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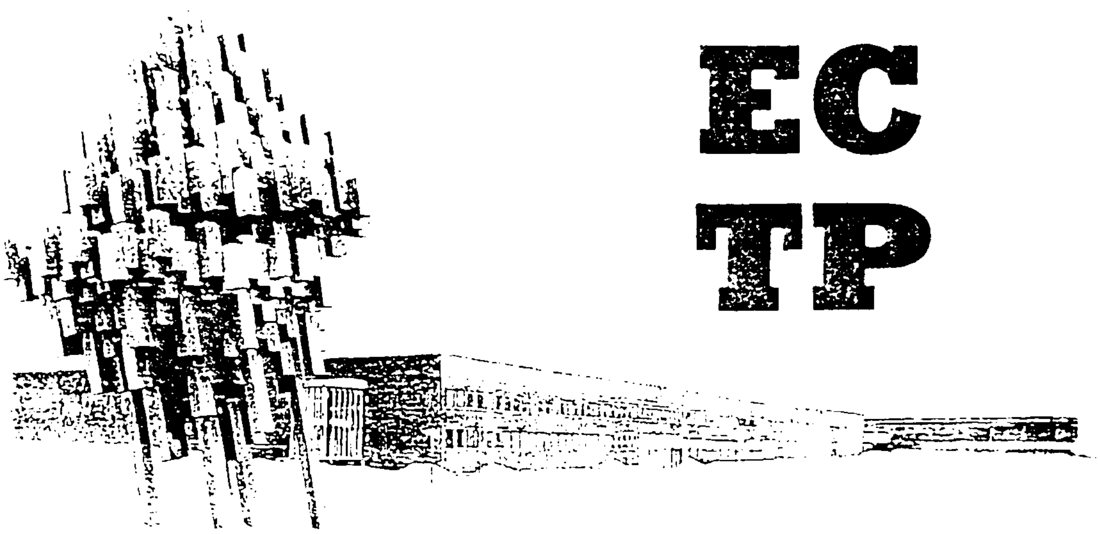

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ABSTRACTS

11th European Conference
on
Thermophysical Properties

13—16 June 1988

University of Umeå, Sweden

11th European Conference on Thermophysical Properties
13-16 June 1988, Umeå, Sweden

International Organizing Committee

Chairman	G. Bäckström, Umeå, Sweden
Vice Chairman	G. Ruffino, Rome, Italy
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Members	P. Andersson, University of Umeå A. Claesson, University of Umeå H. Forsman, University of Umeå Å. Fransson, University of Umeå G. Grimvall, Royal Institute of Technology, Stockholm S.E. Gustafsson, Chalmer's University, Gothenburg R. Ross, University of Umeå/UEA, U.K. O. Sandberg, University of Umeå B. Sundqvist, University of Umeå I. Wadsö, University of Lund

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Ministry of Education

Volvo

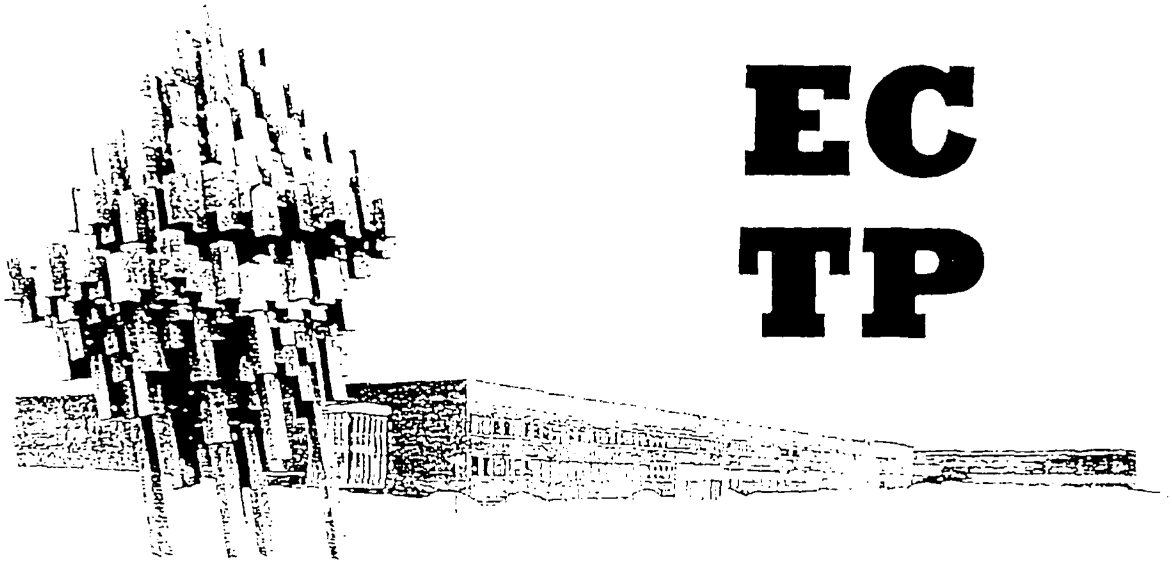
Polish Academy of Science

This volume contains the abstracts of the contributions to the 11th European Conference on Thermophysical Properties, held at the University of Umeå, Sweden, 13-16 June 1988.

The contents of this volume are intended for the guidance of the registered participants in this conference. It is not an open publication, and it is asked that no formal reference be made to any of the papers listed herein unless permission has been obtained from the respective author(s).

The papers presented at the conference will be subjected to normal refereeing procedures prior to publication in "High Temperatures - High Pressures". Full instructions for authors are given elsewhere in the conference information. A proceedings volume will be produced comprising a collection of reprints and made available to participants who have paid the full fee. Note that only papers actually presented at the conference will be included in the proceedings.

This volume contains only abstracts of oral (invited and contributed) and poster presentations, plus an author index. In the interest of maximum accuracy the final programme will be produced separately as late as practical, and thus cannot be included here.



EC
TP

PROGRAMME

11th European Conference
on
Thermophysical Properties

13—16 June 1988
University of Umeå, Sweden

~~90 01 18 050~~

****
*** Monday 13 June ***
****

09:10
Opening remarks and announcements

CHALLENGES AND DEVELOPMENTS AT THE FRONTIERS OF THERMOPHYSICS
(Chairman: R Taylor)

09:20
* **J C Verneuil**, MARCEL-DASSAULT, St Cloud, France: "Thermophysical Problems Linked to the Design of the HERMES Thermal Protection system" ①

09:55
* **H Reiss**, Brown Boveri, Heidelberg, West Germany: "Recent Advances in Thermal Superinsulation" ⑳

10:30
***************** Refreshments ****************

THEORY OF HEAT CONDUCTION
(Chairman: C Grimvall)

11:00
* **G D Mahan**, Knoxville, TE, USA: "Nonlocal Theory of Thermal Conductivity" ②

11:35
Orals: Pettersson ④ , **Hoff** ⑤ ,
Bisio ⑥

12:30
******************* Lunch **********************

WITHDRAWN CONTRIBUTIONS

The following contributions, appearing in the Abstract booklet, are expected to be withdrawn:

R P Tye, The Impact of New Materials and Applications on Measurements of Thermal Transport Properties ②

S D Preston, C Barrett & D Gustard, Thermal Conductivity of Irradiated Boron Carbide ⑩

V V Roschupkin, Thermodynamical Proeprties of Alkali Metals ⑪

J P Coutures & J C Rifflet, High Temperature, Fast Response, Drop Calorimeter for the Measurement of Thermodynamical or Thermophysical Properties on Solid or Liquid Oxides ⑫

L P Mezhov-Deglin, Hydrodynamic Effect in Solids ㉒

K D Maglic, A S Dobrosavljevic & N Lj Perovic, Transport Properties of Copper SRM ㉝

V V Mirkovich, Correlation of Thermophysical Properties of Brittle Materials with their Fragmentation Characteristics ㊺

R Boehler, Thermophysics of B_1-B_2 Phase Transitions ㊻

I I Novikov, V V Roschupkin, M A Pokrasin, A I Chernov & N A Semashko, The Experimental Study of the Sound Speed and the Attenuation Coefficient in Titanium including the Region of Polymorphic Phase Transformation ㊾

S R Atalla & H F Hassan, Analysis of the Plane Temperature Wave Technique for the Measurement ofThermal Properties of Absorbing-Emitting Media (61)

H P Tan & M Lallemand, Transient Pulse Heat Transfer in Semi-Transparent Materials (107)

M Marinelli, U Zammit, F Scudieri, R Pizzoferrato & S Martellucci, Photoacoustic Study of Thermal Parameters Critical Behaviour near the Smetic A-Nematic Phase Transition in Octylcyanobiphenyl Liquid Crystal (113)

S Suknarowski, Influence of the Contact Heat Resistance between Grain and Matrix on the Thermal Conductivity of a Composite (212)

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11th EUROPEAN CONFERENCE ON THERMOPHYSICAL PROPERTIES
13-16 JUNE 1988; University of Umeå, Sweden

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S Suknarowski	Institut Fizyki Politechnika Krakowska Podchorazych 1 30-084 Krakow POLAND	212

LATE PROGRAMME CHANGES

L N Dzhavadov, Behaviour of $(\partial T/\partial P)_s$ near γ-α Transformation of Cerium (214)

CHANGED from Poster Session II to Oral Presentation at Universum, Tuesday 14 June, 13:30 - 15:00

N B Vargaftik, D I Arnol'd, E B Gel'man, O I Ghirney, E V Grodzinsky & V F Kozhevnikov, Sound Velocity and Thermodynamic Properties of Liquid Cesium at High Temperatures and Pressures (114)

WITHDRAWN from Poster Session I

V E Peletsky, Thermophysical Properties of Different Purity Iron Specimens at High Temperatures (115)

WITHDRAWN from Poster Session I

PROGRAMME CHANGES

AT

MONDAY 13 JUNE

W Hemminger & W Neumann, Thermal Conductivity Measurements with the Hot Wire and Steady State Method (56)
CHANGED FROM ORAL PRESENTATION TO POSTER SESSION II

V V Kechin, On the Melting Law at High Pressure (72)
ADDED TO POSTER SESSION II

V E Peletsky, Thermophysical Properties of Different Purity Iron Specimens at High Temperatures (115)
ADDED TO POSTER SESSION II

A G Shashkov, V I Krylovich & A S Konovalov, Methods of Studying Thermal Phenomena Using Unsteady Frequency Methods (216)
ADDED TO POSTER SESSION II

[Abstracts of contributions (72), (115) & (216) will be available at the conference secretariat under the heading ADDITIONAL ABSTRACTS]

VISIT TO THE PHYSICS LABORATORIES

On Monday, 13 June, a visit to the Physics laboratories of the University of Umeå will be arranged in parallel with Poster Session I (13:30 to 15:00), and all interested conference participants are invited. Since the two buildings are so close together, we hope that it will be possible to take part in both events.

The visit will **not** take the form of a guided tour, starting and ending at some definite time and place. Instead, all interested visitors are invited to the main experimental area of the Physics building (see map of the University campus; the way between this building and Universum will be clearly signposted) where a small poster session, manned mainly by research students, will be set up. If possible, several experiments will be shown "live" during the time of the visit. We hope that this model will offer greater flexibility for each visitor to discuss the project of most interest to him/her than would a guided tour.

The various projects and experiments to be displayed include:

A. High pressure equipment
(G Andersson and M Forsgren)

B. 3-coordinate CNC precision measuring machine
(S Elmå)

C. Computerized communication and measurement system
(G Bäckström and B Forsström)

D. Thermophysical measurements under pressure by the hot wire method
(O Andersson, P Andersson, B Håkansson, R G Ross, and G Bäckström)

E. Thermal conductivity and heat capacity of single crystals under hydrostatic pressure
(S Andersson and G Bäckström)

F. Thermal diffusivity of metals under hydrostatic pressure
(P Jacobsson and B Sundqvist)

G. Differential Scanning Calorimeter
(Å Fransson)

H. Conducting polymers
(B Lundberg, H Forsman, Å Fransson, A Lundin, C Johansson)

I. Research on new "metallic" materials
(O Andersson, B Sundqvist)

J. Dielectric relaxation at high pressure
(H Forsman)

K. District heating
(H Wiklund and O Sandberg)

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M Friesel, B Baranowski & A Lundén, Phase Transitions of the System Ag_2HgI_4-Cu_2HgI_4 at Normal and High Pressure Studied by Differential Scanning Calorimetry 112

N B Vargaftik, D I Arnol'd, E B Gel'man, O I Ghirney, E V Grodzinsky & V F Kozhevnikov, Sound Velocity and Thermodynamic Properties of Liquid Cesium at High Temperatures and Pressures 114

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POSTER SESSION II

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O Andersson, P Andersson, R G Ross & G Bäckström, Thermophysical Properties of Glassy Crystals (201)

N Araki, N Kubo & Y Sasahara, Measurement of Thermal Diffusivity of Semi-transparent Material (202)

R de Coninck & A J Flipot, Thermal Diffusivity Measurements on Li_2SiO_3 Using the Modulated Electron Beam Technique and Discovery of some Electrical Phenomena (204)

S Azizi, J C Batsale, C Moyne & A Degiovanni, Measurement of the Thermal Conductivity of Non-saturated Porous Media. Theoretical Analysis and Experiments (205)

B O Haglund & A Hallén, Thermal Diffusivity and Conductivity of Powder Compacts and Sintered Specimens of Cemented Carbide (206)

B Håkansson, P Andersson, R G Ross & G Bäckström, Thermophysical Measurements under Pressure by the Hot-wire Procedure (207)

P Jacobsson & B Sundqvist, Transport Properties of Gadolinium from 40 - 340 K (208)

D Banner, S Klarsfeld & C Langlais, Temperature Dependence of Optical Characteristics of Semitransparent Porous Media (209)

A Lanciani, P Morabito, P Rossi, F Barberis, R Berti, A Capelli & P G Sona, Thermophysical Properties Measurements of Structural Materials in Laboratory and _in situ_: Methods and Instrumentations (210)

V B F Mathot & M F J Pijpers, Heat Capacity, Enthalpy and Crystallinity of LPE, LLDPE and VLDPE as a Function of Temperature by a Continuous DSC Method (211)

H A Tasman, Thermal Conductivity of Liquid UO_2 (213)

L N Dzhavadov, Behaviour of $(\partial T/\partial P)_s$ near γ-α Transformation of Cerium (214)

J M Roux, Temperature Measurements on Both Sides of a Flat Sample Illuminated with a Flash, Leading to the Determination of Thermal Conductivity and Heat Capacity (215)

13:30

POSTER
SESSION I

15:00
*************** Refreshments *************

13:30

VISIT TO
THE PHYSICS LABORATORIES

15:00
*************** Refreshments **************

NUCLEAR MATERIALS
(Chairman: H E Schmidt)

15:30
* **M Beauvy**, CEN, Cadarache, France: "Thermophysical Properties of Nuclear Oxide Fuels" ⑦

16:05
Orals: Martin ⑧ , **Breitung** ⑨ , **Preston** (70)

17:00
Discussion of topics for future meetings
(Chairman: G Bäckström)

17:30
Reception at "Universum"

18:30 Coaches depart for hotels
22:30 Coaches depart for "Universum"

23:00
Lecture on the Aurora Borealis (R Lundin), followed by "son et lumière"

24:00 Coaches depart for hotels

****
* Tuesday 14 June *
****

HEAT TRANSPORT AND PHASE TRANSITIONS
(Chairman: G K White)

09:00
* **I A Smirnov,** Leningrad, USSR: "Influence of Paramagnetic Rare Earth Ions on Thermoconductivity of Ordered and Disordered Materials" ㉓

