KfK 2653
Dezember 1979

On the Determination of the Optical Constants and Radiative Heat Conductivity from Reflection Experiments on Nuclear Fuel Materials in the Liquid Phase up to above 4000 K

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ISSN 0303-4003

Abstract

The report deals with the following questions:

1) Study of the optical constants $n_\lambda(T)$, $k_\lambda(T)$ and of the radiative heat conductivity $\kappa_{rad}(T)$ of liquid nuclear fuel in the light of the problems of radiative heat conduction and heat transfer in reactor safety analysis.

2) Study of the optical constants in relation to the questions of the physical structure and chemical bonding character of nuclear fuel materials in the solid and liquid state.

3) Measuring methods for the determination of the optical constants of opaque non-scattering materials at elevated temperatures.

4) High-temperature measuring technique for determining $n_\lambda(T)$, $k_\lambda(T)$, $\kappa_{rad}(T)$ of nuclear fuel materials up to above 4000 K from reflection measurements using a special integrating-sphere laser reflectometer.

Methode zur Bestimmung der optischen Konstanten und der Strahlungswärmeleitung von Kernbrennstoffen im flüssigen Zustand bis über 4000 K mittels Reflexionsmessungen

Kurzfassung

Der Bericht macht Aussagen zu folgenden Fragen:

1) Relevanz der optischen Konstanten $n_\lambda, k_\lambda(T)$ und der Strahlungswärmeleitung $\kappa_{rad}(T)$ von flüssigem Kernbrennstoff in Reaktorsicherheitsproblemen (Strahlungswärmetransport und Wärmeübergangsfragen).

2) Untersuchung der optischen Konstanten in Bezug auf die Festkörperstruktur und den chemischen Bindungscharakter der Kernbrennstoffmaterialien im festen und flüssigen Zustand.

3) Meßmethoden zur Bestimmung der optischen Konstanten von opaken nicht-streuenden Stoffen bei höheren Temperaturen.

4) Hochtemperatur-Meßtechnik zur Bestimmung von $n_\lambda, k_\lambda(T)$ und $\kappa_{rad}(T)$ von Kernbrennstoffmaterialien bis über 4000 K durch Reflexionsmessungen mit einem Laser-Kugelreflektometer.

1. Study of the Optical Constants $n_\lambda(T)$, $k_\lambda(T)$ and of the Radiative Heat Conductivity $\kappa_{rad}(T)$ of Liquid Nuclear Fuel in the Light of the Problems of Radiative Heat Conduction and Heat Transfer in Reactor Safety Analysis

The major thermophysical properties of a nuclear fuel include its thermal conductivity κ. Regarding the normal fuel element operating range it is important to know the temperature dependence of $\kappa(T)$ for the solid phase of the fuel. Besides, the reactor safety analysis calls for the knowledge of $\kappa(T)$ of the liquid phase up to sufficiently high temperatures. The thermal conductivity of the fuel must be known the more reliably the smaller κ is for the respective material and the more dependent κ is, respectively, on the temperature, structure, stoichiometry, purity, and burnup of the fuel.

The oxide fuels and the advanced ceramic fuels (carbide, etc.) are characterized by a complicated and, to-date, partly unsafe $\kappa(T)$ plot in the temperature range $\gtrsim$ 2000 K. The state of knowledge concerning the heat conduction mechanisms of these materials at temperatures beyond 2000K is still unsatisfactory and partly marked by contradictions. This applies even more to the liquid phases of ceramic nuclear fuel materials [1,2,3].

Above all it has not been clearly elucidated so far whether and to which extent the thermal radiation transport contributes to the heat conduction of the ceramic fuels at high temperatures ($\gtrsim$ 2000). This question is absolutely open as regards the liquid phase of oxide and carbide fuels, which, however, has to be answered for reactor safety analysis [1]. This seems to be possible only by experimental determination of the optical transmittance and the spectral radiation absorption, respectively, of the nuclear fuels at temperatures extending far into the liquid range ($\lesssim$ 4000K). The optical material constant characteristic of this situation is the spectral absorption constant (and extinction constant, respectively) K_λ and the spectral absorption coefficient k_λ, respectively. The latter coefficient is the imaginary part of the complex (usually temperature dependent) refraction index N_λ of the material.+)

$$N_\lambda = n_\lambda - ik_\lambda \qquad (1)$$

The absorption constant $K_\lambda(T)$ is directly related to k_λ by:

$$K_\lambda (T) = 4\pi\, k_\lambda(T)/\lambda \qquad (2)$$

The ultimately sought and wavelength dependent mean free path of thermal radiation in the nuclear fuel under consideration is

$$\ell_\lambda (T) = 1/K_\lambda(T) \qquad (3)$$

The range of wavelengths of interest extends from ultraviolet (~0.3 μm) to the far infrared (≳5 μm). (Complications related to the scattering of radiation in polycrystalline material in the solid phase will be left out of consideration here).

