NEW METHODS OF TREATMENT AND PRODUCTION OF MATERIALS WITH REQUIRED PROPERTIES

A Model of Uranium Dioxide Thermal Conductivity

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Abstract—Existing models for calculation of thermal conductivity of uranium dioxide are analyzed. Anomalous growth of the thermal conductivity coefficient of nuclear fuel in the high-temperature region is explained. Models of specific heat at constant volume and thermal conductivity are proposed. It is demonstrated that the contribution of degrees of freedom of charge carriers to the observed thermal conductivity coefficient of admixture-free stoichiometric UO_2 can be neglected up to the melting point.

Keywords: uranium dioxide, phonon spectrum, electron contribution to thermal conductivity, thermal conductivity coefficient, thermal diffusivity

INTRODUCTION

Most phenomena taking place with oxide nuclear fuel under irradiation (swelling, fission gas release, radiation induced densification, etc.), together with irradiation, are determined by its temperature. The temperature distribution in the pellet is a calculated quantity. The temperature difference between the center and the surface is determined by the thermal conductivity coefficient. In spite of a large number of publications concerning thermal conductivity of oxide nuclear fuel and its dependence from burnable neutron absorbers, initial density (porosity), degree of deviation from uranium dioxide stoichiometry, and degree of burnup, there exist a small number of studies containing the results of measurements of this quantity. In surveyes [1,3] the approximate formulas usually contain the parameters fitted to the experimental points by means of least squares method.

Traditionally, the uranium dioxide thermal conductivity is expressed in the following form [4–7]:

$$\lambda(T) = \frac{1}{A + BT} + \frac{C}{T^x}\exp\left(-\frac{D}{T}\right), \qquad (1)$$

where $x \approx 2$. The first term is connected with the phonon contribution to thermal conductivity, and the second term involves the contribution of electrons and holes in the conduction band and valence band, respectively. It is assumed that the phonon contribution to thermal conductivity of uranium dioxide describes well this thermophysical quantity in the temperature range $298 < T < 1300$ K, while the term describing the contribution of electrons and holes to the heat transfer should be taken into account in the range of higher temperatures $1300 < T < 3100$ K.

The coefficients A, B, C, and D in formula (1) are the fitting parameters whose values are given in [1–3]. The parameters A and B, however, have a physical interpretation. For temperatures satisfying the inequality $k_B T \gg \hbar\omega_{max}$, most phonons in the spectrum of normal modes of the dielectric have the energy $\hbar\omega \approx \hbar\omega_{max}$. The average number of phonons in states with the frequency $\sim\omega_{max}$ increases linearly with temperature. In this limiting case, it follows from the solution of the linearized Boltzmann equation for the phonon distribution function in a solid [8, 9] that the thermal conductivity linearly decreases with temperature,

$$\lambda(T \gg \hbar\omega_{max}/k_B) \sim \frac{1}{BT}. \qquad (2)$$

Concerning the coefficient B, studies [8, 9] devoted to investigation of thermal conductivity of solids give a parametric estimate to a constant factor obtained for a crystal with a monatomic unit cell.

In [9], the coefficient B was calculated for the case of a face-centered cubic lattice in the Debye approximation,

$$\lambda(T > \theta_D) \approx \lambda_0 \frac{\theta_D}{T}, \qquad (3)$$

where $\lambda_0 = 5 \times 10^{-8}\ \bar{A}a\theta_D^2/\gamma^2$ W/(m K), θ_D is the Debye temperature, γ is the Grüneisen constant, $\bar{A}$ is the average atomic weight in the unit cell, and a is the lattice constant.

Let us not that the Debye approximation does not statisfactorily describe the real ionic or covalent crystals in which optical branches of the phonon spectrum can be excited even at room temperatures. Practically all theoretical estimates of the lattice thermal conduc-
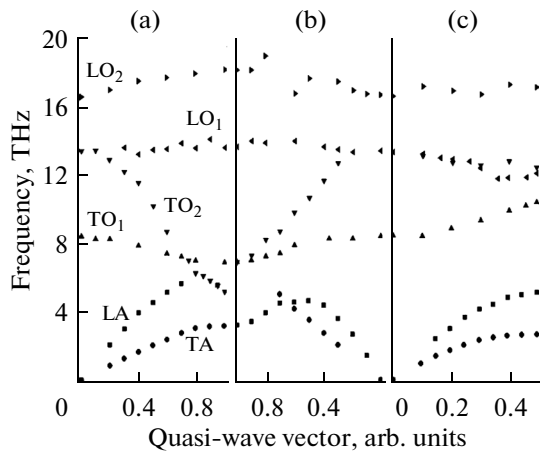
Fig. 1. Experimental phonon spectrum of uranium dioxide along three directions in the Brillouin zone [10]: (a) $\Gamma(0, 0, 0) \to X(0, 0, 1)$; (b) $M(1, 1, 0) \to \Gamma(0, 0, 0)$; and (c) $\Gamma(0, 0, 0) \to L(1/2, 1/2, 1/2)$. The x axis shows the coordinate along the straight line between two typical points of the Brillouin zone.

tivity coefficient use the approximation of a simple monatomic crystal whose oscillation spectrum contains only acoustic phonon branches. The maximum frequency in the spectrum of normal modes is close to the Debye one. The parameter θ_D in (3) occurs because of the approximation of a simple monatomic crystal. In real crystals, the temperature corresponding to the maximum frequency may differ from the Debye one by several hundred degrees, $\hbar\omega_{max}/k_B \gg \theta_D$.

Figure 1 shows the phonon spectrum of uranium dioxide [10] experimentally measured using the neutron scattering method. It can be seen that, at temperatures above 300 K, optical branches are excited in the spectrum of normal modes of the UO_2 crystal, but the temperature corresponding to the maximum longitudinal optical frequency is ~900 K. Therefore, it can be expected that, at $T > 900$ K, the behavior of uranium dioxide thermal conductivity is Debye-like.

For these reasons, the calculation of the coefficient B in formula (3) for dielectrics and semiconductors does not provide agreement with experimental data on thermal conductivity. The values of this coefficient for a particular substance can be determined only by fitting using the least squares method.

The constant A in the expression for thermal resistance W is usually connected with the processes of scattering of thermal phonons on isotopes and admixtures,

$$W = \frac{1}{\lambda} = W_I + W_U = A + BT, \qquad (4)$$

where $W_I = A$ is extrinsic thermal resistance in high temperature range, and W_U is the thermal resistance determined by the Umklapp processes (U processes).