09:35
Orals: M A White ㉔ *Lundén* ㊼ **Karawacki** ㊽

*************** Refreshments **************

THERMOPHYSICAL PROPERTIES OF METALS
(Chairman: G D Mahan)

11:00
* **N. Wiser,** Ramat-Gan, Israel: "Electron-electron Scattering and the Heat Transport Properties of Metals" ⑭

11:35
Orals: Grimvall ⑮ , **Binkele** ⑯ , **Hemminger** ⑰

12:30
****************** Lunch ******************

(Social Science Building)

HETEROGENEOUS AND TECHNOLOGICAL MATERIALS
(Chairman: J F Sacadura)

11:00
* **P Demo,** Czechoslovak Academy of Sciences, Prague: "The Influence of External Fields on the Thermophysical Properties of Technological Materials" ㉕

11:25
Orals: van Haneghem ㉖ , **Morabito** ㉗ , **Saxena** ㉘ , **Laurent** ㉙

12:30
****************** Lunch ******************

THERMOPHYSICAL PROPERTIES OF METALS (... continued)

(Chairman: G D Mahan)

13:30
Orals: Rhee ⑱ ; Hemminger ⑲

15:00
**************** Refreshments ***************

13.30

POSTER
SESSION II

15:00
*************** Refreshments **************

15:30
Coach departures from conference to hotels

16:30
Coach departures from hotels for "Raft on the Waves" or "Orienteering"

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* **Wednesday 15 June** *
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STANDARDS AND DATA
(Chairman: R E Taylor)

09:00
* **T J Quinn**, Sèvres, France: "The International Temperature Scale of 1990" ㉚

09:35
* **T Arai**, NRLM, Ibaraki, Japan: "A Thermal Conductivity Data Base for Solid Materials" ㉛

10:00
Orals: Cabannes ㉜ , **Maglic** (71)

10:30
*************** Refreshments **************

PYROMETRY AND HIGH TEMPERATURE THERMOPHYSICS
(Chairman: G Ruffino)

11:00
* **A Cezairliyan**, N.B.S., Gaithersburg, MD, USA: "Subsecond Pyrometry and Its Applications to Thermophysical Measurements" ㉞

11:35
Orals: Hiernaut ㉟ , **Babelot** ㊱
Ronchi ⑬

12:30
****************** Lunch ******************

(Social Science Building)
GLASSES AND GLASSY CRYSTALS
(Chairman: C A Nieto de Castro)

11:00
* **H Suga**, Osaka University, Japan: "Heat Capacity of Glassy Crystals" ㊿

11:35
* **A Sjölander**, Chalmers University, Sweden: "Microscopic Model of Glass Transitions" (51)

12:10
Oral: Hampton (203)

12:30
****************** Lunch ******************

LASER FLASH AND PHOTOTHERMAL METHODS

(Chairman: K D Maglic)

13:30
* **D L Balageas**, ONERA, Chatillon, France: "Thermal Diffusivity Measurements by Pulse Methods" ㊲

14.05
Orals: R Taylor ㊳ , **Kumashiro** ㊴ , **Balageas** ㊵

15:00
*************** **Refreshments** **************

VOLUMETRIC PROPERTIES

(Chairman: A Degiovanni)

15:30
Orals: G K White ㊶ , **Nieto de Castro** ㊷ **Henderson** ㊸ , **Test** ㊹

17:00
************* **End of session** **************

(Social Science Building)

THERMOPHYSICAL PROPERTIES & THE ELECTRICAL INDUSTRY

(Chairman: F Cabannes)

13:30
* **G Slack**, General Electric, Schenectady, N.Y., USA: "Thermophysics in the Electrical Industry" (53)

14:05
Orals: Dworkin (54) , **Hampton** (55) , **Neumann** (56)

15:00
*************** **Refreshments** **************

OPTICAL METHODS

(Chairman: A Cezairliyan)

15:30
* **C Hartung**, Akademie der Wissenschaften der DDR, Berlin: "Optothermal Laser Spectroscopy" (57)

15:55
Orals: Nagashima (58) , **Bedford** (59) , **Bein** (60) , **Sacadura** ㉑

17:00
************** **End of session** *************

17:05 Coach departures for hotels

18:45 Coach departures for "Universum"
19:00
**************** **Banquet** ******************

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* Thursday 16 June *
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THERMAL CONDUCTIVITY OF FLUIDS AT HIGH PRESSURE

(Chairman: H Suga)

09:00
* **W A Wakeham,** Imperial College, London: "Thermal Conductivity of Liquids under Pressure" (62)

09:35
Orals: Nieto de Castro (63), Nagasaka (64) Vesovic (65)

10:30
*************** Refreshments **************

THERMAL CONDUCTIVITY OF SOLIDS AT HIGH PRESSURE

(Chairman: A Lundén)

11:00
* **R G Ross,** University of East Anglia, Norwich, U.K.: "Thermal Conductivity of Solids under Pressure" (66)

11:35
Orals: G K White (67), Nilsson (68), Schloessin (69)

12:30
****************** Lunch ******************

(Social Science Building)

09:00

WORKSHOP ON NUCLEAR MATERIALS
directed by
G J Hyland, University of Warwick, UK

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10:30
*************** Refreshments **************

11:00

WORKSHOP
(... continued, if required)

12:30
****************** Lunch ******************

************ End of conference ************

ORAL PRESENTATIONS

(INVITED AND CONTRIBUTED)

THERMOPHYSICAL PROBLEMS LINKED TO THE DESIGN OF THE HERMES THERMAL PROTECTION SYSTEM

by J.C. VERNEUIL
Avions Marcel Dassault
Saint-Cloud (FRANCE)

The future European space shuttle HERMES will have to face a very severe thermal environment during atmospheric re-entries and consequently needs a very high-performance thermal protection system, the design of which raises a certain number of thermophysical problems.

The thermal protection will be constituted of different subassemblies adapted to the expected heat flux areas:

-The very hot parts (nose-cap, wing leading edges control surfaces) will be fully working hot structures made of SiC or carbon composite ceramic materials.

-The medium heat flux areas (front-fuselage, windward side) will be covered with a thermal protection system of original design made of a patchwork of thin stiff ceramic shingles fixed to the cold structure and covering a very light alternate felt-metallic multiscreen insulation (which decouples the mechanical function from the thermal insulating function).

The concept of a multiscreen insulation system has been retained because radiative transfer is predominant at high temperatures; so, as a result, the use of highly reflective screens can lead to very high performance insulations which are also light in weight. The main problem is to find the appropriate screens, which have to keep a good resistance against oxidation at high temperatures (coatings may have a catastrophic effect on the reflectivity).

The choice of the interfacing felts is also delicate, due to the necessary compatibility with the metallic foils. The felts also have great importance in the global performance of the insulation, since they work as a semi-transparent medium. The constituent material, as well as the size of the felt fibres and the density, will have to be optimized.

The development and characterization of ceramic hot structures will need the use of high temperature test facilities, able at least to simulate the thermal cycles Hermes will be exposed to, and there is a choice of several techniques. Heating may be achieved by a solar furnace, a quartz lamp, a graphite resistance, a flame or a laser.

2

THE IMPACT OF NEW MATERIALS AND APPLICATIONS ON MEASUREMENTS OF THERMAL TRANSPORT PROPERTIES

By

Ronald P. Tye
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Cambridge, MA 02139, USA

Modern technologies have stimulated significant development and use of new materials together with new and different applications of existing materials in various forms. These activities have had a resultant impact both on existing methods of measurement of transport properties and development of new and modified measurement techniques for the new or different forms of materials.

This impact on measurement methodology will be discussed and illustrated with examples relating to both new materials and new applications. These will include:

- methods for composites of different types and forms, including fiber reinforced matrix materials, layered systems and evacuated high thermal resistance insulation products and systems;
- modified methods for quality control and quality assurance needs; and
- new or improved methods for materials in different forms including those suitable for very thin films, and for materials in very small quantities.

Related issues of variability, accuracy and relevance of results to material bulk properties and applications will also be discussed and recommendations regarding future needs will be included.

NON-LOCAL THEORY OF THERMAL CONDUCTIVITY

G.D. Mahan

Department of Physics of the University of Tennessee, and
Solid State Division of Oak Ridge National Laboratory.

Thermal transport is caused by the motion of excitations such as electrons, phonons, photons, etc. When the excitation has a short mean free path (mfp), the motion of heat can be described by a local theory such as the diffusion equation

$$C(T)\,\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[\,K(T)\,\frac{\partial T}{\partial x}\,\right]$$

where C is the heat capacity and K is the thermal conductivity. However, when the temperature change ∂T/∂x is rapid on the distance scale of the mfp of the excitations, then one must employ a non-local theory of thermal motion. The right-hand side of the above equation is replaced by a term of the form[1]

$$\frac{\partial}{\partial x}\left[\,\int dx'\;H(x-x')\,\frac{\partial T(x')}{\partial x'}\,\right]$$

We discuss the forms for H(x) when the heat current is given by long wavelength phonons.

Recent neutron scattering experiments have provided accurate temperature profiles of the silicon substrate during laser annealing[2]. Conventional modeling of this data revealed a deficit in the thermal current at high temperature gradients[2]. We show that this anomaly is due to the non-local nature of the thermal transport.

1. G.D. Mahan and F. Claro, Phys. Rev. B (in press).
2. B.C. Larsen, J.Z. Tischler, and D.M. Mills, J. Mater. Res. 1, 144 (1986).

④

Pressure Dependence of the Thermal Conductivity of Alkali Halides

Sune Pettersson, Department of Theoretical Physics,
University of Umeå, S-901 87 Umeå, SWEDEN

Accurate dispersion relations have been used for the first time in a calculation of the pressure dependence of the thermal conductivity. We have calculated, using the deformation dipolar model, phonon dispersion relations throughout the whole first Brillouin zone for different values of the lattice constant. These have been used to solve the Boltzmann equation by a variational method and to obtain the thermal conductivity for different lattice constants.

We find (1) that the Bridgman parameter

$$g = -\left(\frac{\partial ln\lambda}{\partial lnV}\right)_T \tag{1}$$

is in good agreement with room temperature experiments. (2) Differences between alkali halides is mainly caused by the changes in the three-phonon scattering rate with pressure. Various contributions to g are discussed in detail.

Nonlinear Heat Conduction And Phenomena of Heat Flow Rectification

Heinrich Hoff, Sektion Kalorimetrie der Universitaet, Oberer Eselsberg, D-7900 Ulm, F.R.G.

Although Fourier's law of heat conduction expresses a linear relation between the heat flow density and the temperature gradient, there are certain nonlinear properties which are caused by the temperature dependence of the heat conductivity. The latter is well known but is usually negliged because it leads to a nonlinear field equation instead of the well known second Fourier's law and thus requires a more difficult mathematical framework. This nonlinear partial is resolved for the simplified case of one dimensional steady state transport by perturbation theory and numerically, thus yielding unknown phenomena like heat flow rectification. The solution permits understanding the conditions under which these effects should occur and how they could be maximized. Recently the theoretical predictions have been verified by experimental observation. This theory of nonlinear heat transport has been generalized to an arbitrary number of coupled processes, e.g. diffusion across a multicomponent system, thus yielding similar phenomena of rectification and certain unknown symmetries of nonlinear coupling.

THERMAL CONDUCTIVITY DEPENDENCE UPON SOME VARIABLES AND CORRESPONDING THERMODYNAMIC EFFECTS IN ONE-DIMENSIONAL HEAT CONDUCTION

GIACOMO BISIO
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Prigogine and others examined continuous systems with time independent boundary conditions and found out the validity of the known inequality:

$$\delta_X P = \sum_n J_n \, dX_n \le 0$$

where P is the entropy production rate, J_n are the the "generalized fluxes" and X_n the "generalized forces" .

A steady state in the heat conduction does not correspond to the state of minimum rate of entropy production. On the other hand Li drew attention to the fact that a different function, by him called "thermokinetic potential", has only a decreasing trend with time; the condition of minimum thermokinetic potential corresponds exactly to the one of steady state . Li derived a thermokinetic potential for various problems of heat conduction, finding an appropriate integrating factor for the contribution of the "generalized forces" change to the variation of the entropy production rate ($\delta_X P$).

In previous notes the author has examined the one-dimensional heat conduction in systems with time independent boundary conditions from two different points of view:

(i) Considering all the possible distributions of the temperatures, with some specified constraints, the conditions were determined under which the differentials of the entropy production rate, P, and of other functions are zero.

(ii) Starting from any initial temperature distribution, the time evolutions of the above functions and of their derivatives were studied, pointing out in particular that in no case the value of the entropy production rate at the steady state coincides with the minimum value determined in (i) .

We propose in this paper for the above problems to study the influence of the various type of thermal conductivity (k) dependence:

(i) Thermal conductivity can be increasing or decreasing with temperature. In some cases for the parameter $G = k\, t^2$ we have $G'(t) < 0$.

(ii) Thermal conductivity can depend directly upon the coordinate in the heat flux direction (e.g. owing to the variation of pressure), and present a finite number of discontinuities (e.g. owing to different materials in series).

(iii) Thermal conductivity can be function directly of time.

The main results are the following.

In a homogeneous system in which the separation of the variables holds for conductivity, as it generally happens, dP is zero for one, and only one, temperature distribution and P is minimum, when dP=0 .

For two-component systems, in which the separation of the variables is valid for the conductivity of every layer, there is always one temperature distribution for which dP=0 , but there is not always a single solution. We can have e.g. two minima and a "saddle point".

For a system consisting of three (or more) layers in general neither the existence nor the uniqueness of a temperature distribution for which dP=0 can be warranted.

It is noteworthy that some coupling of materials in a system can produce time evolutions having the maximum of the entropy production rate at the steady state.

A thermokinetic potential similar to Li's is easily drawn, when for conductivity it is possible to separate the variables.

When the above separation cannot be done, a substantially different expression is found out for thermokinetic potential.

If thermal conductivity is time dependent, obviously it is impossible to draw a thermokinetic potential.

The sign of G'(t) (where $G(t) = k(t)\, t^2$) results a discriminating element for a comparison between the temperature distributions at the steady state and at the state of minimum entropy production rate and also for a comparison of the time evolutions of the entropy production rate during the heating and the cooling of a system.

THERMOPHYSICAL PROPERTIES OF NUCLEAR OXIDE FUELS

M. BEAUVY

COMMISSARIAT A L'ENERGIE ATOMIQUE
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FRANCE

The thermal conductivity, one of the most crucial properties of nuclear fuels, is very difficult to measure on mixed oxide of uranium and plutonium in the range of temperature normally or incidentally reached in nuclear reactor. The purpose of the present paper is to review the main thermal conductivity studies on oxide fuel and point out the reasons of the differences between the published results.

Considering the data from out-of-pile investigations it is demonstrated that the thermal diffusivity is the best way to get accurate conductivity values. Our equipment for thermal diffusivity measurements from room temperature up to the melting point of UO_2 is described. The results of parametric study of the diffusivity on mixed oxide up to more than 2000°C are reported, and recommendations presented on the influence of density, stoichiometry and plutonium concentration. The effect of simulated fission products has also been analysed.

Critical review of the heat capacity measurements on UO_2 and PuO_2, and new results on mixed oxides are proposed.

Attention is drawn to a new thermal conductivity relationship in accord with the majority of the published results and theoretical developments on the nature of conduction mechanisms in mixed oxides.

⑧

Recommendations for some Thermophysical Properties of Nuclear Oxide Fuels

D G Martin
Theoretical Physics Division, Harwell Laboratory, UKAEA, Oxon OX11 0RA, UK

The thermophysical properties of UO_2 and $(U,Pu)O_2$ possessing a range of O/M ratios are required if we are to understand how nuclear fuels behave during irradiation in thermal or fast reactors. In this paper recommendations are developed for the elastic constants and coefficient of thermal expansion (c.t.e.) of the above mentioned range of fuels up to the solidus temperature; in addition the thermal conductivity of hyperstoichiometric UO_2 is discussed.

