Gamma_i n_i, \end{aligned} \tag{18}$$

$$\begin{aligned} S_{\text{defects}}^{(\text{R})} &= \sum_{\text{defects}} S_i^{(\text{R})} \equiv \frac{\Lambda_0}{\upsilon_0}\sum_{\text{defects}} \sigma_i^{(\text{R})} n_i \\ &= 36\left(\frac{1-2\nu}{1+\nu}\right)^2 \sum_{\text{defects}} \Gamma_i n_i \left(\frac{\upsilon_i}{\upsilon_0}\right), \end{aligned} \tag{19}$$

$$\Gamma_i = \frac{1}{3}\,\frac{(\Delta M_i/\overline{M})^2}{\left(1-\frac{2}{3}\Delta M_i/\overline{M}\right)^2} + \frac{16}{9}\left(\frac{\Delta\upsilon_i}{\upsilon_0}\right)^2. \tag{20}$$

Here $S_i^{(\text{L})}$, $S_i^{(\text{R})}$ represent partial strength function for particular defect type; υ_0 is the average volume per atom of the crystal; n_i is the fraction of atoms (point defects) with characteristic size R_i, mass variation ΔM_i and atomic volume variation $\Delta\upsilon_i$, $\overline{M}$ is the average mass of the constituent lattice atoms.

Substituting derived strength functions into the Callaway model equation (12) allows to obtain the analytical solution for the lattice thermal conductivity. In apparent form the solution is given in [5]. The analytical solution can be considerably simplified by neglecting strength function of Rayleigh scattering ($S_{\text{defects}}^{(\text{L})} \ll S_{\text{defects}}^{(\text{R})}$) because of the forth power of frequency dependence: $(\omega/\omega_{\text{D}})^4 \ll 1$ for all long-wave phonons ($0 < \omega < \omega_{\text{D}}$). With derived strength functions $S_i^{(\text{R})}$, the corresponding partial $A_i^{(\text{R})}$, and total extrinsic resistivities $A_{\text{defects}}^{(\text{R})}$ can be expressed in the following forms: $A_i^{(\text{R})} = S_i^{(\text{R})}/K_{\text{class}}$ and $A_{\text{defects}}^{(\text{R})} = \sum_i A_i^{(\text{R})}$ with summation over all defect types.

4. Burnup-induced and self-irradiation effects

The term $\sum_i \Gamma_i n_i$ in formulas (18) and (19) represents the sum of cross-sections of all the phonon-defect scattering centres. In the mixed actinide oxides based on urania or thoria the minor actinide atoms introduce additional scattering centres for phonons because of their mass and ionic size differences leading to an increase in the defect-induced thermal resistivity. Mass and ionic size differences between all minor actinides and uranium or thorium are really small, nevertheless, it determines the start-up value of defect-induced thermal resistivity, which can be calculated accurately for all particular cases based on specifications of actinide content oxides. In oxide fuels with high content of americium and/or curium an additional factor to be considered is the effect of self-irradiation as described by Schmidt et al. [9] and Bakker and Konings [10]. (For instance, it was observed that the lattice conductivity of americium oxides considerably decreases due to a-decay until saturation is reached after three days.)

It also appears that under irradiation fission fragments cause a damage to the lattice (in the form of vacancies, interstitials, and fission products), which can affect the thermal conductivity. The review by Belle and Berman [11] of the irradiation studies at low exposures has shown that lattice damage in urania and thoria as a result of irradiation indicates that this damage is largely confined to the formation and saturation of vacancies and interstitials. Olander [1] gave a quantitative estimate of the effect. To the first approximation the concentration of vacancies and interstitials due to fission fragments can be estimated as a number of atoms displaced in the track by fission fragment: $n_{\text{f}} = 2\pi(\bar{a}/d_{\text{track}})^2$. For ionic solids such as urania and thoria the characteristic diameter of fission track is ~10 nm [1]. Vacancies are the major contributors to the scattering of phonons on point defects since for the vacancies mass difference factor in Eq. (20) has the largest value ($\Gamma_{\text{v}} = 3$ [6]).