Another thermophysical problem in reactor safety analysis concerns the radiative heat transfer between two different condensed material phases. This actually involves the heat transfer from liquid nuclear fuel in direct contact with (liquid) steel or sodium at a lower temperature [4,5]. As long as there is no vapor layer between the two condensed material phases, the thermal radiation transfer is not governed by the total emittance $\varepsilon_\lambda(T)$ of the hotter material and by the total absorption $\alpha_\lambda(T)$, respectively, of the colder material. The transmission of heat radiation through the phase boundary is rather determined by the Beer reflection law, provided that the contacting materials are strong absorbers optically, which is generally the case:

$$R_\lambda = \left(\frac{N_\lambda^{12} - 1}{N^{12} + 1}\right)^2 \quad \text{with } N_\lambda^{12} = N_\lambda^{2}(T_2)/N_\lambda^{1}(T_1) \qquad (4)$$

+) The radiative conductivity $\kappa_{rad}(T)$ can be calculated from the spectral plot of $k_\lambda(T)$ by use of Rossland's diffusion approximation (Sect. 4.).

where $N_\lambda^1(T_1) = n_\lambda^1(T_1) - ik_\lambda^1(T_1)$ is the complex refraction index of the hotter material having the temperature T_1. A similar relation applies to the refraction index $N_\lambda^2(T_2)$ of the colder material having the temperature T_2.

So, the solution of this radiation-heat transfer problem calls for the knowledge of both the absorption coefficient k_λ and of the real refraction index n_λ of these materials which are normally dependent on the temperature.+) The thermal radiation spectral range again extends from the ultraviolet (0.3 μm) to the middle infrared region (~ 3 μm).

The significance in other respects of the optical constants n_λ, k_λ of the oxide and carbide fuels as well as possible measuring methods allowing to determine them will be discussed in the following sections.

2. Study of the Optical Constants $n_\lambda(T)$, $k_\lambda(T)$ in Relation to the Questions of the Physical Structure and the Chemical Bonding Character of Nuclear Fuel Materials in the Solid and Liquid State

In Section 1 (and in the following Section 3) the optical "constants" $n_\lambda(T)$, $k_\lambda(T)$ of the solid or liquid nuclear fuel are considered together with other thermo-optical problems: thermal radiation transport, heat transfer by thermal radiation, thermal emittance, and thermal reflectance. However, knowledge of the absorption spectrum k_λ and of the optical density n_λ would allow in addition that fundamental statements can be made on the bonding character and the electronic conductivity. For the liquid phase of oxide and carbide fuels experimental studies have so far been missing as regards the liquid structure and the type of chemical bonding which essentially determine the thermochemical behavior and the thermophysical properties of the fuel melts.

+) In case, however, where the two condensed phases are seperated by a layer of vaporized material, the radiative heat transfer is governed by the emittance and absorptance of the hotter and colder condensed phase, resp., and by the limited transmittance(!) of the vapor layer /18/.

Consequently, the theoretical extrapolations concerning the behavior of molten fuel under accident conditions so far performed for reactor safety analysis still need experimental support regarding questions related to the physical structure of the fuel melt. The open questions relate e.g. to the homeopolar and ionic portion, respectively, of the chemical bonding, the concentrations of free electrons and defective electrons or polarons, respectively, and the charge carrier mobility in the fuel melt as a function of the temperature. But also regarding solid oxide fuel the experimental statements so far available are incomplete and partly contradictory with respect to these questions. Even for UO_2 measurements are still to be done of the absorption spectrum $k_\lambda(T)$ or of the optical density $n_\lambda(T)$ at elevated temperatures ($T >> 300K$) where these thermo-optical studies could validate the thermochemical findings on the chemical bonding of UO_2 and clarify contradictions.