A set of self consistent recommendations for the four elastic constants (E, G, B and ν) as a function of temperature, porosity, plutonium content and O/M ratio is proposed. At high temperatures, elastic constant values for UO_2 up to 2929K have been derived from the single crystal neutron inelastic scattering measurements of Hutchings et al. It is pointed out that at such high temperatures adiabatic and isothermal bulk moduli differ quite appreciably.

From a review of the literature, recommendations for the c.t.e. of oxide fuels as a function of temperature, plutonium content and O/M ratio are put forward. Data for hypostoichiometric $(U, Pu)O_2$, which is of considerable technical importance, was found to be sparse and rather variable. Further recent neutron diffraction data by Hutchings et al on UO_2 has enabled a far more satisfactory recommendation to be made at high temperatures than hitherto. Agreement between diffraction and macroscopic measurements in the region of 2500K suggests that at least up to this temperature Schottky defects make a negligible contribution to the thermal expansion.

A recommendation for the thermal conductivity of fully dense, hyperstoichiometric UO_2 up to the solidus temperature, which is based on an expression that includes contributions from the lattice and small polarons, is proposed. Although it is difficult to produce an expression which is entirely satisfactory on theoretical grounds, it would appear that such uncertainties do not affect actual thermal conductivity values too markedly. In particular there is reasonable agreement between our recommendation and measured in-reactor integral to melt conductivity values. A method of obtaining further experimental integral to melt values, based on a simple, well proven power to melt tecnique using a Materials Testing Reactor is suggested.

A Measurement of the Density and Compressibility of Liquid (U,Pu)-mixed Oxide at 7400 K.

W. Breitung

K.O.Reil

In a transient in-pile heating test a sample of (U,Pu)-mixed oxide was heated under constant volume conditions. At room temperature the sample filled about 50% of the test volume. The $(U,Pu)O_2$ sample was heated in 10 milliseconds up to about 7400 K. The system pressure was measured continuously, showing first the oxide saturation vapor pressure $p_{sat}(T)$, and late in the test, a sudden liquid phase pressure excursion. At this point in time the $(U,Pu)O_2$ sample had filled the test volume completely by thermal expansion. The data evaluation resulted in a liquid density of 4900 kg/m^3 at 7400 K. From the measured rise rate of the liquid pressure excursion the corresponding isothermal compressibility was estimated to $(3 \pm 2) \cdot 10^{-4}$ MPa^{-1}.

Based on these new data and previously existing measurements, new relations are proposed for the density, thermal expansion, and isothermal compressibility of liquid (U,Pu)-mixed oxide between 3120 and 7400 K.

THERMAL CONDUCTIVITY OF IRRADIATED BORON CARBIDE

S D Preston, C Barrett, D Gustard.

UKAEA Northern Research Laboratories, Springfields, Salwick, Preston, UK.

The operation of large Fast Reactors is controlled by the movement of control and shut-off rods containing a neutron absorber. The preferred absorber material in the UK and elsewhere is boron carbide. It is used in the form of a cylindrical stack of solid pellets in metallic cladding. Naturally occurring boron carbide contains almost 20% of the ^{10}B isotope with the remainder being ^{11}B. Neutron absorption occurs entirely in the ^{10}B isotope which fissions, producing helium and lithium with a release of energy, generating heat.

The fission products cause swelling of the boron carbide with eventual pellet-cladding interaction and the generation of cladding stresses. To model the performance of the absorber pin it is necessary to define both the irradiation induced strains and the thermal strains. For the latter, the thermal properties of the pellet are important parameters.

The ^{10}B burn-up also causes a reduction in the thermal conductivity of the boron carbide. There is, therefore, an increase in thermal gradients with ^{10}B burn-up which could lead to melting in the pellet centre, particularly if the boron carbide is enriched in the ^{10}B isotope to increase the absorption density.

The thermal conductivity of the boron carbide is therefore an important design parameter in modelling pellet behaviour and absorber pin performance. This paper describes the results of high temperature measurements of the thermal diffusivity/thermal conductivity of both unirradiated and irradiated boron carbide to examine the changes produced in this important parameter. Measurements are made on both natural and 40% enriched boron carbide pellets irradiated to a ^{10}B burn-up of 7×10^{21} cap/cm^3 for comparison with the unirradiated data.

⑪

THERMODYNAMICAL PROPERTIES OF ALKALI METALS ALLOYS

Roschupkin V.V.

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The saturated vapor pressure is one of the most important thermodynamical parameters of liquid alloys characterizing phase equilibrium. These data make it possible to investigate the shape of the border curve, the mutual dissolubility of metals, to ascertain substantially the diagram of state for alloys. The report describes precise measuring technique for the saturated vapor pressure, pVT-properties and compressibility of alloys in the temperature range of 500-1800 K.

The basis of this technique is the variant of the static method that maximally satisfy the metals equilibrium condition. The absence of systematic errors (they are eliminated experimentaly) and the usage of the most precise pressure and temperature sensors can be regarded as the advantages of the described technique. The study of the saturated vapor pressure for binary alloys of alkali metals is carried out, as a result of which the temperature and concentration functions are gained and the tables of recommended reference data for the studed systems are made. The question of execution of Raoult law for the binary alloys of alkali metals is of special interest. The stated data demonstrate that the law is true only in the limited area of state. In most cases Raoult law gives essential difference (up to 10%) from the experimental data and entirely different concentration functions for the saturated vapor pressure of alkali metals. Thus the main way of obtaining data on the saturated vapor pressure for the binary alloys of alkali metals is the experimental one.

The report also presents data on the expansion coefficient and the density of alkali metals alloys in the temperature range of 300-1300 K with high accuracy. These data allowed to conclude that the additivity law for the density value is satisfied in the systems under study with accuracy enough for practical purposes. As for the expansion coefficient this law is satisfied only in the limited temperature range. Further experiments are neccessary for the final conclusion about this matter.

⑫

High temperature, fast response, drop calorimeter for the measurement of thermodynamical or thermophysical properties on solid or liquid oxides.

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The high temperature community needs, for the development of oxides high temperature processes, thermodynamical and thermophysical data with reasonable accuracy. For such a purpose, the Research Center for High Temperature Physic has developped an aerodynamic levitation device associated to a CW CO2 laser as heating source and a constant temperature bloc calorimeter (T = 298 K). The aerodynamic technique allows to work in containerless conditions and avoid any limitations due to the sample holder (usually W or Mo), therefore work under pure oxygen are authorized.The sample (spheric shape)/calorimeter distance is around 50 mm and the radiation losses compared to classical drop calorimeters are minimized. Also the sample could be heated by the CO2 laser beam during the first 35 mm of its fall. As the sample weight is between 50 and 120 mg, a large number of runs are carried out during a working day. In term of quality of the heat content, Cp or Δ H phase transition measurements the limiting factor is the accuracy of the temperature measurement on small samples (diameter around 3 mm) with unknown emissivity. Improvements have been obtained using a multiwavelength pyrometer working with monochromatic filters in the 1 to 10 um range and allows to detect "anomalies" on ε_λ (liquid) at constant T. As no internal calibration is used, the heat of fusion of α Al_2O_3 is used to calibrate the calorimeter.

After a discussion of the main parameters governing a stable levitation regime (surface tension, vaporization behaviour) examples are given on H_T-H_{TO}/Δ H of melting, Cp(liquid) data obtained with such a set up and compared to the available literature results. A special emphasism is given on the liquid $\rightarrow$ solid transition in the scope of:a)the effect of the temperature of the liquid, b)the absence of heterogeneous nucleation reference state problem) and c)on the possible use of the aerodynamic levitation in the high temperature instrumentation.

[+] Directeur du Centre de Recherches sur la Physique des Hautes Températures

USE OF ACOUSTIC LEVITATION IN HIGH-TEMPERATURE HEATING EXPERIMENTS WITH PULSED-LASER

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The study of the behavior of nuclear reactors under hypothetical core disruptive accidents has led to the development of advanced techniques for the measurement of the thermophysical properties of nuclear fuels and reactor materials up to temperatures where the sample containment becomes problematic, involving disturbing chemical reactions or hardly controllable thermal conditions.

Acoustic levitation in a high-pressure autoclave was therefore implemented to enable metallic and ceramic materials to be heated with multibeam laser pulses up to extremely high temperatures, the only limiting factor being in fact the rate of evaporation of the sample. This effect was reduced by increasing as much as possible the gas pressure in the autoclave. After having effectively reduced the sample losses to mere thermal exchanges with the gas of the autoclave, specific heat and enthalpy evaluations could be carried out from the experimentally measured curves of temperature vs. time. The precision of these evaluations is strictly dependent on the assessment of the operating heat-loss rates. Under acoustic levitation conditions convective losses may be dramatically high compared with the radiative losses up to temperatures as high as 5000 K. This problem has been thoroughly investigated by using a 70-Hz levitator in an autoclave filled with various gases at pressures up to 500 bar. The results have been analyzed in view of establishing general formulae to deduce the mentioned thermodynamic quantities.

14

Electron-Electron Scattering and the Heat Transport Properties of Metals

Nathan Wiser

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A review will be presented of the contribution of electron-electron scattering to the thermal resistivity $W_{ee}(T) = B_{ee}T$ for the non-transition metals. The discussion will include the following topics:

(i) Status report regarding the experimental values of B_{ee} for the transition metals.

(ii) Comparison between theory and experiment for B_{ee} for the non-transition metals.

(iii) Wiedemann-Franz ratio for electron-electron scattering.

(iv) Phonon-mediation contributions to B_{ee}.

(v) Relationship between high-temperature values and low-temperature values of B_{ee}.

(vi) Unsolved problems.

THERMODYNAMIC PROPERTIES OF TECHNETIUM

Göran Grimvall

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Armando Fernández Guillermet

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The thermodynamic properties of technetium, e.g., the enthalpy, the entropy and the heat of fusion, have been poorly known. On the other hand there has recently been a considerable progress in the theoretical understanding of the microscopic basis for the thermodynamic properties, i.e. a description in terms of electrons and phonons. That includes accurate results for the electron density-of-states and a description of anharmonic effects at high temperatures. We show how the rather meagre experimental information for technetium can be combined with a theoretical approach in order to yield reliable estimates of thermodynamic quantities. The general ideas of our analysis are applicable to any metal or alloy. Our discussion includes superconductivity and the electrical and thermal conductivity.

⑯

Transport Properties of Yttrium and Seven Rare Earth Metals in the Range 300 - 1000 K

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Over many years, rare earth metals have been the subject of special interest in science and industry. To day, for example, they are playing an important role in connection with the development of thin films for magneto-optical data storage with very high capacity. On the other side, investigations concerning these metals are handicapped because of a very poor oxydation stability, especially at temperatures above 300 K. Nearly no directly measured thermal conductivity data are known in this temperature range. This paper discribes the adaption of an earlier designed modified Kohlrausch measuring technique for measuring the thermal and electrical conductivity of polycrystalline Er, Dy, Gd, Ho, Nd, Sm, Yb and Y samples. Measuring data together with calculated (total) Lorenz functions will be presented and discussed.

Apart from Yb and Y, all metal samples show with increasing temperature a monotonic increase of the specific electric resistance $\rho(T)$ and the thermal conductivity $\lambda(T)$. Typical values at 300 K are $100\,\mu\Omega$ cm and 0.1 W/cm^{o}C. For Y, the absolute values are on a similar level whilest $\lambda(T)$ shows a flat minimum at 700 K in this case. Yb was found to be the best conductor from this series (factor 2 to 3). It is felt that some curve features indicate two phase transitions of Yb at 560 and 700 K. Unfortunately up to now no further results supporting this assumption are available (for example X-ray diffraction data).

In accordance with earlier Lorenz function results received for nineteen pure transition metals, the calculated Lorenz functions were found to approach certain discrete and equidistant levels at high temperatures (2.9; 2.7 and 2.5 $10^{-8}\ V^2/K^2$). It is assumed that thermal conductivities in temperature regions which are characteristic for such levels are of pure electronic nature.

⑰

The thermal conductivity of Pb from -180 °C to 500 °C

W. Hemminger,
Physikalisch-Technische Bundesanstalt
Braunschweig, FRG

The thermal conductivity of 99.999% pure Pb has been measured by means of three different steady-state set-ups. All three techniques utilize identical cylindrical samples. The temperature difference created by the axial heat flow is measured on the axis of the cylinder. From -180 °C to 100 °C an unguarded double-cylinder device with a transverse heater is used. From room-temperature to 100 °C as well as from room temperature to 500 °C the measurements are performed with guarded single-cylinder devices. In the overlapping temperature intervals a systematic deviation not greater than 2% was found. The uncertainty for the solid material is about 2.5%, for the liquid it is estimated to be 3%. This is a result of the uncertainties of the corrections due to the sample container.

The thermal conductivity drops at the temperature of fusion from 29.7 W/k m to 15.6 W/k m. The ratio of the values is 1.90 which is in good agreement with the change in electrical conductivity which has a ratio of 1.94. The thermal conductivity of the solid material can be described by means of a first or second order polynominal which shows a maximum deviation of 1.7% between the calculated and measured values. The molten metal shows a scatter less than 0.1%.

Measurements of the Thermal Conductivity of Copper by Twin-Rod Method

by

Sang Woo Park and Chunghi Rhee
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Measurements have been made of the thermal conductivity of commercial grade copper (99.95 % pure) in the temperature range 30 to 800 °C by using a twin-rod method. Twin specimen rods joined by a screw connection have specimen heater inside the central connection area so that heat generated from the specimen heater may be fully transferred to the specimen. The amounts of heat input to each specimen rod are unknown but can be determined by solving the two sets of simultaneous Fourier transport equations derived from each specimen rod. The heat leakage from the specimen to the insulator was reduced by matching the temperature profile of guard to that of the specimen and the amount of heat leakage was calculated to correct the heat input to the specimen. The data given by this method yield good agreement with those of other experiments and show the thermal conductivity of copper to be a smoothly decreasing function of temperature in the measured range.

⑲

An apparatus to measure the thermal conductivity of metals from -180 °C to 100 °C

W. Hemminger,
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The steady state method works with a linear heat flow through two cylindrical specimens. The heat is generated in a central transverse heater between the two specimens. The unguarded cylinders are situated inside a thermostatically controlled vessel which is cooled by means of liquid nitrogen. The total temperature range of the apparatus can be scanned automatically. even non steady-state periods can be used to evaluate the thermal conductivity if the heat capacity of the sample is known. The effect of the heat generated in the input leads of the heater has also been evaluated. The total uncertainty in the thermal conductivity measurements is estimated to about 1.5%.

Regarding the new instrument three points of interest may be stressed:

- the cooling device which uses the enthalpy of vaporization of liquid nitrogen
- the transverse heater which is formed galvanoplastically
- the procedure to evaluate the influence of Joule heating in the input leads by means of variation of the current.

RECENT ADVANCES IN THERMAL SUPERINSULATIONS

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Load bearing, evacuated, fibrous superinsulations show very low thermal conductivity also at elevated temperatures (values as low as 4 mW/(m*K) have been measured for boundary temperatures of 650 and 300 K and under an external load of 1 bar). Analysing the usual conductivity versus radiative temperature diagrams shows that half of the total heat transfer is caused by solid thermal conduction via contacting fibers whereas the remaining part is due to radiative transport. Attenuation of radiative flow by scatterring and absorption processes within the fiber network delivers extinction coefficients of about 50 m^2/kg for pure (conventional) glass fiber insulations.