Thus both, the self-irradiation effect and the effect of thermal conductivity degradation at low exposures can be attributed to the additional concentration of vacancies. A more detailed analysis of these effect has been carried out in [5] where the strength function has been derived accounting for self-irradiation or saturation of fission track network:

$$S_{\text{tracks}}^{(\text{R})} = \frac{54}{49}\cdot\frac{\pi}{2}\cdot\left(\frac{1-2\nu}{1+\nu}\right)^2 \approx \frac{\pi}{2}\cdot\left(\frac{1-2\nu}{1+\nu}\right)^2. \tag{21}$$

For uranium dioxide $K_{\text{class}} \approx 2.0\ \text{W}\,\text{m}^{-1}\,\text{K}^{-1}$; Poisson ratio at low temperatures $\nu \approx 0.314$, thus for partial extrinsic resistivity, $A_{\text{tracks}}^{(\text{R})}$, caused by track network saturation one can obtain an estimate $A_{\text{tracks}}^{(\text{R})} \approx 0.0675$ $\text{m}\,\text{K}\,\text{W}^{-1}$, which is very close to the experimental values [1,12].

The solid swelling (volume increase of the solid phases) in the actinide oxides is a fundamental burnup dependent property important for the modelling of the lattice thermal conductivity, because it produces additional and continuously increasing amount of the phonon scattering centres. The theoretical solid swelling (and consequently $\sum_i \Gamma_i n_i$ factor) can be calculated from the partial volume of each fission product species (including associated oxygen) and its cumulative fission yields. The analysis of solid swelling in oxides of our interest has been carried out by several authors [1,13,14]. Following the Schrire et al. [14], it is assumed in the model that fission products in solid solution do not cause a net change in the lattice parameter of the fuel, thus only mass-difference factors are important. For simple consideration it may be assumed that two peak symmetrical mass distribution of fission products with atomic weights of 95 and 140. Concentrations of solid fission products are linear function of local burnup, thus partial strength function due to solid swelling can be easily calculated based on these parameters [5]. However, the main burnup-induced degradation of lattice thermal conductivity is to be due to gaseous fission products. If the fission gases are present as interstitials atoms, they are expected to make an additional contribution to the solid swelling of 0.43–0.52% (based on the partial volume of 0.085 nm^3) at.% burnup (see [14]). Both, mass differences and size differences, are important in case of gas fission products. Together with the other fission products this would give a total solid swelling rate of 0.75–0.99% per at.% burnup. In terms of burnup and total solid swelling rate corresponding strength function of the phonon scattering on solid fission products, $S_{\mathrm{sw}}^{(\mathrm{R})}$, can be expressed in the form [5]:

$$S_{\mathrm{sw}}^{(\mathrm{R})} = 128 \cdot \left(\frac{1-2\nu}{1+\nu}\right)^2 \dot{S}_{\mathrm{sol.\,sw}} \cdot Bu, \tag{22}$$

where Bu is the local burnup in GWd/tHM, and $\dot{S}_{\mathrm{sol.\,sw}}$ is the total solid swelling rate per unit burnup (it is this default value, 9×10^{-4} per GWd/tHM, which is used in the model). For uranium dioxide corresponding extrinsic resistivity calculated with this strength function is of $(35–45) \times 10^{-4} Bu$ $\mathrm{m\,K\,W^{-1}}$ for total swelling rate ranging from 7×10^{-4} to 9×10^{-4} per GWd/tHM, which is in a good agreement with experimental value estimated in [12].

Effect of stoichiometry ratio (O/M) is also important. Deviation from the exact stoichiometry causes an additional atomic scale defectness of crystal in the form of vacancies and interstitials. The two defects, for instance, in the hypostoichiometric mixed oxides are oxygen vacancies and metallic ions where oxygen vacancies are most important for accounting for the lattice thermal conductivity degradation. It is interesting to note that effect of deviation from exact stoichiometry is almost symmetrical regardless the sign of deviation [1]. For the hypostoichiometric mixed oxides, MO_{2-x}, atomic fractions of vacancies and metallic ions are x and $2x$ respectively. Based on general formula (19) theoretical estimate of this effect can be expressed as follows [5]:

$$S_{x}^{(\mathrm{R})} = 36\Gamma_{\mathrm{v}}\left(\frac{1-2\nu}{1+\nu}\right)^2 x. \tag{23}$$

Using $\Gamma_{\mathrm{v}} = 3$ and taking Poisson ratio of uranium dioxide the corresponding extrinsic resistivity of mixed $(\mathrm{U,Pu})\mathrm{O}_{2-x}$ oxides yields an estimate $\Lambda_{x}^{(\mathrm{R})} \approx 4.2x$ $\mathrm{m\,K\,W^{-1}}$.