The constant contribution to the thermal resistance at temperatures $T \gg \hbar\omega_{max}/k_B$ was first obtained

in [11] in the Debye approximation for a monatomic crystal,

$$W_I = \frac{\pi}{6} \frac{\Omega\Gamma}{c^2} \frac{\theta_D}{\hbar}, \qquad (5)$$

where Ω is the atomic volume, c is the average Debye speed of sound, $\Gamma \equiv f\Delta m/m$, f is the fraction of isotopes in the solid, and $\Delta m/m$ is the mass defect for isotopes. If the solid contains several isotopes of the same element, the value of Γ is equal to the sum of contributions from each group of isotopes.

The approximate mean free path in the form of the product of the relaxation time τ_k and the phonon group velocity with the quasi-wave vector k,

$$L_{\vec{k}} = \left| \frac{\partial\omega_k}{\partial\vec{k}} \right| \tau_{\vec{k}}, \qquad (6)$$

was used for determination of extrinsic thermal resistance in [11].

However, the τ approximation is inapplicable for description of phonon collision processes. It is known [12] that, for normal processes (N processes), the exact solution to the Boltzmann collision equation can be chosen in the form

$$N_{\vec{k}, s}(T) = \left[\exp\left(-\frac{\hbar\omega_s(\vec{k}) - \vec{k}\vec{v}}{k_B T} \right) - 1 \right]^{-1}, \qquad (7)$$

where $\omega_s(\vec{k})$ is the phonon branch of the spectrum and $N_{\vec{k}, s}$ is the phonon distribution function.

Distribution function (7) results in the zero collision integral [12], that formally means a lack of thermal resistance. In this case, the thermal flux generated by the function of form (7) is nonzero, and therefore, the thermal conductivity for N processes is infinite. It was noted in [9] that, in the τ approximation, the collision integral for normal processes does not vanish, since formally in the approximation of the mean free path even N processes contribute to the thermal resistance. Thus, the application of the method [11] for derivation of the high-temperature part of the admixture thermal resistance is unfounded. Moreover, for most dielectrics, Debye law (2) is very well satisfied [9, 12], and the isotopic contribution to the thermal conductivity becomes considerable only in the low-temperature region, $0 < T \ll \hbar\omega_{max}/k_B$.

ELECTRON CONTRIBUTION TO THERMAL CONDUCTIVITY OF URANIUM DIOXIDE

The last term in formula (1) was derived in [4, 5, 7] on the basis of the Wiedemann−Franz law connecting the thermal conductivity of degenerated electron gas in metals and its conductivity. The Wiedemann−Franz law, however, is inapplicable for dielectrics and semiconductors, since the number of charge carriers in the conduction band and the valence band for them is

small, and the chemical potential of a metal differs from the chemical potential of a semiconductor and a dielectric [8]. Stoichiometric uranium dioxide is a typical dielectric. The band gap in UO_2 is large, $\varepsilon_G \approx 2.7-3$ eV [13]. The number of charge carriers (electrons and holes) in the conduction band and the valence band is exponentially small up to the melting point [14],

$$n(T) = \frac{2}{[2\pi\lambda^2(T)]^{3/2}} \exp\left(-\frac{\varepsilon_G}{2k_B T}\right), \qquad (8)$$

where $\lambda(T) \equiv \sqrt{\lambda_e \lambda_h}$, $\lambda_{e,h}(T) = \hbar/\sqrt{m^*_{e,h} k_B T}$ is the de Broglie wavelength of the electron (e) or hole (h) moving with thermal velocity, k_B is the Boltzmann constant, $m^*_{e,h}$ is the effective electron (hole) mass, and $\hbar$ is the Planck constant.

The effective electron mass in the conduction band is usually smaller than or equal to the electron mass, $m^*_e \leq m_0$, and the effective hole mass is smaller than m_0 by at least a factor of two; therefore, the de Broglie wavelength in the temperature range $1000 < T < 3100$ K varies within $0.5 < \lambda < 0.9$ nm, and the number of electrons (holes) in the conduction (valence) band is $4 \times 10^{12} < n < 3 \times 10^{18}$ cm^{-3}. Such concentration of charge carriers even at melting temperature is by four orders of magnitude smaller than the number of electrons in conducting band of metal.

In the temperature range $100 < T < 3100$ K all optical branches of the phonon spectrum are excited. Therefore, electron scattering mainly takes place on optical oscillations (phonons). The electron mean free path determined by scattering on optical phonons is independent of temperature and can be estimated as [14]

$$\bar{l} = \frac{3}{2}\varepsilon\frac{m_0}{m^*_e}a_0, \qquad (9)$$

where $a_0 = 0.053$ nm is the Bohr radius and ε is the dielectric permittivity of UO_2. For uranium dioxide, the mean free path of the electron or hole is just several lattice constants.

The average number of electrons in the conduction band at any temperature is much smaller than the number of states therefore the electron velocity in the conduction band can be estimated in the classical way. If the bottom of the conduction band is taken as the zero energy of charge carriers, the average electron velocity in the band coincides with the thermal velocity $\bar{v}_{e,h} \simeq \sqrt{3k_B T/m^*_{e,h}}$.

The contribution to the specific heat from charge carriers is proportional to their number in the conduction band and the valence band. This yields that the ratio of the specific heat of the electron and hole subsystems of a dielectric to the lattice specific heat is a negligible quantity [14],
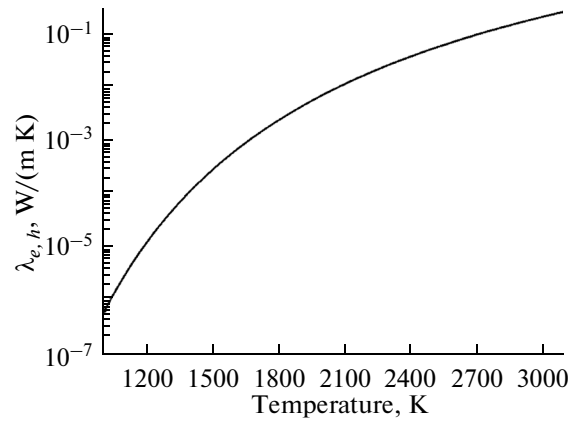

Fig. 2. Electron and hole thermal conductivity of stoichiometric uranium dioxide.

$$\frac{C_{e,h}}{9k_B n_0} = \frac{n(T)}{9n_0}$$
$$\times \left[\frac{15}{2} + 3\left(\frac{\varepsilon_G}{k_B T}\right) + \frac{1}{2}\left(\frac{\varepsilon_G}{k_B T}\right)^2\right] < \frac{1}{n_0\lambda^3(T)} \ll 1, \qquad (10)$$

where n_0 is the average atomic density of uranium dioxide.