We have thoroughly studied the potentials for a reduction of heat losses that result from both transport mechanisms. Following an interesting prediction of Mie theory of scattering, a strong improvement of radiative extinction can be expected from application of very thin, pure metallic or metal coated glass fibers. With a fiber diameter of about 0.3 μm, extinction coefficients of more than 1500 m^2/kg have been achieved. These findings will drastically reduce radiative losses in comparison with conventional glass fiber insulations. The corresponding extinction measurements have been performed with a FTIR spectrometer. In a second (parallel) step, we have investigated a reduction of the solid conduction by means of peg-supported insulations. The remaining solid conductivity amounts to about 0.5 mW/(m*K) only, which is an improvement by a factor of 4 compared with non-segmented (conventional) glass fiber boards. These experiments applied two evacuated, load-controlled, guarded hot plate devices.

Realization of these new findings on a technical scale will strongly increase the thermal performance of superinsulations in a variety of low and high temperature applications.

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IDENTIFICATION OF RADIATIVES PROPERTIES RESPONSIBLE FOR THERMAL PERFORMANCE OF FIBROUS INSULATIONS

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The heat transfer in thermal insulations takes place by a complex mechanism associating the conduction or convection through the gas surrounding the fibers, to the thermal radiation propagating through the pores by an emission, absorption and scattering process.

To improve the performance of these materials, without increasing their density, a good knowledge of the heat transfer mechanisms is necessary, particularly that of the thermal radiation which is the most complex and yet less explored mechanism. So, a performance improvement can be hoped through a better characterization of the radiative properties of such materials.

The light porous materials, widely used as thermal insulations, behave -from the radiative view point- as anisotropic scattering semi-transparent media, presenting a highly forward-peaked phase function.

To identify the radiative properties of these materials, i.e. the coefficients of spectral absorption and diffusion (or the albedo), it is necessary to :

- develop a model for the radiative transfer in an homogeneous medium equivalent to the real medium, from a radiative view point ;
- elaborate an experimental technique to obtain certain results leading to the identification of these properties.

The identification technique used here is based on an experimental determination of the bidirectional spectral transmission in the infra-red range (2-10.5 µm), combined with a radiative transfer model of the discrete ordinates type. The Henyey-Greenstein representation for the phase function has been used.

This technique can be used in a temperature range varying up to 400°C from the ambient temperature. In this range, it has been experimentally found, for the first time, that the spectral radiative properties of ordinary fiberglasses slightly vary with the temperature.

The results presented here for ordinary fibrous insulations are compared with the hardly existing results, obtained through other less elaborated models, and experimental techniques.

The observed deviations, particularity for the albedo -a parameter difficult to identify- have been analysed, and the intended improvements are indicated.

This technique can be applied to a variety of diffuse participating media, in addition to the fibrous thermal insulations.

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For her contribution to that work, Mrs. Geneviève UNY was awarded in 1987 with the "Prix A.F.M.E. 1987 de la meilleure these en Sciences de l'Energie".

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HYDRODYNAMIC EFFECT IN SOLIDS

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If the hydrodynamic conditions $l_R/l_N \gg 1$, $d^2/l_R l^N \gg 1$ are fulfilled, the motion of the quasiparticle gas in large perfect crystals under the action of an applied electrical field or temperature gradient is analogous to Poiseuille flow of viscous gas (space nonuniform flow along a tube) which might manifest itself in significant changing of the dimension and temperature dependence of the proper kinetic coefficients. Here l_R and l_N are the quasiparticle mean free path for resistive and normal scattering, d is the diameter of the crystal. The behaviour of electrical conductivity of noncompensated metals and thermal conductivity of compensated metals, magnetics and dielectrics was calculated firstly by R.Gurzhi (and independently by Sussman and Thellung for the phonon system), and of the phonon drag thermopower by V.Kozlov and E.Nagaev. Numerical calculations of the effective mean free path of the quasiparticles (V.Kopylov, L.Mezhov-Deglin) by Monte-Karlo method had shown the existance of well known Knudsen minimum as the temperature is reduced and the Poiseuille flow is replaced by Knudsen flow of the quasiparticle gas in the large crystals.

INFLUENCE OF PARAMAGNETIC RARE EARTH IONS ON THERMOCONDUCTIVITY OF ORDERED AND DISORDERED MATERIALS

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A new effect in thermal conductance - resonance phonon scattering on paramagnetic levels of rare earth ions split by crystal field - is investigated experimentally and theoretically.

Inner shells of paramagnetic ions are filled only partly.Their orbital (L),spin (S) and full (J) moments are not equal zero. A state of a free paramagnetic ion with full moment J is (2J+1) degenerated. In a lattice these degenerate levels are split by crystal field.Lattice vibrations can transfer ion from one to another level with annihilation of a phonon. So paramagnetic ions - are defects decreasing thermoconductivity of a crystal lattice ($\varkappa_L$).

Unfilled f-shells of rare earth lie deeply in atoms.Their splitting in crystal fields is ~ 100K. Hence an effect of decreasing $\varkappa_L$ can be observed in a mean temperature range. This is practically important.

In this report we discuss the influence of rare earth ions on in next cases:

- they are impurities;
- they form regular ordered lattice;
- they form regular lattice with defects;
- they are components of a glass.

Experimentally decrease of $\varkappa_L$ due to resonance phonon scattering by paramagnetic rare earth ions ($-\Delta\varkappa_{res}$) is measured as difference between $\varkappa_L$ of crystals containing paramagnetic rare earth ions and $\varkappa_L$ of crystals containing the same concentration of rare earth ions with zero L or J (such as La^{3+}, Eu^{3+}, Gd^{3+}, Lu^{3+})

Thermoconductivity has been measured in:

$Y_{1-x}Ln_xAl_5O_{12}$ (Ln= Gd,Tb,Dy,Er,Tm,Lu);

PrS, Pr_3Te_4, Pr_2Te_3 ;

$Pr_2S_3 \cdot X(Ga_2O_3)$.

As reference were used LaS, La_3Te_4 , La_2Te_3, $La_2S_3 \cdot X(Ga_2O_3)$
All crystal materials have cubic symmetry, valence of rare earth ions is +3. In the investigated temperature range 4-400K there are no magnetic ordering.

Experimental results show:

a) ($-\Delta\varkappa_{res}$) has a maximum at T_{max} connected to a splitting of paramagnetic levels Δ (a direct dependence of T_{max} on Δ_1 - energy of the first split level - is observed);

b) a character of temperature dependence of ($-\Delta\varkappa_{res}$) at $T \gtrsim \theta$ (θ - Debye temperature) and $T \gtrsim T_{max}$ is related with rare earth ion concentration in a lattice with a neighbourhood, with a phonon scattering mechanism and degree of perfectness of a lattice;

c) a size of effect is rather large and ($-\Delta\varkappa_{res}$) is more in a defect lattice (and in completely disordered system - in a glass) than in a perfect lattice;

d) temperature dependence of ($-\Delta\varkappa_{res}$) is in general similar to $C_{sch}(T)$ (C_{sch} - Schottky effect in thermal capacity). T_{max} of both effects coincide. So the observed effect of decrease of a lattice thermoconductivity due to resonance phonon scattering on paramagnetic rare earth ions is analogue of the Schottky effect - increase of the thermal capacity of the same systems.

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THERMAL PROPERTIES OF SOME INCLUSION COMPOUNDS.

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The guest-host structures of inclusion compounds allow the study of several unusual aspects of thermal properties, including the interactions of unlike molecules in well-defined environments and the additivity of these interactions.

In this paper we will present our recent findings concerning heat capacities and thermal conductivities of two systems of inclusion compounds - clathrate hydrates and clathrates of a large organic molecule (Dianin's compound).

The work on clathrate hydrates has allowed us to formulate an explanation for their exceptionally-low thermal conductivity, in terms of the interactions between the guest lattice and the host species.

Our recent studies of the thermal properties of clathrates of Dianin's compound allow us to investigate the thermal properties of a small cluster of guest molecules, and also to examine the additivity of the properties of the guest and host species.

The influence of external fields on the thermophysical properties of technological materials.

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Since the physical properties of given material are closely connected with the conditions of its technological preparation, two problems are theoretically studied:

a) How the variations of the temperature may change the coexistence conditions of the appropriate volume phases within the system in which the first-order phase change takes place (viz., solidification). The problem of the so-called striations in solid is solved with use of the bifurcation theory; as example, the striations distribution in the Fe-Si system is computed.

b) How the thermophysical properties (such as, e.g., coefficients of thermal conductivity) of solid of given texture (e.g. lamellar eutectic) can be influenced by the external fields (gravitational, thermal etc.). Using the method of the singular perturbation of bifurcations it is shown the strong dependence of the growing solid phase on the external fields. The stable states of the system under consideration are presented. As example, the changes of the global thermo-conductivity coefficient of the lamellar system are determined under various values of the external fields.

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A new model for the non-steady-state probe method to measure thermal conductivity of porous and granular materials

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Starting point is the modified Jaerger model. This cylindrical model takes into account the major properties of the probe, the thermal conductivity and the heat capacity of the medium and the contact resistance between the probe and the medium. Because the mathematical description results in nonlinear functions of these three thermal parameters, the Gauss-Newton iteration method has been used. To obtain a better description of the measurement for small time values, a second order time correction has been added. The experimental test results in an inaccuracy of 0.5 to 2% for the thermal conductivity, while the other two parameters were accurate to within 5 to 15%.

THERMAL PROPERTIES MEASUREMENT OF DIFFERENT CONCRETES

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This paper presents an experimental work concerning the evaluation of the thermal properties of different concretes with particular reference to their dependence on some other parameters of the material such as density, water content, temperature, type of aggregate.

Both mortar samples of different density and concrete samples have been tested. For these last ones the following aggregates have been employed: expanded clay and sintered pulverized fuel-ash for lightweight concretes, natural gravel for normal weight concrete and barytes for heavy weight concrete.

Thermal properties measurements have been performed on each sample from fully saturated to oven dry condition.

In order to avoid water migration during the run time of the thermal tests a transient measurement method has been used.

It employs two linear and parallel probes inserted in the specimen and allows to measure simultaneously thermal conductivity and diffusivity in few minutes.

The results exhibit that thermal conductivity increases with the density and the moisture content of the concrete and that the rate depends on the type of concrete.

In this respect a comparison with some relationships reported in literature is made.

Moreover, thermal diffusivity shows an increase with the density while it does not seem to depend on the moisture content.

As regards the effect of the temperature, some preliminary results show that both thermal conductivity and diffusivity of the concrete decrease with the increase of it.

TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITIES AND THERMAL DIFFUSIVITIES OF COMPOSITES USING TRANSIENT HOT STRIP-METHOD

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Simultaneous measurement of thermal conductivity and thermal diffusivity of four composite building materials viz., Black marble stone, Normal building stone, Red sand brick and cement brick have been done at room temperature using transient hot strip method. Power supplied to these samples is quite large as compared to loose building materials owing to their composite (brick) nature. Temperature dependence of thermal conductivity and thermal diffusivity of these materials has also been investigated in a temperature range from 10°C to 60°C. Temperature stability is assured within 0.1°C by using Platinum resistance thermometer, in the chamber containing samples, and a digital voltmeter to record any variation in resistance. Results of these experiments exhibit that there is a very slight variation in thermal conductivity and thermal diffusivity of these materials in this temperature range.

KEY WORDS. Transient hot-strip characteristic-time Thermal-
Conductivity Thermal-Diffusivity

DURUM HEAT PASTA THERMOPHYSICAL PROPERTIES

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Two transient methods were used to determine thermal conductivity of extruded durum wheat pasta : the flash method and the hot wire method. The experimental results were obtained in the humidity range lying between 12 to 33 percent, between 20 to 80°C.

Thermal diffusivity data obtained with flash method decreased when temperature and pasta moisture content increased; that property was fitted with and empirical relationship $a = f(x_E,T)$ with a mean error of two percent.

Besides, pasta thermal conductivity determined with hot wire method slightly increased with moisture content and was almost independent of temperature.

Results with the flash method were compared with thermal conductivity values measured with the hot wire probe; despite the differences of sample geometry and heat transfer models, the results were almost consistent.

Thermal conductivity data analysis with different conduction models showed that the series model was the best appropriate to fit our experimental results.

Intrinsic conductivity values were in agreement with literature and almost independent of temperature.

The International Temperature Scale of 1990 (ITS-90)

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It now seems likely that the International Practical Temperature Scale of 1968 (IPTS-68) is going to be replaced by a new international temperature scale, the International Temperature Scale of 1990 (ITS-90), expected to come into force on January 1st 1990.

In this lecture I shall show why a new international temperature scale is necessary, describe the work that has gone into the preparation of the new scale, give an outline of the probable form of the new scale and give the numerical differences $\underline{T}_{68}$ and $\underline{T}_{90}$ as far as they are known at present.

Before the new scale can be finalized, however, there remains a considerable amount of work to be done by the Comité Consultatif de Thermométrie and its Working Groups. I shall discuss the various points still at issue and give the timetable that will have to be met if ITS-90 is indeed to come into force on January 1st 1990.

THERMAL CONDUCTIVITY DATABASE FOR SOLID MATERIALS

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A thermal conductivity database for metals, ceramics, and other inorganic solid materials is under construction. Specific heat, thermal diffusivity, emissivity, coefficient of thermal expansion, electrical resistivity, and sound velocity are included as supplementary information. To evaluate and utilize thermophysical property data of solid materials, we require sufficient information about characterization of solid material which is much more complicated than that of fluid. So we are making study what scheme the database should have for effective storing, retrieving, and maintaining numerical data with material characters.

Description of material characters is divided into two levels. One is general characters of material which is chiefly used for material searching. The other is deatiled characters and information about individual specimens including experimental conditions. The database has individual data tables corresponding to each property, which allows quick search of materials identified by a temperature range and/or property range. The database allows to identify data of different properties that are taken for a specimen or specimens cut from a lot. This will facilitate multiproperty investigation of material in which exactly the same characters are ensured for the data.

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Thermal Conductivity and Thermal Diffusivity of a Cordierite-based Ceramic. Results of a CODATA Measurement Program.

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The objective of the CODATA Task Group on Thermophysical Properties was to improve the quality of thermophysical property data on solid materials generated worldwide.

Initially a measurement program was focused on thermal transport property determination on pure metals (Fe and W), austenitic stainless steel and polycristalline graphite, which were designated as standard reference materials (SRM). For the broad class of ceramic materials, there is practical interest in technology and industry for developing SRM's with conductivities in the low conductivity range and usuable across a broad temperature spectrum. The measurement methods themselves are generally well established, but improvements in precision and accuracy are needed. SRM's are also required to facilitate reliable, relatively high accuracy measurements. That is why a methods/SRM's program was initiated in the low conductivity materials.

Materials identified as potential SRM's included Pyroceram 9606, black Vycor and a sintered cordierite-based ceramic. The initial program was performed with the cordierite-based ceramic provided by Lafarges Refractaire Co (France).

Four laboratories (France, Germany, U.S.A., Yougoslavia) used the hot-guarded-plate method, and two others (Austria, U.S.A.) used comparative method for the thermal conductivity measurement.

Nine laboratories (Canada, France, Germany, Sweden, U.K., U.S.A., Yougoslavia,) participated in the thermal diffusivity program, using the flash or modulated-beam methods. The results of the thermal diffusivity measurements fit a fifth-order polynomial, with a standard deviation of about 5 %. The deviations were lower above 600 °C than below these temperature. Any systematic deviation could not be ascribed to the method of measurement.

The deviations for the thermal conductivity results were larger than for the thermal diffusivity results. A good approximation for all the results is the linear relationship : $\lambda = 1.45 - 2.00 \cdot 10^{-4} \cdot t$ (W/mK - °C)

TRANSPORT PROPERTIES OF COPPER SRM

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The paper presents the results of an experimental study of transport properties of the copper candidate standard reference material (NBS). Thermal diffusivity was measured by the laser pulse technique in the 550 to 1200 K temperature range. Electrical resistivity was measured by the four probe technique in the 295 to 1300 K range. The experimental results are compared with the literature and recommended transport property data for copper. Experimental and averaged results are presented and discussed.