5. Model parameters

The classical limit of the lattice thermal conductivity can be expressed in terms of lattice constants and basic thermodynamic properties [15]:

$$\begin{aligned} K_{\mathrm{Class}} &= \frac{1}{3}\rho\bar{c}_{\mathrm{S}}^2\Lambda_0(c_{\mathrm{V}}/c_{\mathrm{P}})\frac{\alpha_{\mathrm{V}}}{\gamma_{\mathrm{G}}}\bigg|_{T\approx T_{\mathrm{M}}} \\ &= \frac{1}{3}\Lambda_0\bar{c}_{\mathrm{S}}B_{\mathrm{S}}\frac{\alpha_{\mathrm{V}}}{\gamma_{\mathrm{G}}}\bigg|_{T\approx T_{\mathrm{M}}} \\ &= \frac{1}{3}\frac{(c_{\mathrm{V}}/c_{\mathrm{P}})-1}{c_{\mathrm{V}}/c_{\mathrm{P}}}\cdot\frac{\rho\Lambda_0\bar{c}_{\mathrm{S}}^3}{\gamma_{\mathrm{G}}^2 T}\bigg|_{T\approx T_{\mathrm{M}}}. \end{aligned} \tag{24}$$

From the Slack expressions, one can concludes that

$$K_{\mathrm{Class}} = K_{\mathrm{Class}}^{(0)}\left(\frac{T_{\mathrm{M}}}{T_{\mathrm{M}}^{(0)}}\right)^{1/2}\left(\frac{\bar{a}}{a_0}\right)\left(\frac{\bar{a}}{c}\right)^3\frac{q}{q_{(0)}}, \tag{25}$$

where index '0' is to refer to the uranium dioxide (for instance) and other values are as follows: $\bar{a}$ is the cell average lattice parameter: $\bar{a} = V_{\mathrm{cell}}^{1/3}$; c is the largest lattice parameter; other definitions as above; since the adiabatic compressibility modulus $B_{\mathrm{S}} \sim c^{-4}$ [10], $\Lambda_0 \sim \bar{a}$, and $\bar{c}_{\mathrm{S}}^3 \propto \theta_{\mathrm{D}}^3 \propto T_{\mathrm{M}}^{3/2}$ due to the Lindemann's criteria [6]; q is the number of atoms in the chemical formula of solid.

The adiabatic sound wave velocity (c_{S}) for many solids can be calculated quite accurately based on stiffness constants, however, as the first estimate it can be also correlated to the classical Debye limit by using the equivalent definitions given by Eqs. (10) and (11) as above.

Thus, the main model parameters are as follows: melting temperature, lattice constants of oxides; theoretical density (TD), thermal expansion coefficient and Poisson ratio. In all model calculations below these parameters, except Poisson ratio, for oxides of our interest have been taken following recommendations by Mignanelli and Thetford [16]. Macro-porosity (P) effect on the lattice thermal conductivity, i.e. F_P function of the basic model equation (12) is accounted by using the simplest Halden reactor project (HRP) recommendation [12]:

$$F_P = (1-P)^{1.8}.$$

Thermal expansion of the actinide oxides can be also correlated with the melting temperature and basic lattice constants, i.e. calculated from the first principles. However, for simplicity, the experimental measurements for actinide oxides reported by Yamashita et al. [17] are optionally used in the model. The thermal expansion for mixed actinide oxides are then calculated with Vegard's law, using the experimental values for simple oxides.

6. Comparison with available experimental results

A first validation of the developed model has been made with the experimental results on thermal conductivity of the uranium dioxide with 95% of TD, which are contained in the HRP database partially published in [12]. Fig. 1 shows a rather good agreement between the model predictions and the recommended values for thermal conductivity of the fresh and of irradiated UO_2 up to burnup levels of 60 MWd/kgHM.

The degradation effect in these calculations was simulated using the assumption that a total volumetric solid swelling rate of UO_2 fuel is of 0.75% per 1 at.% burnup, which was reported by Schrire [14]. This value was used in calculations as a fixed input parameter.