Thus, the thermal conductivity of the electron and hole subsystems of a dielectric (or a pure semiconductor) in the high-temperature region can be estimated as

$$\lambda_{e,h} \approx \frac{1}{3}C_{e,h}\bar{l}\bar{v} \sim T^2 \exp\left(-\frac{\varepsilon_G}{2k_B T}\right). \qquad (11)$$

Figure 2 shows the thermal conductivity of the electron–hole subsystem for stoichiometric admixture-free UO_2 as a function of temperature calculated using (11) for $\varepsilon_G = 3$ eV and $\bar{l} = 2a$. It can be seen that, even in the vicinity of the melting point the electron–hole contribution to the thermal conductivity is ~0.2 W/(m K), while the experimental thermal conductivity at $T \approx 2800$ K is ~2 W/(m K). Since the experimental accuracy of the thermal conductivity measured using the laser flash method in the high-temperature region ($T > 1800$ K) is not lower than 10%. Therefore the contribution to the total thermal conductivity of pure uranium dioxide with stoichiometric composition from the electron and hole subsystems can be neglected.

EXPERIMENTAL DATA ON THERMAL CONDUCTIVITY COEFFICIENT FOR ADMIXTURE-FREE STOICHIOMETRIC UO_2

The thermal conductivity of uranium dioxide was experimentally measured, as a rule, using two techniques, the radial heat flow method [15] and the laser flash method (Parker's method) [16].
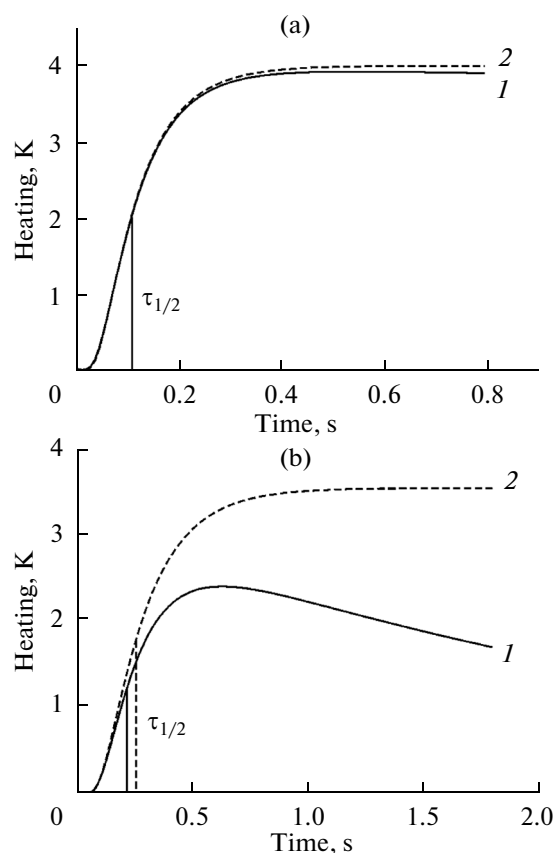
Fig. 3. Heating of uranium dioxide sample as a function of time [17] (*1*) with and (*2*) without allowance for infrared radiation at an initial temperature of (a) 600 and (b) 1500 K.

The radial heat flow method is a stationary measurement method. In this method the thermal conductivity coefficient is derived from the solution of the inverse problem of temperature distribution in a cylindrical sample with the generatrix length L. The axial heater situated at the center of the sample transmits the thermal power P to the sample [15],

$$\lambda(T_0) = \frac{P}{2\pi L(T_1 - T_2)} \ln\left(\frac{r_1}{r_2}\right), \qquad (12)$$

where T_1 and T_2 are the temperature values at the radial distances r_1 and r_2, respectively, measured by thermocouples, and T_0 is the temperature at the sample surface. The quantity $\lambda(T_0)$ formally represents the average thermal conductivity in the temperature range from T_0 to $T_0 + \Delta T$, where $\Delta T = P\Delta t/C_P$ is the maximum heating during the time Δt and C_P is UO_2 specific heat at constant pressure. It is assumed that thermal losses from the sample surface are absent. At temperatures above 1000 K, however, infrared (in vacuum) or convective (in a gaseous medium) thermal losses in the installation chamber containing the sample become considerable. Therefore, the temperature distribution along the sample cannot be considered stationary. In

these conditions, formula (12) is inapplicable, and the temperature distribution in the sample should be calculated on the basis of the solution of the nonstationary problem of heat conduction taking into account thermal losses to infrared radiation and convective flows. Therefore, usually the stationary heat flow method is used for measurement of the thermal conductivity of ceramics in the temperature range $300 < T_0 < 1600$ K.

The laser flash method (Parker's method) [16] is a nonstationary method. The essence of this method is as follows: the base of a cylindrical sample with the generatrix $L \sim d/10$ (d is the sample diameter) placed in technical vacuum at the initial temperature T_0 is irradiated by a laser pulse with the duration $\tau \sim 10^{-3}$ s. The width of the laser beam is equal to the base area $\pi d^2/4$ of the sample. The laser transmits the amount of heat $Q = 3-5$ J to the sample, and the pyrometer at the other base of the sample measures its temperature evolution.

In the absence of thermal losses, the time derivative of the heating curve of the sample at half maximum is proportional to the thermal diffusivity coefficient $k(T)$ of the investigated substance [16],

$$\frac{\Delta T_{\max}}{2\tau_{1/2}} = \frac{\partial T(L, \tau_{1/2})}{\partial t} = \frac{\Delta T_{\max}\pi^2 k(T_0)}{2KL^2}, \qquad (13)$$

where $\Delta T_{\max}$ is the maximum sample heating and $K = 1.37$ is the constant. The thermal diffusivity coefficient included in expression (13) on the basis of the laser flash method is determined from the relation [16]

$$k(T_0) = \frac{1.37L^2}{\pi^2\tau_{1/2}}. \qquad (14)$$

It follows that, in order to calculate the thermal diffusivity using the laser flash method, it is necessary to measure the value of $\tau_{1/2}$ at half maximum of the heating curve.