Thus, the problem arises of determining by experiments the spectral plot of the optical absorption coefficient $k_\lambda(T)$ and of the refraction index $n_\lambda(T)$ of oxide fuel up to the liquid state. The relevant range of wavelengths extends from the short-wave ultraviolet until the far infrared ($0.1\ \mu m \lesssim \lambda \lesssim 100\ \mu m$). However, a limitation is imposed to the experiments by the fact that in the high temperature range ($T > 2000K$) only lasers are applicable as reference light sources. To-date, the range from 0.25 µm to 15 µm can be covered by standard type lasers. But also in this restricted range of wavelengths, n_λ, k_λ-measurements allow significant statements to be made on the physical structure and on the chemical bonding of solid and liquid oxide and carbide fuels.

3. Measuring Methods for the Determination of the Optical Constants of Opaque Non-Scattering Materials at Elevated Temperatures

Ceramic nuclear fuels in the solid state are generally opaque at elevated temperatures, which means that they are not at all or only slightly transparent optically. Also in the molten state the nuclear fuels seem to be strong optical absorbers. This results from laser evaporation experiments and measurements of the emissivity of UO_2 and UC up to 4000K [6,7]. For this reason, transmission measurements [8] for determination of n_λ, k_λ in the high temperature range are practically ruled out and transmission measurements on molten nuclear fuels seem to be even less feasible. However, there are several methods of determining the optical constants of opaque materials, which are based on the measurement of the reflection properties of these materials. They will be briefly discussed in the following paragraphs.

The best known method, although but rarely used in practical application and practically disqualified for experimental reasons in the case under consideration, is based on the measurement of the so-called main angle of incidence Φ_λ according to Cauchy, for which the ratio of the reflection factor R_λ^p/R_λ^s gets smallest for light polarized parallel with and vertical to the plane of incidence [9,10]. The calculation yields the relation:

$$n_\lambda = \sin\Phi_\lambda \cdot \mathrm{tg}\Phi_\lambda \cdot \frac{1-(R_\lambda^p/R_\lambda^s)}{1+(R_\lambda^p/R_\lambda^s)} \qquad (5)$$

$$k_\lambda = n_\lambda \cdot \frac{2\sqrt{R_\lambda^p/R_\lambda^s}}{1-(R_\lambda^p/R_\lambda^s)} \qquad (6)$$

with R_λ^p/R_λ^s measured at the angle of incidence $\theta = \phi_\lambda$.

A more convenient experimental method, which is consequently more important in practice, is based on the measurement of the reflection factor with only vertical reflection R_λ and on the determination of the phase change δ_λ of light reflection. δ_λ can be determined by calculation from the spectral plot of the reflection factor R_λ for vertical incidence, using the Kramer-Kronig relation [9]:

$$\delta_\lambda = \frac{2\nu}{\pi} \int_0^\infty \frac{\ln\sqrt{R(\nu_1)}}{\nu^2 - \nu_1^2} d\nu_1 \qquad (7)$$

$\nu = c/\lambda$ = light frequency.

The optical constants n_λ , δ_λ sought are obtained with the following equations of condition: The first equation of condition used is the Beer reflection formula (4). The second equation describes the relationship existing between the reflection phase shift δ_λ and n_λ, k_λ:

$$\mathrm{tg}\,\delta_\lambda = \frac{2k_\lambda}{1-n_\lambda^2-k_\lambda^2} \qquad (8)$$

However, this basically convenient measuring method calls for the reflection factor R_λ being measured for vertical reflection only, although continuously in the greatest possible spectral region. This is not possible with the high-temperature measuring problem considered here since the laser light sources available do not cover the entire spectral region.

A number of other methods for determination of n_λ, k_λ is based on reflection measurements using linearly polarized light of the wavelength λ and one reflection measurement at least to be made with rather oblique incidence of light ($\theta \gtrsim 60^\circ$) [11, 12, 13]. The complex formulae by Fresnel (9) applicable to oblique reflection and the refraction law (10) for absorbing materials with the complex refraction index N are used as the equations of condition for n_λ, k_λ.

$$R^s_\lambda(\theta) = \frac{\sin^2(\theta-\chi)}{\sin^2(\theta+\chi)}, \quad R^p_\lambda(\theta) = \frac{\tan^2(\theta-\chi)}{\tan^2(\theta+\chi)} \qquad (9)$$

$$\sin\theta/\sin\chi = N_\lambda = n_\lambda - ik_\lambda \qquad (10)$$

R^s = reflection factor for light polarized vertical to the plane of incidence
R^p = reflection factor for light polarized in parallel with the plane of incidence
λ = wavelength of light
θ = angle of incidence
χ = angle of refraction

The determination of n_λ, k_λ requires absolute measurements of the reflection factor $R^s_\lambda(\theta)$, $R^p_\lambda(\theta)$ performed at a sufficiently great angle of incidence θ since the system of equations (9), (10) does not provide otherwise an unambiguous pair of values n_λ, k_λ which make up the solution. The evaluation of the measurement calls for some graphical-numerical expenditure since the complex equations of condition cannot be solved explicitly for n_λ, k_λ [11].