The next two runs of the validation calculations have been made with the experimental data on the thermal conductivity of uraniam–gadolinium fuel. Fig. 2 shows a comparison of the model predictions with the HRP data [12] for the non-irradiated uranium dioxide with gadolinium additions. It was assumed in the model calculations that uranium–gadolinium mixed oxide forms the ideal homogeneous solution. The observed effect of the gadolinium addition on the lattice thermal conductivity was attributed to point defect scattering. The effect of burnup-induced degradation was calculated for this type of fuel with 4 and 8 wt% Gd and compared with the HRP recommendations in Fig. 3. One can see a rather good agreement.

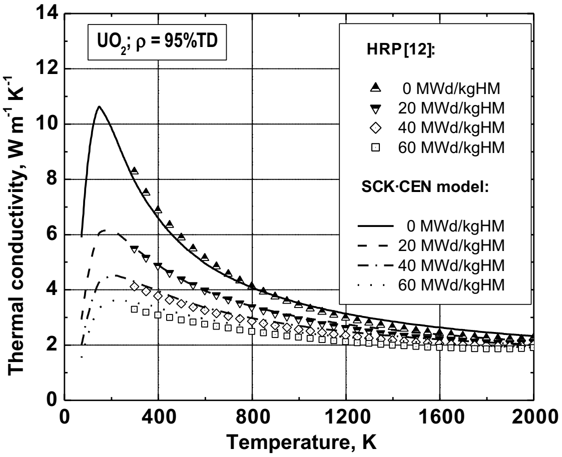

Fig. 1. Thermal conductivity of UO_2: comparison between the SCK · CEN model predictions and the HRP recommendations [12].

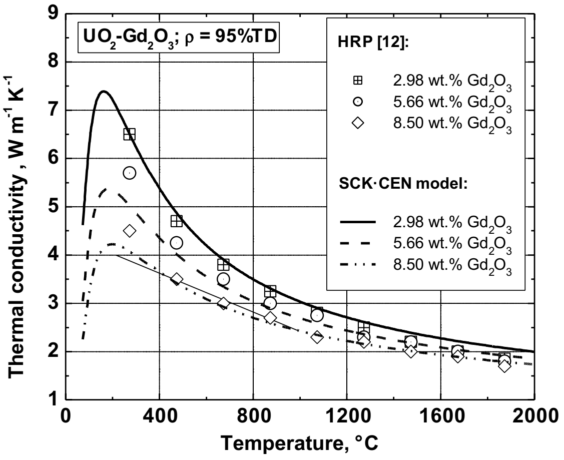

Fig. 2. Thermal conductivity of the fresh UO_2–Gd_2O_3 fuel: comparison between the SCK model predictions and the Lucuta's measurements [12].

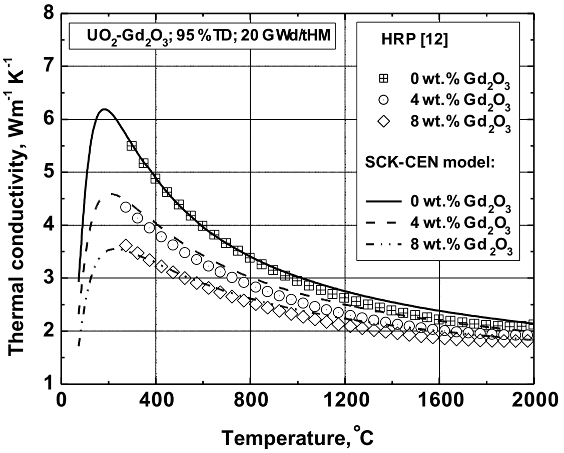

Fig. 3. Thermal conductivity of the UO_2–Gd_2O_3 fuel irradiated up to burnup of 20 GWd/tHM: comparison between the SCK · CEN model predictions and the HRP recommendations [12].