At high temperatures, infrared radiation from the sample surface results in reduction of maximum heating of the irradiated substance. Figure 3 shows the typical heating curves of uranium dioxide samples (dashed lines) measured using the laser flash method [17]. The solid lines in Fig. 3 correspond to the heating curves that would take place for the same initial temperatures T_0 in the absence of losses for "blackbody" radiation. The time $\tau_{1/2}$ at heating half maximum is also shown in this figure. It can be seen that, at 1500 K, thermal radiation results in an error in determining $\tau_{1/2}$ and, correspondingly, in overestimation of the thermal diffusivity of uranium dioxide calculated using (14). Therefore, the original Parker method yields an overestimated value of the thermal diffusivity coefficient [17].

Figure 4 shows the thermal conductivity coefficients of UO_2 pellets with a density of 94–95% of the theoretical density (TD) as functions of temperature reconstructed in [15, 18] using the radial thermal heat
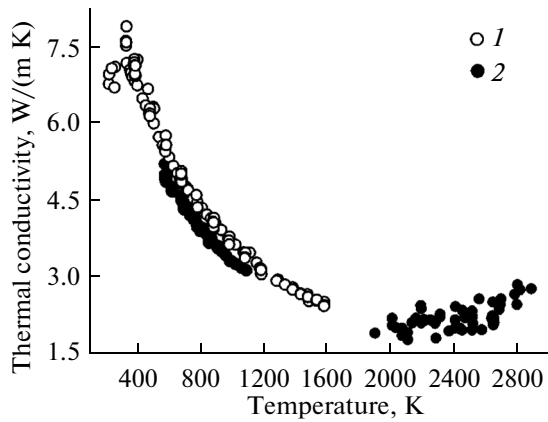
Fig. 4. Temperature dependence of thermal conductivity of uranium dioxide measured using (*1*) the radial heat flow method [15] and (*2*) the laser flash method [18]: (*1*) 94.3% TD, O/M = 2.01 ± 0.01; (*2*) 95% TD, O/M = 2.002 ± 0.002.
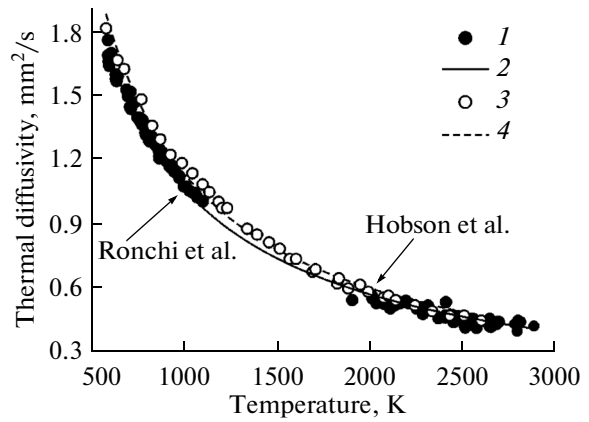
Fig. 5. Temperature dependence of thermal diffusivity of uranium dioxide and its approximation by a power function: (*1*) 95% TD, O/M = 2.002 ± 0.02; (*2*) $424.9 \times 10^{-6}/T^{0.869}$ [18]; (*3*) 94.89% TD, O/M = 2.001; and (*4*) $519.9 \times 10^{-6}/T^{0.889}$ [19].

flow method and the laser flash method. It can be seen that the values of the uranium dioxide thermal conductivity coefficients measured using different methods in the temperature range $T < 1200$ K are close and monotonically decrease with temperature. Moreover, the spread of experimental points for these temperatures is small. In the range $T > 1800$ K, however, anomalous growth of the thermal conductivity coefficient is observed which cannot be explained on the basis of the theory of lattice thermal conductivity or by the contribution to the thermal conductivity from degrees of freedom of charge carriers (electrons and holes).

It should be noted that such anomalous growth of thermal conductivity was experimentally observed in the laser flash method, where the thermal conductivity coefficient is not a directly measured quantity, but is calculated as the product of the specific heat of UO_2 and the thermal diffusivity coefficient (14).

Figure 5 shows the thermal diffusivity as a function of temperature $k(T)$ of uranium dioxide with the composition close to stoichiometric obtained using the laser flash method [19]. Points in Fig. 5 correspond to experimental data and curves correspond to its approximation by power function using the least squares method. It can be seen that, unlike $\lambda(T)$, the experimental thermal diffusivity coefficient $k(T)$ monotonically decreases with increasing temperature up to 2800 K without any anomalies. The thermal diffusivity as a function of temperature in the high-temperature region is well described by the Debye law $1/T^{0.9}$.

The thermal conductivity coefficient of UO_2 by definition is the product of the specific heat of uranium dioxide at constant volume $C_V(T)$, the density ρ, and the thermal diffusivity $k(T)$ [20],

$$\lambda(T) = C_V(T)\rho k(T); \qquad (15)$$

i.e., the thermal conductivity coefficient is a quantity defined at constant volume.

The equation of thermal balance in a dielectric is formulated for the thermal part of internal energy U in a unit volume,

$$\frac{1}{V}\frac{\partial U}{\partial t} = \nabla[\lambda(T)\nabla T]. \qquad (16)$$

Under quasi-equilibrium condition at constant volume, according to the second law of thermodynamics, the variation of internal energy coincides with the variation of the amount of heat,

$$(\Delta U)_V = (\Delta Q)_V. \qquad (17)$$

Substituting thermodynamic relation (17) into the energy conservation law results in the classical form of the thermal conductivity equation,

$$C_V\rho\frac{\partial T}{\partial t} = \nabla[\lambda(T)\nabla T], \quad C_V \equiv \frac{1}{\rho V}\left(\frac{\partial Q}{\partial T}\right)_V. \qquad (18)$$

Sometimes, when calculating the thermal conductivity coefficient using formula (15), the specific heat at constant pressure is used instead of the specific heat at constant volume. According to the second law of thermodynamics the system performs the work

$$(\Delta Q)_P = (\Delta U)_P + (\Delta A)_P. \qquad (19)$$

Substituting second law of thermodynamics (19) into kinetic equation (16) we obtain the thermal conductivity equation in the system at constant pressure:

$$C_P\rho\frac{\partial T}{\partial t} = \nabla[\lambda(T)\nabla T] + \frac{1}{V}\left(\frac{\partial A}{\partial t}\right)_P,$$

$$C_P \equiv \frac{1}{\rho V}\left(\frac{\partial Q}{\partial T}\right). \qquad (20)$$