A version of the method above developed by Avery substantially simplifies the measuring technology and the evaluation [12, 13, 14, 15]. It is based on the measurement of the reflection ratio R^p_λ/R^s_λ for light of the wavelength λ polarized both parallel with and vertical to the plane of incidence at an oblique angle of incidence θ. Absolute measurements of R_λ are not required which substantially augments the accuracy of the results!*

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* The Ditchburn method [16] is likewise based on the measurement of R^p_λ/R^s_λ with the phase change δ_λ of reflection measured in addition.

(Moreover, the function $R^p(\theta)/R^s(\theta)$ depends more on the angle of incidence than $R^p(\theta)$ alone). n_λ, k_λ can be determined more accurately if the reflection ratio R^p_λ/R^s_λ is measured at two angles of incidence θ_1, θ_2, with θ_1 being smaller and θ_2, if possible, greater than the main angle of incidence ϕ_λ. By additional measurements at still other angles of incidence θ_3, θ_4... it is possible to examine the consistency of the solutions n_λ, k_λ and to determine their scattering width. The expensive numerical evaluation of the complex equations of condition

$$R^p_\lambda(\theta)/R^s_\lambda(\theta) = \frac{\cos^2(\theta+\chi)}{\cos^2(\theta-\chi)} \qquad (11)$$

$$\sin\theta/\sin\chi = n_\lambda - ik_\lambda \qquad (12)$$

is suppressed in favor of a relatively simple graphical evaluation [14,15] provided that the measurements are made only at the angles of incidence $\theta = 30^\circ, 60^\circ, 73^\circ, 80^\circ, 83^\circ$ and provided that the optical constants sought lie within the range of values $1 \le n \le 6$, $0 \le k_\lambda \le 60$.

If in this case of application one forgoes unnecessary precision in the determination of the optical constants of nuclear fuels, the process of evaluation under the Avery measuring method can be substantially simplified by use of the Abelès method of approximation [15]. If the reflection ratio is measured at two appropriate angles of incidence, the optical density n_λ is directly obtained with sufficient accuracy as a real solution of a cubic equation and k_λ is derived from a still simpler root expression.

The discussion above leads to the result that the Avery reflection method [14] combined with the numerical evaluation method of Abelès [15] seems to be most appropriate in the determination of the optical absorption and density k_λ, n_λ of nuclear fuels or core materials. In this way, the task gets reduced to the experimental problem of developing a suitable high-temperature measuring method allowing to measure with an adequate accuracy the ratio of the spectral reflection factor $R_\lambda^p(\theta)/R_\lambda^s(\theta)$ of opaque materials up to maximum temperatures ($T \leq 4000$ K).

4. High-Temperature Measuring Technique for Determining $n_\lambda(T)$, $k_\lambda(T)$, $\kappa_{rad}(T)$ of Nuclear Fuel Materials up to > 4000 K from Reflection Measurements

The optical measurements of n_λ, k_λ previously performed on opaque materials under the Avery method or other reflection methods have been limited to a moderately high temperature range ($20K \leq T < 2000K$). The only measuring technology presently known which allows reflection measurements with opaque materials up to above 4000K, is the integrating sphere laser reflectometer /7/ (Fig. 1) developed and used by us at KfK. By use of this technique the spectral emissivity of UO_2, UC, ThO_2 and of other ceramic materials has been determined up to above 4000K, so far at two given wavelengths (0.63 and 10.6 μm).

Using this laser reflectometer it seems possible to measure the reflection ratio R_λ^p/R_λ^s of opaque material samples up to maximum temperatures ($\leq$4000K) at a sufficiently oblique light incidence so as to derive the optical constants n_λ, k_λ as a function of the temperature. The spectral measuring range of the laser reflectometer, which is presently extended, comprises wavelengths between 0.3 μm and 11 μm. (Measurements around λ = 10 μm are possible by means of a tunable CO_2 laser).

The radiative heat conductivity $\kappa_{rad}(T)$ of the opaque material at a given temperature has to be calculated from the measured spectral plot of the absorption coefficient $k_\lambda(T)$ by use of Rossland's diffusion approximation, as described, e.g., in Ref. 17.