The model calculations for thoria fuel are plotted in Fig. 4, where the obtained data are compared with the results of measurements given in [11,18] normalised to 100% TD and with the averaged result of some earlier (except [11]) experimental data [19]. It can be seen that the model predictions are close to the results obtained recently (in 2000) by Pillai and Raj [18] and 10–20% lower than the results of Belle and Berman [11] published 16 years earlier. The recommendations of Bakker et al. [19] are close to [11] at low temperatures and to [18]

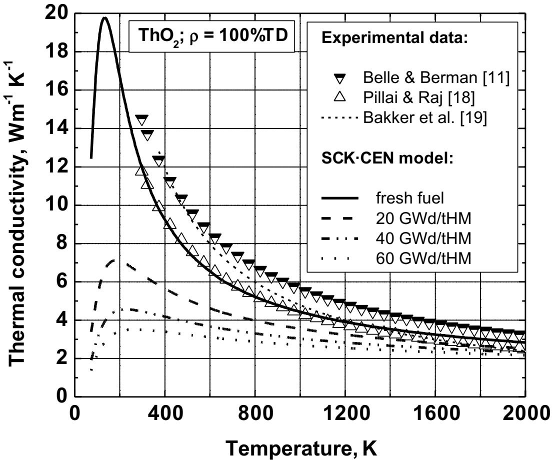

Fig. 4. Thermal conductivity of ThO$_2$: comparison between the SCK · CEN model predictions and the experimental results of [11,18,19].

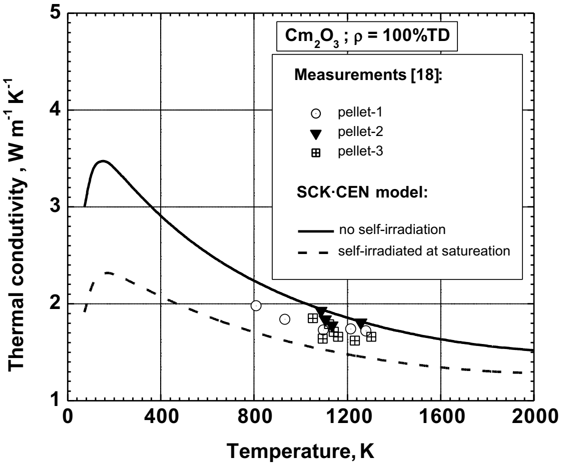

Fig. 5. Thermal conductivity of curium sesquioxide: comparison between the SCK · CEN model predictions and the experimental results of [20].

at high temperatures. Supplementary analysis and more data are needed to understand these results.

7. Self-irradiation effects in curium and americium oxides

Thermo-chemical and thermo-physical properties of curium and its oxides have been studied by Ketchen [20] and Gibby et al. [21], who measured, in particular, the thermal conductivity. Extensive analysis of these experimental results has been made by Konings [22]. Based on arguments given by Konings, the experimental data of Ketchen have been selected for the verification calculations with the developed model.

It is well known, that radiation damage caused of alpha-decay can reduce significantly the thermal conductivity of curium oxides, mainly due to production of point defects. These defects can be partially 'removed' from the atomic scale by annealing at high temperatures. In the case of curium oxides, the temperature during annealing should not exceed the level where phase transformation (monoclinic B–Cm$_2$O$_3$ $\overset{1888\text{ K}}{\leftrightarrow}$ hexagonal A–Cm$_2$O$_3$) may occur with considerable changes in lattice constants [20,22]. Ketchen [20] made the measurements in the temperature range of 773–1373 K with the samples annealed at ~1470 K, i.e. well below the phase transformation mentioned above. However, the annealing temperature is still too low to enable a complete recombination of the self-irradiation induced vacancies and interstitials. Moreover, the time scale of self-irradiation in curium is very short.

Two cases of the model calculations for the Cm$_2$O$_3$ thermal conductivity normalised to 100% TD are presented on Fig. 5: for the pure monoclinic lattice structure and for that self-irradiated at saturation. In the last case, the relative change of the lattice constant $\Delta a/a \approx 3.5 \times 10^{-3}$ was postulated in accordance with [20]. It also was taken into account that the experimental samples contained 2 wt% Pu and Am, and between 0.4 and 0.9 wt% Zr (average values were used in calculations). Comparison with the results of measurements of Ketchen [20] shows that all experimental points are situated well between the two extreme cases (see Fig. 5).