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SUBSECOND PYROMETRY AND ITS APPLICATIONS TO THERMOPHYSICAL MEASUREMENTS

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Developments of millisecond and microsecond resolution pyrometers during the last two decades are reviewed. Emphasis is placed on accurate fast pyrometers designed, constructed, and used at the National Bureau of Standards for rapid temperature measurements above 1000°C.

Operational characteristics of fast pyrometers are discussed and the results of extensive tests performed on both millisecond and microsecond resolution pyrometers are presented.

Examples of applications of fast pyrometers in high temperature research are given. Particular emphasis is placed on the use of these pyrometers in measurements of selected thermophysical properties of solid and liquid substances by rapid pulse heating techniques in the temperature range 1000 - 5000°C.

Ongoing research in developing accurate fast multiwavelength and spatial scanning pyrometers are presented. Further research directions vis-a-vis needs for new fast pyrometers are briefly discussed.

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DETERMINATION OF THE MELTING POINT AND OF THE EMISSIVITY OF REFRACTORY METALS WITH A SIX-WAVELENGTH PYROMETER

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The modern research in the domain of new materials, advanced ceramics, amorphous metals and high temperature alloys urgently requires the development of pyrometers able to measure with a good precision temperatures of samples of unknown emissivities in a millisecond timescale up to 5000 K.

A six-color pyrometer has been used to measure the melting point and the emissivity of nine refractory metals: hafnium, niobium, molybdenum, rhenium, rhodium, tantalum, vanadium and zirconium.

The experiment has shown that at the melting point all these metals behave like grey-bodies, i.e. their emissivities are independent of the wavelength of the emitted light. Though the physical meaning of this property is still obscure, its technological interest for calibration of multi-wavelength pyrometers at high temperatures is evident, especially under difficult working conditions (typically when the samples are heated in optically absorbing atmospheres).

In many metals and conductive ceramics the isotherm of emissivity $\varepsilon_L(L)$ are found to cross each other at a particular wavelength L_x, called X-point, or within a very narrow interval δL_x. These results have been extended up to and beyond the melting point, and it was found that the emissivity at this temperature is independent of the wavelength and equal to the emissivity at the X-point.

A first analysis of this effect is presented

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The Spectral Emissivity of Metals and Non-Metals in the Wavelength Range 400-15000 Nanometers and their Total Emissivity

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The determination of the temperature of a surface from measurements of the spectral radiance at six wavelengths, using the six-color pyrometer, relies on a simple expression for the spectral emissivity variation as a function of the wavelength. The spectral emissivity data of W, NbB TaC, WC, ZrC, HfN, TaN, ZrN, Al_2O_3, Cr_2O_3, MgO and ThO_2 have been investigated, and in the wavelength region 400-3000 nanometers ε can be expressed as $\ln \varepsilon = a + b\lambda$ where a and b are constant with the wavelength, but can vary with the temperature.

In the wavelength range 3000-15000 nanometers, there is a rapid rise and decrease of the spectral emissivity of Al_2O_3, Cr_2O_3, MgO and ThO_2 ; in this range, the variations of the spectral emissivity can be represented by the equation $\ln[\varepsilon/(1-\varepsilon)] = c + d\lambda$. The total emissivity is deduced from these equations, and compared with the experimental value.

Conclusions on the application of six-color pyrometry are presented.

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THERMAL DIFFUSIVITY MEASUREMENT BY PULSED METHODS

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The pulsed method called "flash" method is world-wide used for the determination of the thermal diffusivity. During the last twenty-five years it was progressively improved thanks to the theoretical works of many searchers. The precision was enhanced and the application field widely enlarged. The last developments in these two directions will be developped in the conference.

In other respects, not only this method profited by progresses in the experimental techniques due to the impressive development of the quantum optics, but also new methods appeared, with the generic name of "photothermal methods". In particular the pulsed photothermal methods (by radiometry, mirage effect,...) where applied to the diffusivity determination. They may be considered as complementary to the classical "flash" method as they bring new possibilities and new domains of application -such as very thin layer samples-. A brief description of these new methods will also be given.

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Thermal diffusivity of carbon fibre reinforced silicon carbide matrix composites.

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Thermal diffusivity of a three dimensionally reinforced carbon fibre silicon carbide composite has been measured over a range of temperature up to 1500C using the laser flash method. Samples of varying thickness, diameter and density have been tested. The orientation of the reinforcing fibres is such that four fifths of the fibres lie in one plane and the remaining fifth are arrayed perpendicular to the majority of fibres. Diffusivity measurements have been made on samples where heat flow is either parallel or perpendicular to the plane containing the larger number of fibres.

Samples tested up to 1200C showed either no change or a slight rise in diffusivity on cooling. This increase did not persist to 200C. Heating to higher temperatures (~1350C) resulted in a larger increase in diffusivity on cooling. In this case recovery to the initial value was incomplete. Whilst the increase was partially a hysteresis effect, some permanent increase was observed at 200C. A much greater permanent increase was observed when samples were cooled from 1500C. Possible reasons for this behaviour have been considered.

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Thermophysical Properties of Thick Wafers of Boron Phosphide

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The present paper describes thermoelectrical and thermal characterics of well-characterized boron phosphide single crystalline wafers made by CVD process to clarify intrinstic thermophysical properties. The high light of the present paper lies in the measurement of thermal diffusivity, because conventional lase flash method was many problems to apply thick wafers.

The electric conductivity of the wafers of n-type increases with temperature, becomes constant and then begin to decrease with temperature. In the case of p-type wafers the conductivity increases with temperature and upon further increase of the temperature the intrinstic conduction region is reached.

The absolute thermoelectric power for n-type materials shows almost constant values of 500μV/K, but it begins to decrease at the temperature of 650K due to the creation of acceptors. The thermoelectric power for p-type materials decreases with increasing temperature, indicating that acceptors and donors contribute to the conduction.

We have solved difficulity in laser flash method by using ring flash light, which originates from many-variable analysis based on two-dimentional model. The thermal diffusivity is calculated by fitting temperature profile curve to theoretical equation. The thermal diffusivity thus obtained has large value of 1.8cm^2/s at room temperature and it shows pronounced temperature dependence charactterized by phonon scattering. Thermal diffusivity is also measured by photo-AC method. Thermal conductivity is calculated from the product of the thermal diffusivity and specific heat capacity by DSC method. A fairly good agreement with thermal constants between two methods was established. The thermal conductivity of BP single crystalline wafer is to be 4.0W/cm.°C at room temperature. This value is far larger than that of sintered BP discs(0.08W/cm.°C) and is comparable to that of boron nitride. The thermal conductivity decreases with increasing temperature. Then boron phosphide is a promising material for radiating substrate up to high temperatures.

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FAST PULSED PHOTOTHERMAL METHOD APPLIED TO DIAMOND LIKE AND SiC COATINGS

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We applied pulsed back emission photothermal radiometry to the characterization of a 1.1 µm diamond like coating (DLC) and a 40 µm SiC coating. The first one is used as a nonreflective layer for Germanium infrared windows, the second as a CVD deposited matrix in a SiC composite. In these experiments, we employed a 50 ns pulse duration ruby laser, a HgCdTe detector and electronics with a total bandwidth of 70 MHz. The experiment was validated, using a polished copper sample, in order to find the $1/\sqrt{t}$ theoretical time dependence of the temperature. For the characterization of the first coating, a three layer sample was realized, constituted by an Aluminium substrate, the DLC coating to characterize and a second coating (2.4 µm of Aluminium) to avoid absorption problems. We used for this experiment a hemispherical reflecting cavity for increasing the emissivity of the sample surface.Thermal properties of the coating were found by comparison between the experimental curve and the result of a numerical calculation. For the second characterization, the sample was a 40 µm SiC coating deposited on a graphite substrate. For this experiment, the cavity was needless, because of the good infrared emissivity of the SiC surface. The results seems in this case to indicate that the effusivity of the SiC is equal of the substrate's one.

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RECENT THERMAL EXPANSION MEASUREMENTS AT THE NATIONAL MEASUREMENT LABORATORY

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Recently we have measured the linear thermal expansion of a number of solids which show interesting behaviour.

(a) High T_c superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $Y\ Ba_2Cu_3O_7$ which show small (~1%) changes in α near T_c and more marked anomalies at high temperatures.

(b) CrMn alloys with large magneto volume effects at low temperatures, positive or negative depending on composition.

(c) Zn_2SiO_4 (Willemite) which has negative volume expansion below room temperature.

(d) Other materials of basic or technical interest including TeO_2 (Tellurite).

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DENSITY OF TERPENE MIXTURES OF TURPENTINE FROM *Pinus Pinaster*

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The knowledge of the thermophysical properties of the components of olio resin from *pinus* is very important for the design of chemical processing plants of naval stores industry, both for first generation products and derivatives.

As a first study of an overall program of measurement of the thermophysical properties of the components of olio resins and derivatives initiated by our group, the density of several mixtures rich in beta-pinene and alpha-pinene have been measured as a function of temperature from 298 to 313 K, using a digital densimeter. The densimeter was calibrated with benzene and water and the densities obtained are expected to have an accuracy of 0.3%.

A correlation of the density dependence on temperature and the molecular nature of the components in these mixtures will be presented and discussed.

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MEASUREMENT OF THE THERMOCHEMICAL EXPANSION OF POLYMER COMPOSITE MATERIALS

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The thermochemical expansion of two widely used glass-filled phenol-formaldehyde (phenolic) resin composites was measured using a new high-temperature pushrod dilatometer capable of operation to 2200°C. The dilatometer is equipped with a computer control and data acquisition system. The expansion characteristics of both materials were measured to temperatures in excess of 2000°C at several heating rates. The expansion was found to be a strong function of temperature and heating rate during the low-temperature pyrolysis reactions. During the high-temperature carbon-silica reactions, the expansion was found to be a strong function of temperature, with minimal dependence on heating rate.

The expansion results are presented graphically, depicting expansion as a function of temperature and heating rate. A detailed discussion of these results is presented along with references to other material properties and their influence on the expansion results.

Prior to the study of the expansion characteristics of the composites, the accuracy of the dilatometer was established. This was accomplished by calibration of the instrument for both the temperature and length signals. Because of the very large temperature range of the dilatometer, unique calibration materials and techniques were utilized. Clearly, the calibration procedure is of paramount importance for pushrod dilatometers to insure accurate thermal expansion results. A detailed discussion of both the calibration technique and materials, as well as the accuracy of the measurements, is presented.

Finally, the expansion characteristics of a material must be measured in the absence of any chemical reactions between that material and the dilatometer components. At present, the dilatometer components in contact with the sample material are fabricated from graphite. It has been observed that graphite participates in the high-temperature carbon-silica reactions which these particular materials undergo at temperatures in excess of 1000°C. This requires identification of materials which will not react with the composites at temperatures above 1000°C. A discussion of the compatibility of several high-temperature materials such as Al_2O_3, SiC, HfC, BN, etc. with the composite materials of interest is also presented.

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*Some of the measurements were conducted at Netzsch Geratebau in Selb, Germany.

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EXPERIMENTAL DETERMINATION OF THE PERMEABILITY OF POROUS COMPOSITE MATERIALS

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Permeability, as a property of decomposing polymer composites, is necessary for the prediction of the flow of gases generated within the composite matrix as a result of decomposition. Previous studies on flow characteristics of porous media have been confined solely to the Darcy regime wherein the flow is laminar and the inertia forces are negligible. The present investigation is directed towards the measurement of permeability in the non-Darcy flow regime where the inertia forces play a significant role. Here, attention has been focused on two different glass filled phenol-formaldehyde polymer composites designated as Haveg H41N and MXBE-350.

An experimental apparatus has been designed and constructed to measure the permeability as a function of the decomposition temperature of a composite sample. Pre-decomposed samples were placed in the test section and the volumetric flow rate of gas through the sample as a function of the pressure difference across the sample was measured. The permeability and inertial coefficient of the sample at various stages of decomposition were calculated using the equation for non-Darcy flow in a porous media.

Results are presented for samples preheated to temperatures of 400, 500, 600, 700, 800, 900, and 1000°C. Results indicate that for MXBE-350 the permeability increases steadily up to a decomposition temperature of 600°C and then declines to a constant value as the material becomes fully charred (beyond 900°C). Haveg H41N which has high internal pressures because of its tighter fibrous structure cracks after the onset of pyrolysis reactions during heating. Since there is no way of eliminating propagation of cracks within the Haveg sample, the permeability results for the material show considerable scatter. The results also indicate that the inertial coefficient (β) is large when the permeability (κ) is small.

CORRELATION OF THERMOPHYSICAL PROPERTIES OF BRITTLE MATERIALS WITH THEIR FRAGMENTATION CHARACTERISTICS

by

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Thermal fracturing of brittle materials is a thermophysical process in which thermally induced stresses exceed the strength of the material, causing it to break. A subject of various studies in the past, thermal fragmentation has not only been the topic of scientific curiosity but also, with the advent of advanced ceramics and their use in energy generating devices, of significant technological importance.

Numerous theoretical equations have been formulated by different authors. However, studies of thermal fragmentation of several types of brittle materials made in this laboratory revealed a fundamental variance between accepted theoretical concepts and the experimentally obtained correlation of thermal fragmentation and thermophysical properties.

Keywords: thermal fragmentation, brittle materials, spalling, thermal diffusivity, thermal expansion.

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Thermophysics of B_1-B_2 Phase Transitions

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The prediction of the change in elastic properties through phase transitions of simple oxides that may be present in the deep mantle of the Earth may be modelled from lattice theory and experimental data at moderate pressures of simple ionic compounds such as alkali halides. The bulk modulus change across these transitions is of particular geophysical importance since it is directly related to sound velocity. Serious disagreement exists between experimental data and theory *and* among the experimental data concerning the change in bulk modulus both in sign and magnitude across the B_1-B_2 (fcc-bcc) phase transition. For example, values of the change in the zero pressure bulk modulus, ΔB_0, calculated from X-ray data of NaCl disagree by 400%.

We have accurately measured the change in volume and elasticity through the B_1-B_2 phase transition of KCl, KBr, KI, and RbCl on large samples ($V_0 \cong 15$ cm^3) in a hydrostatic medium in the piston cylinder apparatus. This method yields accuracies in ΔV and change in bulk modulus, ΔB, of 0.1 and 1%, respectively and is, therefore, a good test for simple models that predict the change in elasticity through B_1-B_2 transitions at higher pressures. $\Delta V_{tr}/V_0$ in our experiments ranges from 8.3 to 14.6% and is always larger than the changes in elasticity across the transition. This results in decreases in the bulk modulus of between 3 and 9%, contrary to theoretical calculations. Accurate values of the change in Grüneisen parameter across the phase transition will also be presented.

Pressure dependence of solid-solid and solid-liquid phase transitions in $CsHSeO_4$, $RbHSO_4$ and $RbHSeO_4$ studied by differential scanning calorimetry.

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In the temperature range 350 - 480 K $CsHSeO_4$, $RbHSeO_4$ and $RbHSO_4$ have two types of phase transitions:

1) The first one is transitions with large enthalpy changes, about 5 - 30 kJ/mol, giving large changes in crystal symmetry. These transitions are reversible in the sense that they are detected by DSC technique both when heating and cooling a sample. In $CsHSeO_4$ and $RbHSeO_4$ these transitions, at 400 and 447K respectively, are from a non conducting to a protonic conducting phase. In $RbHSO_4$ it is the melting at 476 K.