It follows from conservation law (20) that at constant pressure the thermal conductivity equation contains an additional energy source connected with the

work performed by the system upon heating. The last term in the right-hand part of Eq. (20) can be represented as

$$
\frac{1}{V}\left(\frac{\partial A}{\partial t}\right)_P = P\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]\frac{\partial T}{\partial t} = \frac{3\alpha\gamma\Delta U}{V}\frac{\partial T}{\partial t}
$$
$$
= (3\alpha)^2 B_T\frac{\Delta U}{VC_V}\frac{\partial T}{\partial t} \approx (3\alpha)^2 B_T T\frac{\partial T}{\partial t}. \quad (21)
$$

The equation of state of a solid in the Grüeneisen form $PV = \gamma\Delta U$ and the thermodynamic relation $3\alpha B_T = \gamma C_V$ [8], where ΔU is the thermal part of internal energy, α is the coefficient of true linear thermal expansion, and B_T is the isothermal compression modulus were used for obtaining relation (21).

Thus, quantity (21) represents the work of anharmonic forces spent for thermal expansion of a solid. This work per unit time is proportional to the rate of change of temperature therefore term (21) can be combined with the left-hand part of Eq. (20),

$$
\left[C_P - \frac{(3\alpha)^2 B_T T}{\rho}\right]\rho\frac{\partial T}{\partial t}
$$
$$
= C_V\rho\frac{\partial T}{\partial t} = \nabla[\lambda(T)\nabla T]. \quad (22)
$$

The following Nernst−Lindemann relation [9] was used for writing equality (22):

$$
C_P - C_V = \frac{(3\alpha)^2 B_T T}{\rho}. \quad (23)
$$

Thus, even for a system at constant pressure taking into account the work of anharmonic forces on thermal expansion of the solid results in the classical equation of thermal conductivity in the solid.

Formally, replacing the heat capacity at constant volume by the heat capacity at constant pressure in formula (15) is equivalent to neglecting the work of anharmonic forces in heat conduction equation (20). The specific heat at constant volume for uranium dioxide at temperatures above 500 K reaches the Dulong−Petit limit $9R$ ($R = 8.31$ J/(mol K) is the universal gas constant). Therefore, according to definition (15) the thermal conductivity coefficient as a function of temperature at temperatures $T > 500$ K should have the same form as the thermal diffusivity as a function of temperature; i.e., the thermal conductivity of the purely stoichiometric uranium dioxide should be described by the Debye law $\lambda(T) \sim 1/T^{0.9}$.

The true linear thermal expansion coefficient (TLTEC), the isothermal compressibility modulus, and the lattice parameter of uranium dioxide weakly depend on temperature. The product of the anharmonic correction and the thermal diffusivity coefficient slowly grows with increasing temperature as

$$
\Delta\lambda = (C_P - C_V)\rho k(T) \sim [3\alpha(T)]^2 B_T(T)T^{0.1}. \quad (24)
$$

The contribution of this term to the thermal conductivity coefficient determines its anomalous nonphysical growth at high temperatures (Fig. 4).

MODEL OF UO_2 SPECIFIC HEAT AT CONSTANT VOLUME

To calculation of the thermal conductivity coefficient of uranium dioxide in a wide temperature range, it is necessary to know the temperature dependence of its specific heat. Note that specific heat at constant volume is a calculated quantity, since it is impossible to provide constant volume in an experiment because of the phenomenon of thermal expansion of solids under heating.

According to Fig. 1 the phonon spectrum of uranium dioxide contains nine branches (all transverse branches of the normal spectrum are twice degenerate); therefore, the number of vibrational degrees of freedom of unit cell for UO_2 is also equal to nine. The specific heat per one mole of uranium dioxide at constant volume by definition is [20]

$$
C_V(T) = 9R\frac{\partial}{\partial(k_B T)}\int_0^{\omega_{max}} d\omega D(\omega)\hbar\omega\bar{n}(\omega, T), \quad (25)
$$

where $\bar{n}(\omega, T) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose−Einstein distribution function for phonons, $D(\omega) = \frac{1}{9N_A}\sum_{s=1}^9\sum_{\vec{k}}\delta[\omega - \omega_s(\vec{k})]$ is the phonon density of states (DOS), $\omega_s(\vec{k})$ is the phonon frequency, index s denotes a phonon branch number, $\deg\{\vec{k}\} = N_A$, and N_A is the Avogadro constant. The plot of the function $D(\omega)$ obtained in an experiment on neutron scattering on a UO_2 crystal [10] is shown in Fig. 6.

It is convenient to derive the expression for the specific heat of uranium dioxide in the form of an analytical function of absolute temperature using a model DOS instead of the real DOS. This approach is founded since the specific heat is an integral quantity with respect to the phonon spectrum. The model phonon density of states should be normalized per unit,

$$
\int_0^{\omega_{max}} d\omega D(\omega) = 1 \quad (26)
$$

and possess characteristic frequencies equal to the characteristic frequencies of the experimental phonon spectrum.

The first and second peaks of the experimental DOS (Fig. 6) correspond to acoustic frequencies: twice degenerate transverse frequency ω_{TA} and longitudinal frequency ω_{LA}. The third and fourth peaks can be correlated with the frequencies $\omega_{TO1} > \omega_{TO2}$ of twice degenerate transverse optical branches (Fig. 1). The

remaining frequencies of longitudinal optical oscillations ω_{LO2} and ω_{LO1}, due to the closeness of their values, are indistinguishable on the plot.

To development of the numerical model of specific heat at constant volume of uranium dioxide, we take into account the contribution to the specific heat from acoustic branches within Debye model and the contribution of optical phonon branches within Einstein model [20].