In the measurements of Gibby et al. [21] samples were heated during the annealing up to ~2270 K. At such temperatures the lattice primary defects can be annealed completely, but at the same time the phase transformations shall certainly cause mixing of different phases, if cooling is not slow enough and, consequently, may cause the considerable atomic scale disturbance of lattice, resulting in a decrease of the thermal conductivity. Indeed, the experimental values (normalised to 100% TD) are in the range of 1.53–1.65 W m^{-1} K^{-1} and show rather a plateau, typical for amorphous solids, than a hyperbolic temperature dependence. In addition, the heat capacity data, used in [21] for calculation of the thermal conductivity from the measured thermal diffusivity, are considered by Konings [22] to be too high. After the correction these results become for about 20% lower: 1.2–1.3 W m^{-1} K^{-1}. The corrected results are very close to the thermal conductivity classical limit (1.2 W m^{-1} K^{-1}) as calculated with the SCK·CEN model for monoclinic Cm$_2$O$_3$. By any reasons, a saturation of the samples by atomic scale crystal defects can be assumed. Since the details of measurements and annealing are missing in [21], it is difficult to assess quantitatively their results.

Thermal and chemical properties of americium oxides and some oxide mixtures have been recently reviewed and analyzed by Bakker and Konings [10] and also by Mignanelli and Thetford [16]. The thermal conductivity measurements of the freshly annealed americium dioxide and americium sesquioxide pellets at temperature 333 K have been reported by Schmidt [23] ($\lambda_{AmO_{2-x}} = 0.69\ \mathrm{W\,m^{-1}\,K^{-1}}$, $\lambda_{Am_2O_3} = 0.82\ \mathrm{W\,m^{-1}\,K^{-1}}$). Based on the analysis by Bakker and Konings [10], three americium oxides were selected for our model calculation: AmO_2 with cubic lattice, the lower limiting form $AmO_{1.62}$ with face-centered cubic lattice, and monoclinic B-Am_2O_3 sesquioxide. The results of these calculations are shown in Fig. 6. The calculations have been performed for two extreme cases: a non-disturbed lattice and that self-irradiated at saturation.

The thermal conductivity of americium oxides was predicted to be low even for 'fresh' dioxide because of low temperature phase transformations. The lowest thermal conductivity was predicted for the $AmO_{1.62}$. This is mainly due to the extremely high concentration of atomic scale point defects existing in the highly non-stoichiometric dioxide, which are the main source of the 'athermal' lattice resistivity. The slight increase of $\lambda_{AmO_{1.62}}$ with temperature above $T = 200$ K can be attributed to the dilatation effect (anharmonic contribution to heat capacity).

Next three plots (Figs. 7–9) show the predicted and measured thermal conductivity of some mixed oxides

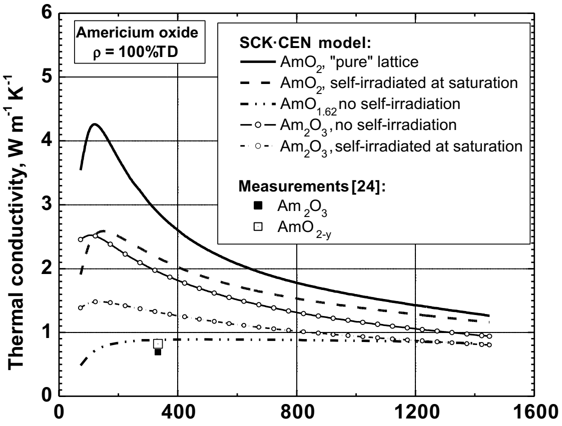

Fig. 6. Thermal conductivity of americium dioxide: comparison between the SCK · CEN model predictions and the experimental results of [23].

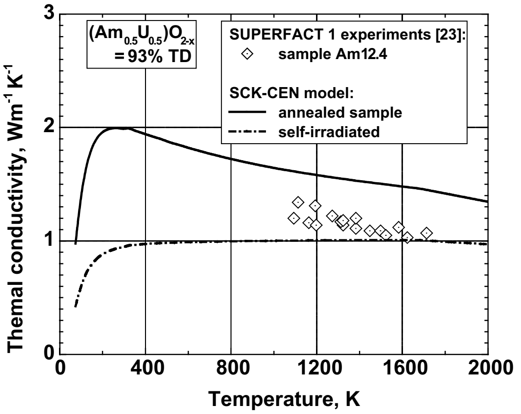

Fig. 8. Thermal conductivity of $(Am,U)O_{2-x}$: comparison between the SCK · CEN model predictions and the experimental results of [24].