2) The second one is transitions with lower enthalpy changes, about 0.5 kJ/mol. These transitions are detected by DSC only during the heating cycle and the reproducibility with respect to transition temperature and enthalpy is less than for the first type. The main difference between these two types of phase transitions is that a special treatment of the material is a condition for appearence of the second type. This treatment can be of exposure of the material to water vapour or mechanical treatment as for example grinding. The transition temperatures are at 355, 372 and 439 K for $CsHSeO_4$, $RbHSeO_4$ and $RbHSO_4$ respectively.

In this study DSC technique was applied for investigations of the two types of phase transitions at normal and high pressure. The dependence on pressure was determined for the transition temperatures and enthalpies and changes in volume were calculated by means of the Clausius-Clapeyron relation.

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HEAT TRANSFER PROPERTIES OF SALTS OF INTEREST FOR ENERGY STORAGE STUDIED BY MEANS OF THE TRANSIENT HOT STRIP (THS) METHOD

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Literature data for the thermal conductivity of a solid refer to large pieces of the material in question, while there are many applications where the effective thermal conductivity is strongly affected by the grain size, packing, porosity, composition changes etc. This is the case for some devices intended for heat storage. E. g. a chemical heat pump operates by means of absorption-desorption processes where the number of ligands attached to some salt is changed continuously during the process. Water and ammonia are examples of ligands considered for heat pump applications. Heat can be stored as latent heat when a suitable substance is melted and released when it solidifies, i. e. the substance is cycled between the solid and the liquid state. Hydrates are the most common candidates for storage at temperatures slightly above ambient.

The transient hot strip (THS) method is very suitable for "instantaneous" determinations of the thermal conductivity and diffusivity of heat storage materials under different experimental conditions. We have studied some heat storage materials based on calcium chloride, sodium sulphide, sodium sulphate, magnesium chloride and magnesium nitrate. The effective thermal conductivity was found to change drastically during some treatments. Some examples will be given to show the relative importance of different parameters.

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THE EXPERIMENTAL STUDY OF THE SOUND SPEED AND THE ATTENUATION COEFFICIENT IN TITANIUM INCLUDING THE REGION OF POLYMORPHIC PHASE TRANSFORMATION

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The original variant of pulse method of measuring the sound speed and attenuation coefficient developed by the authors and used on the wire samples is described. The unit allows to carry out reseacn in the temperature range of 300-1500 K.

The results are given for the experimental study of acoustic properties of pure and doped titanium in the temperature range of 300-1300 K using deformed and annealed samples. The region of polymorphic phase transformation is studed in details. It is shown that the values of sound speed and attenuation coefficient depend on the degree of deformation. The existence of impurities in doped titanium causes substantial changes of the sound speed values.

In the region of polymorphic phase transformation there are three kinks (drastic changes) of the sound speed and attenuation coefficient curves. The attenuation coefficient of doped titanium is higher than of the pure one, and the temperature dependence maximums are lower and less sharp. It is mentioned that the suggested method gives high measurement accuracy.

HEAT CAPACITY OF GLASSY CRYSTALS

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Liquids as the most common representative of disordered systems can solidify in two ways; either discontinuously to a crystalline solid at the freezing temperature or continuously to a non-crystalline solid through the glass transition range. The glassy liquid retains a residual entropy associated with the freezing of remaining disorder. Likely, crystal in orientationally disordered phase can be cooled down in a thermodynamically non-equilibrium state by by-passing the solid-solid phase transition. The undercooled disordered phase shows a relaxational heat-capacity jump at T_g and has a residual entropy. The non-equilibrium, frozen-in orientationally disordered state of crystal is called as glassy crystal.

Enthalpy relaxation around T_g can be studied by observing the calorimetric temperature as a function of time under an adiabatic condition. Relaxation time derived from the heat capacity data and the spontaneous temperature drift rates is well correlated with dielectric relaxation time data of the same polar substance. These studies clarified the wide occurrence of freezing phenomena in crystals as well as in liquids and liquid crystals.

Freezing occurs also in a stable crystal. Ice I_h is a historically famous example exhibiting both T_g and residual entropy. The freezing of water reorientation was found recently to be removed by doping the ice lattice with a minute amount of alkali hydroxides. The incorporated OH^- ions infringe the ice rules and accelerate dramatically the proton configurational motion to induce a first-order phase transition at 72 K in the crystal within a reasonable experimental time.

Glassy crystals are promising substances to renew the concept of glass transition phenomena and to clarify the nature of disorder in non-crystalline materials. The translational invariance of the molecular center of mass is helpful in simplifying the complexity of disorder existing in glassy liquids.

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MICROSCOPIC MODEL OF GLASS TRANSITIONS

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Some kind of phase transition from a liquid to an amorphous solid, a glass, seems to be a very general phenomenon, provided one can prevent crystallization to occur. Computer simulations on hard sphere and Lennard-Jones systems have given strong indications that even such simple systems have a liquid to glass transition, if the cooling rate is high enough. Experimentally one finds that the transition is connected with rather sudden changes in heat capacity, thermal expansion and compressibillity, but the most dramatic changes are for some of the transport properties. Of particular interest is to analyse the density fluctuations, since they can be studied experimentally through a variety of techniques such at neutron scattering, Brillouin scattering, photon correlation measurements, dielectric loss measurements etc.

A dynamical and microscopic model for a simple monoatomic system, which contains a mechanism for liquid-glass transition, will be described. This model makes predictions which are in quite remarkable qualitative agreement with what one finds experimentally for real glass forming systems. Extensive experimental work, particularly through neutron scattering, is going on at various places in order to test the validity of this model. The theory is based on an approach, which nowadays is quite commonly used for calculating various dynamical quantities, particularly the density correlation function, for ordinary liquids and which has been found to work very well.

A large number of phenomenological models for the liquid-glass transition have been presented in the past and a brief discussion is given of how some of them can be connected to the present model.

ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF SAMARIUM PHOSPHATE GLASSES

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The first measurements of the d.c electrical conductivity and the low frequency (static) dielectric constant of samarium phosphate glasses (in the composition range 5 to 25 mole% Sm_2O_3) are reported. A break in the slope of the Arrhenius plot divides the conductivity data into two temperature regimes, the conductivity mechanism at low temperatures having a lower activation energy than that at higher temperatures. Addition of more Sm_2O_3 glass modifier into the P_2O_5 former results in a decrease in the absolute value of conductivity. The data are consistent with a small polaron transport and small polaron theory has been used to establish the characteristic energies of the carriers. The dielectric constants range from 5.4 for a glass containing 5 mole% Sm_2O_3 to 8.1 for that with 25 mole% Sm_2O_3; the temperature dependences of the dielectric constants are linear and positive - usual behaviour for glasses.

THERMOPHYSICS IN THE ELECTRICAL INDUSTRY

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Research studies on thermophysical properties in the electrical industry in the United States, and specifically at the General Electric Company will be reviewed. A discussion will be given of the initial problems requiring answers, the results and their scientific importance, and, in some cases, the final practical applications. Examples will be given from the published literature of studies of thermal contraction and expansion, thermal conductivity, thermal radiation, heat capacity, thermoelectric power generation, and thermoelectric refrigeration.

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QUICK CHARACTERIZATION OF HIGH T_c SUPERCONDUCTORS BY D.S.C.

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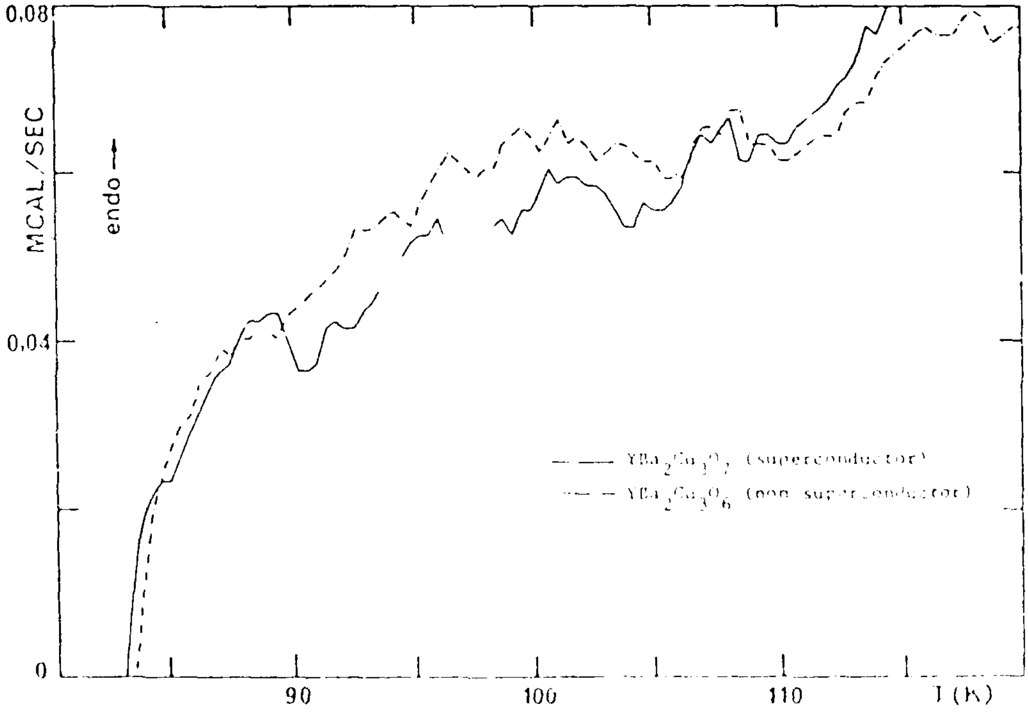
It has been possible to cool down DSC samples down to 83 K thanks to a special device adapted to a commercial Perkin Elmer DSC-2.

This facility opens the way to a survey of the thermal properties of the so called high-T_c superconductors. In that respect DSC presents a lot of advantages as it requires very small amounts of substance (20-50 mg) and gives a quick answer : it is therefore well suited to follow such parameters as the homogeneity of a batch or the influence of a peculiar treatment. The first results are encouraging :

i. the transition is clearly seen when other evidence has proven the existence of superconductivity and not seen in the reverse case (Fig. 1). This observation is reproducible.

ii. the order of magnitude of the transition is in good agreement with other results.

The new transition reported at 220 K has not been observed on the available samples.



THE CONTRIBUTION OF GRAIN BOUNDARIES TO THE ELECTRICAL CONDUCTIVITY OF SOLID URANIA

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The electrical impedance of single crystal UO_2 discs includes a contribution from an electrode layer as well as the bulk material. In polycrystalline material an additional contribution from intergranular conductivities might also be expected. To examine this possibility, complex plane spectroscopy (10Hz - 10MHz) has been used to make measurements of the temperature dependence, between 108 and 380K, of the electrical conductivity.

The impedance profile exhibits a voltage dependence at low frequencies, which indicates the presence of an electrode layer. Two other profile features have been identified and attributed to the bulk material and grain boundary conduction mechanisms. Standard Arrhenius analysis reveals three activation energies (0.13, 0.17, 0.3eV) for the bulk, electrode and grain boundary effects respectively. (Above 273K the dominating resistance is due to the grain boundaries which may have consequences for the high temperature behaviour.) The dielectric constant for the bulk material is 22.5.

Thermal conductivity measurements with the hot wire and steady state method

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The thermal conductivity of good conductive ($k \approx 20\ Wm^{-1}K^{-1}$) and rather poor conductive materials ($k \approx 0,03\ Wm^{-1}K^{-1}$) were measured by the use of the hot wire method and a steady state method. The interlaboratory tests were carried out with regard to the creation of a SRM for insulating material. Using the hot wire method the so called parallel wire as well as the cross wire method was applied. Two experimental set ups with steady state heat flow were also used. The comparison of the obtained results showed a good agreement between the transient and steady state method (~10%). The largest difference was found between the parallel and the cross wire method (<30%). The results and possible explanations for the differences are discussed.

Optothermal Laser Spectroscopy

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Most gaseous molecules are characterized by radiationless relaxation of the excited states in the infrared range. The excitation energy is transformed into kinetic energy by collisions with other gas molecules or with surfaces, leading to rising temperature.
The increase of the gas temperature after radiationless relaxation is used in the optoacoustic detector, well known in the laser absorption spectroscopy at gas pressures higher 10^3 Pa. To measure gas absorption at pressures below 10^3 Pa, direct detection of the temperature modulation by thermal detectors (optothermal detection, OT) is more advantageous.
Moreover, it has been shown by means of heat conducting equations, that there is a very simple relationship between the absorbed light energy in the gas and the heating of the thermal detector. If a cylindrically shaped thermal detector, for instance a thin PVDF-foil, is arranged inside a gas cell so that a light beam is propagating along the axis of the cylinder, the temperature variation ΔT of the detector after light absorption in the gas is the same, as it is after direct absorption of the light.

The following applications has been investigated:
Linear absorption measurements, especially for the atmospheric pollution detection (for this purpose we optimized an OT, by means of which we are able to detect NH_3 concentration in the air under field conditions down to ppb-region);
Sub-Doppler spectroscopy by means of standing optical waves, molecular beams (we placed a PVDF-film in a supersonic molecular beam of SF_6 to study the process of formation of clusters and also the single and multiphoton absorption spectra in the 10 /um region) or travelling waves (selection of excited molecules by means of a system of parallel ring disks perpendiculary to the laser beam);
Spectroscopy with pulsed light (exciting SF_6 molecules by strong CO_2-TEA-laser pulses and registrating the absorption in the gas by an OT it was possible to study the multiphoton absorption behaviour in the wide energy range from 5×10^{-9} Ws absorbed energy per puls up to about 10^{-5} Ws at laser puls energy up to 1 Ws under collisionless conditions).

Conclusions

By means of coupling thermal sensors with other spectral selective absorbers and using the heat transport in the absorbing medium it seems to be possible to open up new application fields in the analysis of materials and radiation.

Optical Measurement of Anisotropic Behavior of Thermal Diffusivity of Oriented Poly(methyl Methacrylate)

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The orientation of polymer molecules causes anisotropy of various physical properties of polymers. Though the oriented polymer is also expected to have the anisotropy of thermophysical properties such as the thermal conductivity or the thermal diffusivity, it is extremely difficult to measure the effect by the conventional experimental methods. The forced Rayleigh scattering method which has been improved by the present authors' group is an optical measuring technique for the thermal diffusivity. With this method, the thermal diffusivity can be determined within a very short time, by a very small sample volume and in contact-free manner. The capability to measure the thermal diffusivity in the particular direction in anisotropic materials is also one of its unique features. In the present study, the anisotropic behavior of the thermal diffusivity of uniaxially stretched poly(methyl methacrylate) was investigated in order to show the applicability of the method to measurement of oriented polymers. The stretch-ratio dependence and the angular dependence of the thermal diffusivity were measured and it was found that the thermal diffusivity along the stretch direction increases sharply with the progress of molecular orientation, whereas the variation of the thermal diffusivity perpendicular to the stretch direction is negligible. Moreover, the temperature dependence of the thermal diffusivity in the temperature range 25°C - 110°C was studied. Although the thermal diffusivity of poly(methyl methacrylate) has a strong temperature dependence in this temperature range, its anisotropic ratio showed little change.

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Calculation of the Effective Emissivity of a Diffuse Plane Surface Below a Specular Hemisphere

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In a previous paper with a similar title[1] we calculated the radiant characteristics of a plane diffuse surface which lay on the base of a specularly reflecting spherical segment at a much lower temperature. The segment became a hemisphere in the limiting case where there was no gap between it and the surface. When the gap is small, blackbody conditions are approached. The effective emissivity (ε_a) of the surface is very high and nearly constant in a region $r < 0.3R$ (where r is the distance on the surface from the centre and R is the hemisphere radius), but decreases substantially and nonuniformly with increasingly larger r.