In order to calculate the Debye frequency ω_D of uranium dioxide it is necessary to calculate longitudinal and transverse speeds of sound in UO_2. In [21] the approximating formulas for calculation of isotopic elastic moduli of oxide nuclear fuel at room temperature depending on the sample porosity P in the interval $0 < P < 0.1$ were proposed,

$$E = 220(1 - 1.45P)\ \text{GPa}, \qquad (27)$$

$$G = 84(1 - 2.25P)\ \text{GPa}. \qquad (28)$$

According to (27) and (28), the values of elastic moduli at 100% density of oxide nuclear fuel are equal to $E = 220$ GPa and $G = 84$ GPa. Then the isothermal compression modulus of uranium dioxide at 100% fuel density and a temperature of 25°C is equal to

$$B_T = \left[-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \right]^{-1} = \frac{EG}{9G - 3E} = 192.5\ \text{GPa}. \quad (29)$$

The longitudinal and transverse speeds of sound are related to the isotropic elastic moduli by the known relations [22]

$$c_l = \left(\frac{3B_T + 4G}{3\rho}\right)^{1/2} = 5271\ \text{m/s}, \qquad (30)$$

$$c_t = \left(\frac{(G/\rho)^{1/2}}{\rho}\right) = 2768\ \text{m/s}, \qquad (31)$$

where the density of the substance is taken to be equal to the theoretical density of uranium dioxide at room temperature $\rho = 10960$ kg/m^3.

The average speed of sound c according to the Debye model can be calculated using relation [8, 9, 20]

$$\frac{3}{c^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3}, \qquad (32)$$

which yields the average value of the speed of sound $c = 3096$ m/s. The Debye frequency represents the product of the average speed of sound and the Debye quasi-wave vector $k_D = [6\pi^2/\Omega]^{1/3} = 3.89/a$ ($\Omega = a^3$ is the volume of unit cell of uranium dioxide) and is equal to

$$\omega_D = ck_D = 2.20 \times 10^{13}\ \text{Hz}. \qquad (33)$$

The Debye temperature for UO_2 is equal to $\theta_D = \hbar\omega_D/k_B = 168$ K.

Since in the proposed model of specific heat of uranium dioxide the acoustic phonon branches are taken into account within the Debye model and the optical branches are taken into account within Einstein
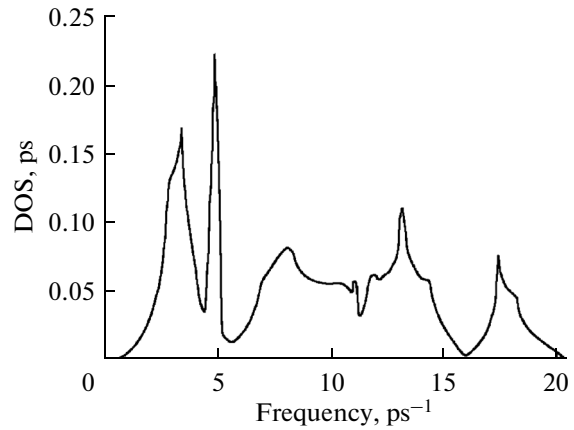

Fig. 6. DOS of UO_2 [10].

model. So, in this approximation the model DOS can be taken as the sum

$$D(\omega) = \frac{\omega^2}{\omega_D^3}\eta(\omega_D - \omega) + \frac{2}{9}\delta(\omega - \omega_{TO1})$$
$$+ \frac{2}{9}\delta(\omega - \omega_{TO2}) + \frac{2}{9}\delta(\omega - \omega_{LO2}), \qquad (34)$$

where $\eta(x)$ is the Heaviside function and $\delta(x)$ is the Dirac delta function. It is obvious that the model DOS satisfies condition (26).

The values of Einstein frequencies for optical branches of the spectrum of normal oscillations (Fig. 6) are given in Table 1.

Substituting DOS(34) into (25) we obtain the final formula for calculation of specific heat at constant volume $C_V(T)$ within the proposed model:

$$C_V(T) = 9R\left[4\left(\frac{T}{\theta_D}\right)^3 I_3\left(\frac{\theta_D}{T}\right) - \frac{\theta_D/T}{e^{\theta_D/T} - 1} \right.$$
$$\left. + \frac{2}{9}\sum_{i=1}^{3}\left(\frac{\theta_{Ei}}{T}\right)^2 \frac{e^{\theta_{Ei}/T}}{(e^{\theta_{Ei}/T} - 1)^2} \right], \qquad (35)$$

where $I_3(z) \equiv \int_0^z dx \frac{x^3}{e^x - 1}$ is is the third order Debye integral and θ_{Ei} are the characteristic Einstein temperatures of the phonon spectrum for UO_2. The values of the parameters in formula (35) are given in Table 2. It follows from this table that, even at room temperature, optical branches are excited in the spectrum of normal oscillations of uranium dioxide.

Experimental data describing the temperature dependence of specific heat at constant pressure for uranium dioxide [23–27] are shown in Fig. 7. This figure also shows model specific heat at constant volume (35). It can be seen that in the temperature range $35 < T < 199$ K the calculated specific heat at constant

Table 1. Characteristic phonon frequencies in formula (34)

ω_D, THz	ω_{TO1}, THz	ω_{TO2}, THz	ω_{LO2}, THz
22.0	51.1	82.3	109.0

Table 2. Characteristic temperatures in the expression for model specific heat of uranium dioxide (35)

| θ_D, K	θ_{E1}, K	θ_{E2}, K	θ_{E3}, K
168	391	629	836

volume practically coincides with the low-temperature part of specific heat at constant pressure C_P. It proves that the choice of the model DOS in form (34) is founded.

It should be noted that formula (35) for calculation of specific heat at constant volume is inapplicable in the vicinity of the Néel point and absolute zero since at $0 < T < 32$ K uranium dioxide is turned into the antiferromagnetic state in which the specific heat is defined mainly by degrees of freedom of antiferromagnetic magnons.