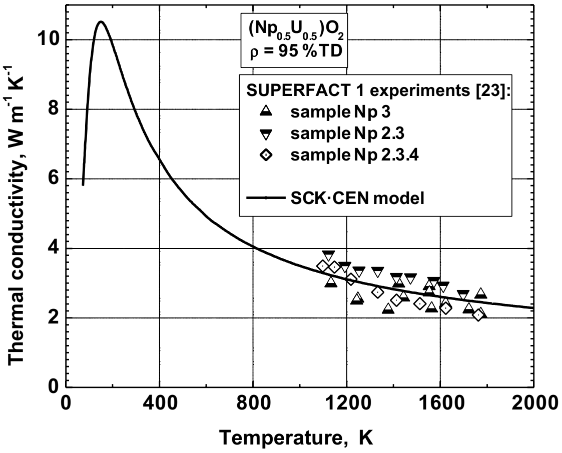

Fig. 7. Thermal conductivity of uranium–neptunium mixed oxide: comparison between the SCK · CEN model predictions and the experimental results of [24].

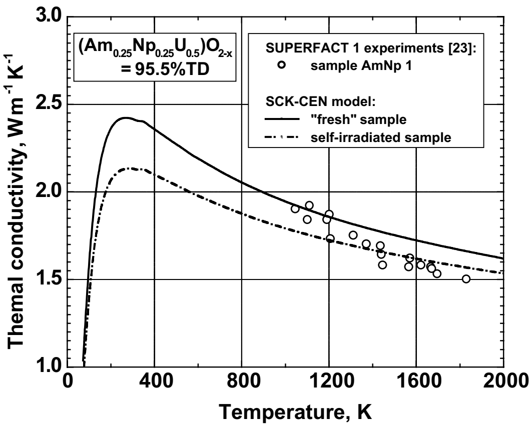

Fig. 9. Thermal conductivity of $(Am,Np,U)O_{2-x}$: comparison between the SCK · CEN model predictions and the experimental results of [24].

with a high content of neptunium and americium. The data from the joint CEA/ITU synthesis report on the SUPERFACT 1 experiments [24] were used in these calculations. A rather good agreement can be observed between the calculated and measured thermal conductivity of $(Np_{0.5},U_{0.5})U_2$ (Fig. 7). For the $(Am_{0.5}U_{0.5})O_2$ sample the experimental points are between two calculated extreme curves but closer to that corresponding to the suturated self-irradiation (Fig. 8). The experimental values for thermal conductivity of $(Am_{0.25}Np_{0.25}U_{0.5})O_2$ are dispersed around two calculated curves: a 'fresh' sample and a self-irradiated at saturation (Fig. 9). A tendency to a stronger temperature dependence for the measured thermal conductivity is observed. A significant fuel restructuring can be expected for americium containing samples. A more detailed analyses of the experiments and of the samples structure is needed for better understanding of the last results.

8. Conclusions

A model is present for the lattice thermal conductivity of pure and mixed oxides based on the Klemens–Callaway's approach for the dialectric heat conductance modelling and on some correlations between thermoelastic properties of solids. The model distinguishes between the effects of momentum conserving interactions such as N-processes, and non-conserving interactions such as U-processes and scattering by point defects. It was assumed that all phonon scattering processes can be represented by frequency-dependent relaxation times. A physical model to calculate the relaxation times for each process was developed. In view of the high temperatures observed in nuclear fuels, the Debye spectrum was applied to solve analytically the Callaway's equation for the lattice thermal conductivity.

The model has been tested by comparison with the results of in-pile and of out-of-pile measurements of thermal conductivity of UO_2, UO_2–Gd_2O_3 and ThO_2 fuels. The comparison of our model predictions with the experimental data was successful for all cases. Even the burnup-induced degradation effect, incorporated in the empirical formulations of thermal conductivity proposed by the Halden project, could be reproduced quite accurately with our physical model.

In addition the model has been successfully applied for thermal conductivity of the minor actinide oxides and their mixtures with urania, such as AmO_{2-x}, Am_2O_3, Cm_2O_3, $(Np,U)O_{2-x}$, $(Am,U)O_{2-x}$, $(Am,Np,U)O_{2-x}$, and the effect of self-irradiation on their thermal conductivity was estimated. Rather satisfactory agreement was obtained with the existing limited experimental data. Given the general approach used in the model, it can also be applied to other types of ceramic fuels, including inert matrix and nitride fuels.

Acknowledgements

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