In this paper we treat the parallel and more practical case of a complete specular hemisphere above a plane diffuse surface. The calculation is considerably more complex and is an excessive consumer of computer time. In order to assess the accuracy of the results for ε_a we have used three different procedures: (a) straightforward numerical solution of the underlying analytical equations; (b) purely geometric projection solution whereby individual rays from an emitting point on the surface are followed through specular reflections back to the surface; (c) a double coordinate transformation that allows the equations of the previous paper[1] to be incorporated. To obtain better than 3-digit accuracy with reasonable computing time we must use a variable grid on the hemisphere such that, for each emitting point, there is a high density of grid points in the region where most energy is incident. The results for ε_a are accurate to a few in the fourth digit.

Compared to the previous geometry, for a given value of intrinsic surface emissivity, hemisphere reflectance, and gap, ε_a is somewhat lower for $r < 0.3R$ and decreases slightly with r. For larger r, ε_a is higher than in the previous case with none of the complicated structure. ε_a decreases more or less uniformly with r, but at an increasing rate as r approaches R.

The paper will set up the underlying equations, describe the methods of calculation in detail, present typical results, and point out the differences that result from the two geometries.

References

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EFFECT OF SURFACE ROUGHNESS AND POROSITY ON THE EFFUSIVITY DEPTH PROFILE OF ARTIFICIAL GRAPHITE *

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In frequency dependent photoacoustic measurements, normalized with the help of reference materials of known thermal and optical properties, depth dependent profiles have been found for the effusivity of various artificial graphites. Based on a geometrical-structural model for opaque random surfaces, these depth profiles of the effusivity, the relevant thermophysical parameter in time-dependent surface heating and cooling processes, have been related to the thermal properties of the respective compact material, to the roughness-increased heat capacity of the surface and to the bulk porosity. For the purpose of calculation of the dynamical thermal response to heat pulses of a duration of several milliseconds as observed for graphite limiters in nuclear fusion research devices, the depth profiles can be approximated by a three-layer model, consisting of

- a thin surface layer with a thermal diffusion time $\tau_s = l_s^2/a_s = 20 - 40\,\mu s$ and an effusivity value $\sqrt{(koc)_s}$ characteristic for the material just at the surface; the quantities l_s and a_s here are the thickness and the thermal diffusivity of this first surface layer, and k, o, and c represent the thermal conductivity, density and specific heat capacity, respectively;
- a second thicker layer with a diffusion time $\tau_r = l_r^2/a_r = 10 - 20$ ms and an increased effusivity value $\sqrt{(koc)_r} > \sqrt{(koc)_s}$, which is characterized by a specific internal surface S_r of the open pores,
- and the bulk region of the material, where the thermophysical properties are affected by the volume porosity, and where thus a lower value of the effusivity is expected, $\sqrt{(koc)_p} \leq \sqrt{(koc)_s} < \sqrt{(koc)_r}$.

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Analysis of the Plane Temperature Wave Technique for the Measurement of Thermal Properties of Absorbing-Emitting Media

BY

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The integro-differential equation which describes the propagation of plane wave in an absorbing-emitting medium is solved for a surface heat source. The distribution of temperature oscillations is calculated for finite and infinite media.

The effect of radiative heat transport on the measured properties is discussed.

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THERMAL CONDUCTIVITY OF LIQUIDS UNDER PRESSURE

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The development of the modern version of the transient hot-wire technique for the measurement of thermal conductivity in the first part of the last decade has had a profound effect upon the accuracy and extent of the data available. In particular, a considerable body of reliable data has now been accumulated for the thermal conductivity of liquids for temperatures in the range 90 to 500 K and pressures from 0.1 to 700 MPa. The paper briefly describes the manner in which these new results have been obtained.

The availability of reliable experimental information has, in its turn, stimulated the development of theoretically-based descriptions of the behaviour of the thermal conductivity of liquids. These developments are reviewed with special emphasis on the role of the hard-sphere model of fluids. It is shown that this model provides the basis of a universal description of the density dependence of the thermal conductivity of a wide class of liquids. Furthermore, the same theory is able to represent other transport properties with a consistent set of parameters.

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Some comments on the theory of the transient hot wire technique for the simultaneous measurement of the thermal conductivity and thermal diffusivity of fluids

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The transient hot wire technique for the measurement of the thermal conductivity of fluids is now recognized to be the most accurate method, outside the critical region.

The theory of the method was formally developed in the middle 70's for its application to the dilute or moderate dense gas. Its application to the liquid phase has been made possible by the development of some modifications of or extensions to the original theory.

In the case of thermal diffusivity several attempts have been made to make the theory of the transient hot wire technique usable to obtain this property with an acceptable accuracy. However, only recently was it possible to solve some of the theoretical and experimental problems to derive from the thermal conductivity measurements values for the heat capacity of the fluids.

It is the purpose of this paper to systematize these separate contributions, with special emphasys in the derivation of the correction to the finite physical properties of the wire, the temperature dependence of the physical properties of the fluid, and the effects of the non-zero compressibility of the liquid.

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MEASUREMENT OF THE THERMAL CONDUCTIVITY OF MOLTEN KNO_3 AND $NaNO_3$ BY THE TRANSIENT HOT-WIRE METHOD USING CERAMIC-COATED PROBES

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The industrial applications of molten salts are increasing in recent years and reliable data of thermophysical properties are required. However, there are restricted number of studies on the measurement of the thermal conductivity of molten salts and their discrepancy is often large. In the present paper, we describe the measurements of the thermal conductivity of molten KNO_3 and $NaNO_3$ by the transient hot-wire method using newly developed probes insulated by ceramics.

In order to apply the transient hot-wire method to electrically conducting liquids such as molten salts, the probe has to be insulated from the liquids. In the present study, aluminum oxide was selected as the insulating material and following techniques were used to insulate the probe ; ion plating for the thin hot-wire and plasma-spray for titanium leads. Furthermore, Si-Ti-C-O ceramic paint was used as top coat on leads. These insulating materials and insulating techniques were chosen by examining their heat-resisting properties and insulating resistance in molten salts at high temperatures. Experimental apparatus was fully automated and onset time of natural convection was determined with care. Measurements were performed on pure KNO_3 and $NaNO_3$ in temperature range from 310 to 450 ℃ and several different probes were used to check an ability of the probe. The accuracy of the results is estimated to be ±3%. The results by the different probes agree well each other within the estimated accuracy.

THERMAL CONDUCTIVITY OF CARBON DIOXIDE

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A new representation of the thermal conductivity of carbon dioxide has been developed. The representation covers the temperature range $220 \text{ K} \leq T \leq 1500 \text{ K}$ and pressures up to 100 MPa in both gaseous and liquid phases. The representation is based, in part, upon a body of critically-evaluated experimental data. In the dilute gas state the critical assessment makes use of the available kinetic theory to check for internal consistency among various gas properties. Experimental information demonstrably inconsistent with the theory, which turns out to be in the majority, is eliminated from the analysis. As a consequence the representation of the thermal conductivity in the dilute gas state is based on a small set of accurate experimental data and theory.

In the dense gas state the available experimental information is more self-consistent and it is possible to develop an empirical representation of the thermal conductivity excess. Owing to the small extent and poor quality of the experimental thermal conductivity data in the liquid phase, it has been necessary to extend the dense gas phase representation into the liquid phase. The behaviour of the background thermal conductivity deduced in this way is then employed to refine a description of the divergent behaviour of the same property near the critical point, using a recent and essentially-complete theory in conjunction with accurate experimental data.

Carbon dioxide is employed as a heat transfer medium in some nuclear reactors. For heat transfer calculations associated with such applications the final representation of the thermal conductivity, which has an accuracy of ± 1% near ambient conditions, deterioriating to ± 5% at the extremes of its range, is a significant advance over earlier work.

Thermal Conductivity of Solids under Pressure

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Thermal conductivity (λ) is a property of central interest in solid state physics. In nonmetals, with which this review is concerned, heat is carried by phonons and it is the scattering of phonons which leads to thermal resistivity (λ^{-1}). Phonons can be scattered by other phonons and/or by structural disorder.

Over many years, numerous data have been obtained for the temperature dependence of λ at zero pressure and these data have provided the basis for considerable theoretical understanding. Fairly recent technical advances which enable reliable measurement of λ under pressure have opened up new areas of investigation. Examples include the possibility of separating the temperature and density dependences of λ (which are both involved in measurements under isobaric conditions) and of studying phases which are stable only under high pressure. A number of phases investigated under pressure have exhibited some kind of structural disorder, and the influence of such disorder on λ will provide an important theme in the discussion.

GRÜNEISEN PARAMETERS AND PRESSURE DEPENDENCE OF THERMAL CONDUCTIVITY

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The pressure dependence of thermal properties of a solid and the thermal expansion coefficient are related through the equation of state. Thus the change in thermal conductivity, λ, of non-metallic crystals with pressure P depends on the volume dependence of the lattice frequencies and of their anharmonic coupling. Measurements of expansion and heat capacity give values for the anharmonicity or thermal Grüneisen parameter $\gamma(T)$ which may be compared with the values of γ deduced from measurements of $d\lambda/dP$. For this comparison we make use of equation-of-state data for alkali halides which indicates $q = d\ln\gamma/d\ln V \approx 1$ and measurements of $\lambda(P)$ at Umea.

Compressed Porous Media - Correlation Between Thermal Conductivity and Young's Modulus.

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As has been found recently from compression experiments with fibrous insulation materials, the solid conductivity, λ_s, and Young's modulus, Y, show the correlation $\lambda_s \propto Y^\alpha$, with $\alpha \approx 0.4$. Those measurements, however, only covered a small density range, $\rho < 300$ kg/m^3. In order to investigate porous materials up to densities of about 1000 kg/m^3, a high pressure piston-cylinder apparatus was constructed. An integrated hot-wire probe allows to measure the thermal conductivity of the compressed specimen in situ. The first measurements with this new system will be presented. If one succeeds to establish the correlation $\lambda_s \propto Y^\alpha$ over a wider range of densities, the development of technical insulation systems could be improved considerably: instead of complicated thermal measurements easy-to-perform elasto-mechanical measurements are possible to estimate the solid thermal conductivity. Furthermore such a correlation would allow conclusions on phonon propagation in porous media.

MEASUREMENT AND MODELLING OF THE TEMPERATURE FIELD IN HIGH p,T-EXPERIMENTS ASSEMBLED IN CUBES WITH INTERNAL HEATING

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The distributions and gradients, mostly in pyrophyllite and boron nitride envelopes, are generated by internal heaters in the form of cylindrical graphite sleeves or rods, Pt- or Nb-foils and Pt-, Nb- or Mo- wires. They are measured by thermocouples at salient positions within the experimental assemblages, the p-transmitting medium and at the boundaries (anvil contacts representing heat sinks with large thermal mass). The T-fields for varying source geometries and stages of heating power output, representing about one dozen furnace designs habitually used in our high p,T experiments with cubic presses, are shown and compared. The analysis consists of (a) the actual T-measurements and fixed point determinations by means of calibration materials, (b) electric field analog plots of isotherms for different designs modelled in two dimensions and (c) computer models obtained by finite-difference solutions of Laplace's and Poisson's equations. All three are in excellent agreement. On the basis of these tests the computer solutions can be relied on as the most expedient and versatile method of determining the boundaries of isothermal zones for given source-probe-sink conditions. They greatly facilitate, and provide one with confidence in, the designing and devicing of experimental assemblages conforming with the required tolerances of isothermality.

THERMAL DIFFUSIVITIES AND CONDUCTIVITIES OF UO_2 AND $U_{1-x}GdO_2$ SOLID SOLUTIONS

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ABSTRACT

Gadolinia is added to urania as a burnable poison to control the reactivity of the fuel in boiling water reactors, however, these materials also have potential applications in pressurised water reactors to extend the fuel cycles to a higher target burnup. In order to assess the performance of these fuels under irradiation it is necessary to have information on the thermal properties of the materials.

The thermal diffusivities of samples of UO_2 and UO_2 doped with 3 and 5 mass Gd_2O_3 (viz. $U_{0.956}$ $Gd_{0.044}$ O_2 and $U_{0.927}$ $Gd_{0.073}$ O_2, respectively) have been measured between 293 and 1631 K using the laser pulse method. Thermal conductivity values for the three materials were calculated from the thermal diffusivity results and the reciprocal of the conductivity (the thermal resistivity) was found to increase linearly with temperature. The thermal resistivity was found to increase with increasing gadolinia addition.

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Completion of Compendium of Thermophysical Property Measurement Methods Series Project

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This paper reports the results of the second phase of the international co-operative programme on standardization of thermophysical property measurement methods realized under the auspices of ETPCs. The outcome of this phase is the second volume of Compendium of Thermophysical Property Measurement Methods: "Recommended Methods and Measurement Practices" which was completed in 1988, four years after its initiation. The volume includes scientific contributions on recommended methods for thermal conductivity (8), electrical resistivity (1), thermal diffusivity (4), specific heat (5), thermal expansion/density (3) measurements, as well as an update for existing thermophysical property reference materials. 37 scientists from 7 countries contributed to the second phase of this programme as authors and 32 as reviewers of individual chapters.

The volume conserves the essence of property measurement philosophy and knowledge acquired during the past 30 years period.

The volume is expected to appear at the beginning of next year, published by Plenum Press, N.Y., USA.

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ON THE MELTING LAW AT HIGH PRESSURE

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Experimental data at static and shock compression and Monte Carlo computer experiments was used to propose a simple relation between melting temperature, T_m , and volume, V_m of solid at the melting line

$$\ln T_m = A + B|\Delta V_m/V_{om}| \qquad (1)$$

The relation (1) generalized the melting law of Kraut and Kennedy for high pressure and helds for wide classes of substances: metals, alkali metals, molecular and atomic gases. The parameter B is nearly constant for the given class of substances.

POSTERS

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A technique for deriving emissivity data for infrared pyrometry

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Knowledge of the target emissivity is a crucial point in practical temperature measurements using radiation techniques.

The techniques for measuring normal spectral emissivity, which is the property involved in pyrometric measurements, can be classified into the two broad categories of direct and indirect techniques, according to whether they directly rely upon the emissivity definition or emissivity is derived from reflectivity.

As a result of a comparative analysis of the two kinds of techniques, a hybrid technique has been devised which combines the advantages of both. Basically, it consists of first deriving at a relatively short wavelength the emissivity of a sample from its reflectivity, then using it for a pyrometric measurement of the sample temperature in a direct measurement of the emissivity at a longer wavelength.

The main advantages in this technique are as follows:

(i) it is simpler than conventional techniques, thus it is suitable for routine measurements;

(ii) the measurements can be performed with a radiation pyrometer, thus obtaining a direct calibration of the target-pyrometer system;

(iii)the measured emissivity exactly matches the spectral characteristics of the pyrometer one is going to use.

Measurements performed on different materials at temperatures from 400°C to 1000°C in the spectral interval from 1 µm to 10 µm proved the viability of the proposed technique.

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LONG TERM PERFORMANCE OF A TRANSFER STANDARD PYROMETER

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The long term performance of the transfer standard pyrometer developed at the Istituto di Metrologia "G. Colonnetti" was evaluated by:

a) testing a calibration technique
b) assessing the capability to maintain the high temperature scale in comparison with high stability tungsten strip lamps
c) checking the absolute stability of the instrument

The calibration technique of the instrument is based on the assumption that the effective wavelength and the linearity of the transfer standard pyrometer are stable for long periods of time. The reference temperature signal depends on the stability of many electro-optical components and might need to be checked regularly. A monthly comparison (for a period of one year) between the transfer standard pyrometer and two sets of high stability lamps at two wavelengths (near 650 nm and 900 nm) indicated that the high temperature scale kept on the pyrometer and that kept on the lamps are equivalent within the reproducibility of the scale on the lamps (± 0.3 K band in the temperature range 1000-2200 K). The absolute stability of the transfer standard pyrometer (900 nm operation) under carefully controlled conditions was evaluated by repeated measurements over a period of one year at the freezing point of copper. During this time the absolute stability of the instrument was better than ± 0.1 K.