MODEL OF UO₂ THERMAL CONDUCTIVITY

In the core of WWER-type reactor, the working temperature interval for oxide nuclear fuel is much higher than the Debye temperature of uranium dioxide. In the range of high temperatures compared to θ_{E3} (Table 2) the thermal diffusivity of uranium dioxide satisfies the Debye law [8, 9],

$$k(T) = k(\theta_{E3})\left(\frac{\theta_{E3}}{T}\right)^{0.89}, \qquad (36)$$
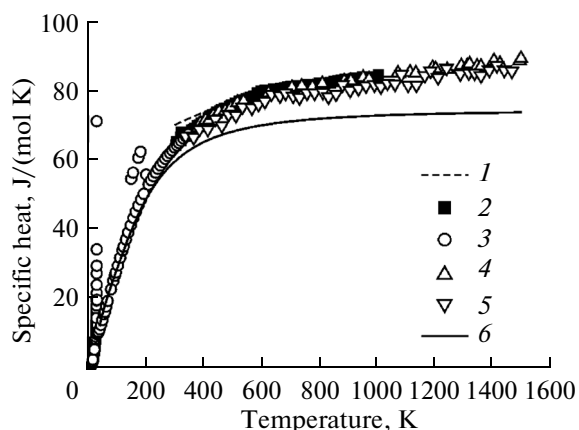
Fig. 7. Temperature dependences of specific heat C_P of UO₂: (*1*) [23], (*2*) [24], $x = 0.017$; (*3*) [25], $x = 0.002 \pm 0.001$; (*4*) [26], $x = 0.004$; (*5*) [27], $x = 0.00$; and (6) specific heat at constant volume C_V calculated using formula (35).

where $k(\theta_{E3}) = 1.3 \times 10^{-6}$ m²/s is the value of the thermal diffusivity coefficient at $T = \theta_{E3}$.

Let us use for calculation of thermal conductivity of UO₂ a model of specific heat at constant volume of UO₂ developed in this work.

$$
\lambda(T) = \frac{9\rho R}{M}\left[4\left(\frac{T}{\theta_D}\right)^3 I_3\left(\frac{\theta_D}{T}\right) - \frac{\theta_D/T}{e^{\theta_D/T}-1} \right.
$$
$$
\left. + \frac{2}{9}\sum_{i=1}^{3}\left(\frac{\theta_{Ei}}{T}\right)^2 \frac{e^{\theta_{Ei}/T}}{\left(e^{\theta_{Ei}/T}-1\right)^2}\right] k(\theta_{E3})\left(\frac{\theta_{E3}}{T}\right)^{0.89}, \qquad (37)
$$

where $M = 0.27$ kg/mol is the molar mass of uranium dioxide and ρ is its density.

The results of comparison of the temperature dependences of the thermal conductivity coefficients of UO₂ calculated using (37) and determined experimentally [15, 18] are shown in Fig. 8. It can be seen that, in the whole temperature range, the calculated dependence $\lambda(T)$ is close to the experimental points. Therefore it is reasonable to use semiempirical formula (37) for calculation of the thermal conductivity of oxide nuclear fuel in the whole temperature range $400 < T < 2800$ K.

In the case of nonstoichiometric uranium dioxide or UO₂ containing alloying dopants, burnable neutron absorbers and simulated fission products the mechanism of heat conduction of uranium dioxide changes. The distance between the dopant-induced state and the bottom of the conduction band is much smaller than the band gap. According to [13] in hyperstoichiometric uranium dioxide the energy gap between the top of the valence band and the energy level of oxygen interstitials—p-type impurity—is $|\varepsilon_G - \varepsilon_A| = 0.4$ eV, while in the case of uranium interstitials or oxygen vacancies—n-type impurity—the energy corresponding to the donor level is $\varepsilon_D = 0.9$ eV. Thus, in the high-temperature region nonstoichiometric uranium dioxide shows semiconductor properties and its contribution to thermal conductivity connected with the charge carriers becomes comparable with the lattice thermal conductivity. In this case, the number of charge carriers in the conduction band or the valence band is proportional to the square root of the number of donor or acceptor dopants $(n_{D,A})^{1/2}$ [14]. If alloying elements, Al, Cr, Gd, and Nb oxides are introduced into uranium dioxide, the number of either acceptor dopants (interstitial oxygen) or donor dopants (oxygen vacancies) increases depending on the ratio of the number of oxygen atoms (O) to the metal atoms (M) in the chemical formula of the metal oxide in the alloying dopants. If the ratio O/M in the chemical formula of the alloying dopant is less than 2 dissolution of such dopant in the UO₂ lattice increases the number of holes in the valence band and therefore the amount of oxygen interstitials. If the ratio O/M in the chemical formula of the dopant is larger than 2 the correspond-
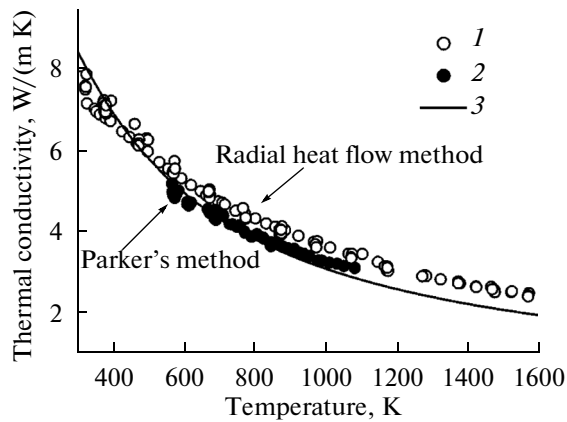
Fig. 8. Comparison of temperature dependences of calculated (using formula (19)) and experimental thermal conductivity coefficients of uranium dioxide: (*1*) 95% TD, O/M = 2.002 ± 0.002, measurement using Parker's (laser flash) method [15]; (*2*) 94.3%, O/M = 2.01 ± 0.01, measurement using the radial heat flow method [18]; (*3*) 94.89% TD, calculation, O/M = 2.00.

ing dopant in the uranium dioxide lattice is the source of additional electrons in the conduction band.

The thermal conductivity coefficient specified by the processes of phonon scattering on isolated point defects or isotopes is known [12] only for the case of their small concentration $n_{D,A}/n_0 \ll 1$, when the amplitude of phonon scattering on admixtures and isolated defects is much smaller than the average distance between them $(n_{D,A})^{1/3}$. Only in this case can phonon scattering on admixtures be considered coherent and the scattering probabilities be independent from each other. Therefore, the phonon part of the thermal conductivity coefficient for nonstoichiometric uranium or uranium with alloying dopants is at present unsubstantiated.

CONCLUSIONS

A model of specific heat of uranium dioxide at constant volume C_V describing both the experimental data on specific heat of UO_2 at constant pressure C_P in the low-temperature region and the limiting transition $C_V = 9R$ in the high-temperature region (the Dulong–Petit limit) was proposed.

It was established that the contribution of electron and hole thermal conductivity of pure (admixture-free) uranium dioxide with stoichiometric composition in the whole temperature range up to the melting point is negligible as compared to the lattice thermal conductivity coefficient.