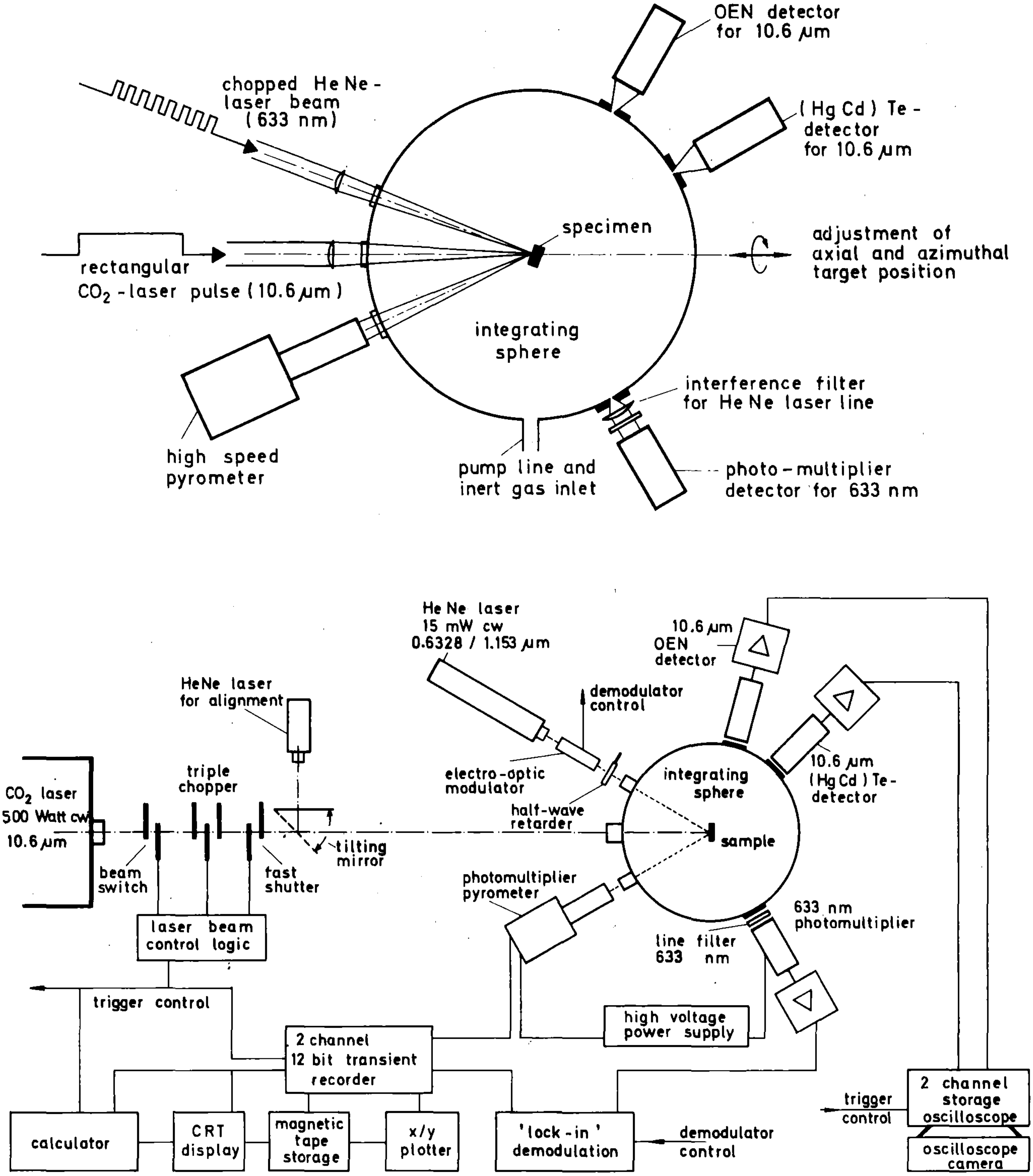

Fig. 1: Principle of measurement and block diagram of the integrating sphere laser reflectometer

In this way n_λ,k_λ-measurements on nuclear fuel materials performed up to ≳4000K by use of the laser reflectometer in the spectral range between 0.3 µm and 10 µm will do to get answers to the problems indicated in Sections 1 and 2, validitated experimentally for reactor safety analysis.

Acknowledgement

I am indebted for helpful discussions to Professors F. Cabannes and B. Piriou, Orléans Research Center on High Temperature Physics.

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