It was demonstrated that the thermal conductivity of uranium dioxide follows the Debye law. The contribution to the resulting thermal conductivity of UO_2 in the high-temperature region $T > 900$ K due to phonon scattering on admixtures and isotopes can be neglected.

The anomalous growth of the thermal conductivity coefficient of uranium dioxide in the high-temperature region $T > 1800$ K is the systematic error caused by neglecting of the work of anharmonic forces upon thermal expansion of a solid during analysis of measurement results of UO_2 thermal conductivity using Parker's method.

REFERENCES

1. Martin, D.G., A re-appraisal of the thermal conductivity of UO₂ and mixed (U, Pu) oxide fuels, *J. Nucl. Mater.,* 1982, vol. 110, pp. 73–94.
2. Carbajo, J.J., Yoder, G.L., Popov, S.G., and Ivanov, V.K., A review of thermophysical properties of MOX and UO₂ fuels, *J. Nucl. Mater.*, 2001, vol. 299, pp. 181–198.
3. Brandt, R. and Neuer, G., Thermal conductivity and thermal radiation properties of UO₂, *J. Non-Equilib. Thermodyn.,* 1976, vol. 1, pp. 3–23.
4. Hyland, G.H., Thermal conductivity of solid UO₂: Critique and recommendation, *J. Nucl. Mater.*, 1983, vol. 113, pp. 125–132.
5. Harding, J.H. and Martin, D.G., A recommendation for the thermal conductivity of UO₂, *J. Nucl. Mater.*, 1989, vol. 166, pp. 223–226.
6. Fink, J.K., Thermophysical properties of uranium dioxide, *J. Nucl. Mater.*, 2000, vol. 279, pp. 1–18.
7. Lucuta, P.G., Matzke, Hj., and Verral, R.A., Modelling of UO₂–based SIMFUEL thermal conductivity. The effect of burnup, *J. Nucl. Mater.*, 1994, vol. 217, pp. 279–286.
8. Ashcroft, N.W. and Mermin, N.D., *Solid State Physics* Harcourt College, 1976.
9. Ziman, J.M., *Electrons and Phonons: The Theory of Transport Phenomena in Solids*, Oxford: University Press, 2001.
10. Dolling, G., Cowley, R.A., and Woods, A.D.B., The crystal dynamics of uranium dioxide, *Can. J. Phys.*, 1965, vol. 43, pp. 1397–1413.
11. Ambegaokar, V., Thermal resistance due to isotopes at high temperatures, *Phys. Rev.*, 1959, vol. 114, no. 2, pp. 488–489.
12. Lifshitz, E.M. and Pitaevskii, L.P., *Fizicheskaya Kinetika* (Physical Kinetics, Vol. 10 of Theor. Phys. Course), Moscow, FizMatLit, 2007.
13. Willardson, R.K., Moody, J.W., and Goering, H.L., The electrical properties of uranium oxide, *J. Inorg. Nucl. Chem.*, 1958, vol. 6, pp. 19–33.
14. Anselm, A.I., *Introduction to Semiconductor Theory* Prentice Hall, 1982.
15. Godfrey, T.G., Fulkerson, W., Kollie, T.G., Moore, J.P., and McElroy, D.L., Thermal conductivity of uranium dioxide from −57°C to 1100°C by a dadial heat flow technique, *J. Amer. Ceram. Soc.*, 1965, vol. 48, pp. 297–305.
16. Parker, W.J., Jenkins, R.J., Butler, C.P., and Abott, G.L., Flash method of determing thermal diffusivity, heat capacity and thermal conductivity, *J. Appl. Phys.*, 1961, vol. 32, pp. 1679–1684.
17. Baranov, V.G., Devyatko, Yu.N., Tenishev, A.V., Khlunov, A.V., and Khomyakov, O.V., New method for

determining the temperature dependence of the thermal conductivity coefficient of dielectrics, *Inorg. Mater.: Appl. Res.*, 2010, vol. 1, pp. 167−173.

18. Ronchi, C., Sheindlin, M., Musella, M., and Hyland, G.J., Thermal conductivity of uranium dioxide up to 2900 K simultaneous measurement of heat capacity and thermal diffusivity, *J. Appl. Phys.*, 1999, vol. 85, pp. 776−789.

19. Hobson, I.C., Taylor, R., and Ainscough, J.B., Effect of porosity and stoichiometry on the thermal conductivity of uranium dioxide, *J. Phys. D: Appl. Phys*, 1974, vol. 7, pp. 1003−1016.

20. Landau, L.D. and Lifshitz, E.M., *Statisticheskaya Fizika* (Statistical Physics. Vol. 5 of the Theoretical Physics Course), Moscow, FizMatLit, 2012.

21. Roque, V., Cros, B., Baron, D., and Dehaudt, P., Effects of the porosity in uranium dioxide on microacoustic and elastic propertie, *J. Nucl. Mater.*, 2000, vol. 277, pp. 211−216.

22. Landau, L.D. and Lifshitz, E.M., *Teoriya uprugosti* (Theory of Elasticity. Vol. 7 of Theoretical Physics Course) Butterworth−Heinemann, 1986, 3rd ed.; Moscow, FizMatLit, 2001.

23. Engel, T.K., The heat capacities of Al_2O_3, UO_2 and PuO_2 from 300 to 1100 K, *J. Nucl. Mater.*, 1969, vol. 31, pp. 211−214.

24. Gronvold, F., Kveseth, N.J., Sven, A., et al., Thermodynamics of $UO_{(2+x)}$ phase. 1. Heat capacities of $UO_{2.017}$ and $UO_{2.524}$ from 300 to 1000 K and electronic contributions, *J. Chem. Thermodyn.*, 1970, vol. 2, pp. 665−679.

25. Huntzicker, J.J. and Westrum, E.F., The magnetic transition, heat capacity, and thermodynamic properties of uranium dioxide from 5 to 350 K, *J. Chem. Thermodyn.*, 1971, vol. 3, pp. 61−76.

26. Inaba, H., Naito, K., and Oguma, M., Heat capacity measurement of $U_{(1-y)}Gd_yO_2$ (0.00 < y < 0.142) from 310 to 1500 K, *J. Nucl. Mater.*, 1987, vol. 149, pp. 341−348.

27. Takahashi, Y. and Asou, M., High-temperature heat-capacity measurement on $(U, Gd)O_2$ by drop calorimetry and DSC, *J. Nucl. Mater.*, 1993, vol. 201, pp. 108−114.

Translated by E. Baldina