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INVESTIGATION ON TOTAL EMITTANCE OF METALS AND STEELS SUBJECTED TO MECHANICAL SURFACE TREATMENTS

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Numerous emittance data for metals and steels are reported in the literature. Owing to the strong effect of surface conditions (surface damage, roughness, oxidation etc.) all such data are subject to large uncertainty that is of particular relevance when the surface condition may vary from micropolished to rough as a consequence of mechanical treatments or oxidation processes.

Since the surface conditions of a material usually change during its use, it is of great importance to keep in mind this large uncertainty in radiative properties data, whenever the thermal behaviour by radiation of the material is of primary interest.

Several analyses have been made with the intent of predicting the effect of a given surface roughness on the radiative properties of materials. The results of these analyses have provided the basis for understanding some of the observed roughness effects, but a conclusive phase does not seem to have yet reached. The main difficulties concern the precise definition of the surface characteristics by suitable parameters, and the attempts to extend the experimental results obtained on a particular material to a larger number of cases.

In this work, an investigation has been performed on some metals and steels subjected to different mechanical surface treatments (sandblasting, grinding, polishing) at the aim of finding a connection between them and the consequent thermal emittance properties, measured in a temperature range from 200 °C to 600 °C.

The research activity concerns the measurements of total normal emittance of each material for the surface condition resulting from the mechanical treatment experienced, and the search of suitable parameters for the definition of the surface characteristics, and the modified emission property of the base material as a consequence of a surface damage.

By means of these parameters, an analysis is then performed to develop a correlation of the experimental data suitable to understand the observed effects and possibly to include the results of a larger number of cases.

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EXPERIMENTAL STUDY OF TRANSPORT AND THERMODYNAMIC PROPERTIES OF COBALT

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The paper presents experimental results for the heat capacity, electrical resistivity and thermal diffusivity of high purity cobalt. Heat capacity and electrical resistivity were measured by the millisecond resolution pulse heating technique in the 300 to 1700 K range. Thermal diffusivity was measured by the laser pulse technique in the 550 to 1500 K range. The applied measurement techniques allowed the study of the structural and magnetic phase transitions in cobalt. The measurement uncertainties were estimated to be 3% for heat capacity and thermal diffusivity and 1% for electrical resistivity, except in the vicinity of phase transitions. The obtained results are tabulated, plotted and compared with literature data.

THERMAL CONDUCTIVITY OF INCONEL 600 AND Ti6Al4V FROM 360 K TO 900 K.

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Thermal conductivity measurements have been performed on Inconel alloy 600 and on Ti6Al4V alloy in the temperature range 360 K - 900 K by means of a computer-controlled comparative axial heat flow apparatus.

Experimental results show that the thermal conductivity increases with increasing temperature both for Inconel 600 and for Ti6Al4V and can be described by linear equations.

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THERMAL DIFFUSION IN COMPOSITES

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Previously the author has presented review articles on thermal diffusivity measurements of composites. The present paper is designed at updating thermal diffusivity studies of composites with special emphasis on degrading systems and on thermal insulations. The use of techniques capable of obtaining data on small samples over a large temperature range rapidly or of reaching and holding a prescribed temperature almost instantaneously creates the possibility of studying time-temperature changes on physical properties. Thermal diffusivity studies using the laser flash technique conducted on a wide variety of materials have shown that information concerning the previous time-temperature history of materials can be obtained and that degradation studies can be performed even on fairly unstable systems. Several examples are presented. The laser flash method is not suitable for fibrous insulations. However, a step-heating technique, which is suitable for such materials, has been developed. The technique which requires rather inexpensive apparatus except for the data acquisition and computation, involves the use of measured quantities in place of mathematical assumptions for initial and boundary conditions. Results on several fibrous insulations are reported.

Transient Pulse Heat Transfer in Semi-Transparent Materials.

by

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Modeling of the thermal respons of a slab of semi-transparent material submitted to a flash irradiation is proposed.

From a metrological point of view this problem is of importance, since many non-metal materials of practical interest are semi-transparent in the infrared, and the popular laser flash method cannot be used without caution in order to carried out the thermal diffusivity.

A plan parallel layer of absorbing-emetting-non-scattering S.T.M is considered. It is bounded either by opaque or semi-transparent surfaces characterized by a specular reflection model, including the natural vitreous reflection case.

By a nodal analysis based on Hottel 's zonal method extended to geometrical optic concepts, the transient combined conductive-radiative heat transfer, 1D, problem is worked out in non-grey semi-transparent materials, more especially glasses, subjected to a square pulse of radiant energy. The thermal boundary conditions are different when the wave lenght of the light belongs either to the opacity range or to the semi-transparent range of the material.

The model is tested for its sensitivity against the absorption properties of the medium and against the diffusivity coefficient.

Comparison is made between thermal respons for a non-grey and a grey model (averaged in the Rosseland and Planck sense), as well as between opaque and semi-transparent materials. One notices, that the increase in temperature of the rear face is higher in a S.T.M than in an opaque material and that the raising times are quite different. The numerical simulation shows also the dependence of the thermograms against the optical nature of the interfaces.

When the sample is heated at a high temperature, the influence of the external convective and radiative heat interchanges conditions is examined. In certain situations it can to mask the internal conductive phenomenon.

It is concluded that in the flash method when the rear face thermogram is used as source of information, irrelevant results, in the infered value of the thermal diffusivity coefficient, may be obtained if the basic heat transfer model is not able to take into account radiative-conductive coupling.

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Calculation of the Electron-Electron Contribution to the Thermal Resistivity of Alkali Metals under Pressure.

The electron-electron contribution to the thermal resistivity has been calculated for Li, Na and K from 0 to 120 kbar at room temperature. The Boltzmann equation has been solved for a Fermi liquid. The scattering rate in the collision integral has been approximated by a sum over Landau parameters, which depend on the Wigner-Seitz radius r_s, or the electron density. The Wigner-Seitz radius has then been modified to take account of the background of positive ions.

The thermal resistivity W_{ee} is explicitly proportional to $r_s^5 m_b^2$, where m_b is the band mass. This has been calculated by the LMTO-method for different pressures, and it is shown that it has a pronounced effect on W_{ee}. This is especially true in the case of potassium, where the band mass increases by almost a factor of 2. Consequently the thermal resistivity first decreases, due to the effect of pressure on the r_s^5 term, until a pressure of 40 kbar is reached where upon it becomes constant. After 60 kbar the resistivity increases, because of the rapidly increasing band mass, m_b.

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Temperature Dependence of the Thermal Conductivity of Alkali Halides

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The thermal conductivity of 17 alkali halide crystals have been calculated in the temperature range 5 K up to the melting point. This has been done by calculating phonon dispersion relations throughout the whole first Brillouin zone with a deformation dipolar model. The Boltzmann equation including only three phonon scattering processes has been solved by a variational method.

We compare our results with experimental data that have been corrected to constant volume. We find good agreement (within 10-20%) in most crystals at temperatures above the Debye temperature. At low temperatures we find good agreement with experiments in isotopically pure crystals. In crystals with a gap between the acoustic and optic branches we predict an unusual temperature dependence of the thermal conductivity at medium temperatures which has also been observed in NaI and over a limited temperature range in LiBr.

THERYST, a Database with Program System for Thermophysical Properties.

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THERSYST is a system data base designed to store and evaluate thermophysical property data of solid materials together with all relevant informations describing the material characteristics and experimental conditions.
A scheme of categories has been developed comprising material designation, material characterisation, experimental description, property description and bibliography. The whole content of a publication is related to the category scheme by means of THERSYST-descriptors and thus transformed into a structured set of standardized data, which permits further data processing.

THERSYST provides a number of program-moduli, which allow to arrange the data base content under various criteria in order to investigate the dependence of thermophysical properties on different material parameters and measuring conditions. Also the calculation of thermophysical properties out of other properties is possible by the aid of physical formulae (e.g. thermal conductivity from thermal diffusivity, specific heat capacity, and density). Beyond that theoretical models describing the temperature or porosity dependence of thermal conductivity can also be disscused using program-moduli specially designed for this purpose. These moduli facilitate a critical selection and evaluation of data.

The data can be represented in manifold ways in graphical or table form, or using regression formula.

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MICROCOMPUTER PREDICTION OF TEMPERATURES IN FOODSTUFFS

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This paper describes the heat equation solver (HES) being developed by Torry in collaboration with AFRC Institute of Food Research, Bristol, England, to predict temperature profiles in foodstuffs during thermal processing.

HES solves the nonlinear heat equation and thus can model freezing and thawing of water-containing foodstuffs.

When the specific heat and thermal conductivity values required as input by HES are not known, they can be generated by COSTHERM, a program predicting the thermophysical properties of foodstuffs from their composition (water, carbohydrate, protein, fat, etc), developed by Miles, van Beek and Veerkamp (1983).

When even the composition is unknown, COSTHERM provides a set of default values for a number of food commodities.

Calling COSTHERM from HES enables users with no prior knowledge of thermophysical properties to model heat transfer in their products.

HES is operated from user friendly menus and runs on the IMB PC/XT/AT compatible microcomputers. HES can be used for the design, monitoring or control of thermal processing of food.

Reference

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Phase transitions of the system Ag_2HgI_4-Cu_2HgI_4 at normal and high pressure studied by differential scanning calorimetry.

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Differential scanning calorimetry (DSC) has been applied for studying the system Ag_2HgI_4-Cu_2HgI_4 at both normal and high pressure. It is confirmed that there is a miscibility gap in the ordered phase, and that the order-disorder phase transition has an eutectoid point at 307 K and 42.7 mol% Cu_2HgI_4 at normal pressure. This transition is of first order character over the whole composition range, thus ruling out a claim by an author that it should change its character with composition, to be of second order character in the middle part of the composition range. The obtained values of enthalpy and volume change as well as temperature for the eutectoid point are compared with values calculated from an ideal solution model. A phase transition, not reported previously, was found at 488 K in samples with the eutectoid composition of Cu_2HgI_4 at normal pressure.

The pressure dependence of the temperature and enthalpy for the order-disorder phase transition has been determined up to 0.75 GPa and 330 K for samples with the eutectoid composition. The effect of the pressure on the eutectoid point and on the solubility is discussed using a theoretical model proposed by van Laar. At 0.4 GPa order-disorder phase transition splits into two branches. The effect is discussed qualitatively in terms of the theory of modulated phases proposed by Bak.

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PHOTOACOUSTIC STUDY OF THERMAL PARAMETERS CRITICAL BEHAVIOUR NEAR THE SMECTIC A-NEMATIC PHASE TRANSITION IN OCTYLCYANOBIPHENYL LIQUID CRYSTAL.

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The study of the critical behaviour of thermal parameters near phase transitions requires high resolution in temperature as well as in thermal parameters determination. A photoacoustic approach to such an investigation is presented near the Smectic A-Nematic phase transition in octylcyanobiphenyl liquid cristal. The sample (~ 40 mg) surface temperature oscillations necessary to obtain an adequate signal to noise ratio were estimated to be ~ 4mk r.m.s. thus meeting the requirements of high temperature resolution. Moreover the technique allowed a simultaneous determination of the thermal conductivity k, specific heat capacity c and therefore thermal diffusivity $D=k|c\rho$ behaviour near the phase transition. ρ is the sample density.

In the optically and thermally thick sample approximation the expression for the photoacoustic signal amplitude A, and phase ϕ |1| become very simple |2| only depends on D, while A depends on D and $e=(kc\rho)^{\frac{1}{2}}$. Thus D, k and c can be evalueted as a function of temperature from the ϕ and A data.

Values of A and ϕ were recorded as a function of temperature every 0.01°C. Near the transition temperature (33.5°C) the sample temperature change rate was 1 mK|min.

A sharp critical increase in c and a critical decrease in D were observed over the transition temperature (T_c) while k only showed a discontinuity.

The critical exponents α ($T < T_c$) and α' ($T > T_c$) for c were calculated and a value $\alpha = \alpha' = 0.3$ in agreeement with existing data |3||4| was found. The critical experiments for D were $b=b' = -0.3$. No data are available in literature for comparison with the D and k critical behaviours.

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THERMAL DIFFUSIVITY MEASUREMENTS OF TUNGSTEN STANDARD REFERENCE MATERIAL

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Presented at the Eleventh European Conference on Thermophysical Properties
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ABSTRACT

Reported measurements of thermal diffusivity of arc cast tungsten NBS thermophysical property Standard Reference Material 1468 were performed as a part of CODATA international cooperative program in development of property reference materials. Measurements were effected employing laser pulse technique in the 585 to 1620 K temperature range. The estimated measurement uncertainty did not exceed 3.5% in the whole measurement range. The table of experimental results is presented, and the results are compared with CINDAS recommended thermal diffusivity function and the values computed from NBS standard reference data on thermal conductivity. Agreement with the CINDAS recommended data is very good. Thermal diffusivity values calculated from NBS reference thermal conductivity data lie about 3% above the two sets.

THERMOPHYSICAL PROPERTIES OF DIFFERENT PURITY IRON SPECIMENS AT HIGH TEMPERATURES

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An interest towards the properties of Iron can be explained with its wide technical applications and with the unique opportunity to study anomalies of various solid-solid phase transformations on the same specimen.

The objective of this paper is to describe the measurements of thermal and electrical conductivity, thermal diffusivity, hemispherical total and normal spectral emissivity of Iron.

Specimens under investigations were fabricated from the electrolitic Iron rod furnished by the NBS as a SRM 1464 and from the rod of an low-alloyed steel used as a SRM in the USSR.

The temperature range investigated included the Curie point, bcc/fcc and fcc/bcc transformations.

Our results confirmed the validity of the NBS thermal conductivity data for SRM 1464 in the temperature range 300-1000 K.

The temperature dependence of transport properties in the vicinity of the phase transition points are discussed. The Lorenz function calculated is analized from the point of view of the purity metal influence.

The electrical resistivity and emissivity data were used to evaluate the role of the relaxation time and interband transitions in the thermal radiation of heated Iron.

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THERMOPHYSICAL PROPERTIES OF GLASSY CRYSTALS

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The thermal conductivity and heat capacity per unit volume has been measured for the glassy crystal former cyclohexanol. A glassy crystal state is produced by supercooling a plastic crystal phase. In this glassy state the molecules have translational order but they may be frozen at different orientations. Results for measurements on the glassy crystal state and the different phases of cyclohexanol will be presented. The results of the glassy crystal state will be compared to those of a normal glassy state.

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MEASUREMENT OF THERMAL DIFFUSIVITY OF SEMI-TRANSPARENT MATERIAL

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In measuring thermal diffusivity of a semi-transparent material, an apparent thermal diffusivity which includes the error due to thermal radiation heat transfer is obtained in general and the apparent value changes in accordance with the measuring conditions such as the temperature level and the heating method. In this paper the influence of thermal radiation on the thermal diffusivity measured by the stepwise heating method has been theoretically analysed and the corrected values for a soda glass have been discussed.

The stepwise heating method is based on the measurement of temperature response at the surface of a sample when the other surface is heated in step-function. The thermal diffusivity is obtained from the ratio of the temperature response at the different time which is expressed as a function of Fourier number.

Transient heat transfer by simultaneous thermal conduction and radiation in a semi-transparent material is analysed when the front surface is stepwisely heated. Consideration is given to a one-dimensional system consisting of an absorbing and emitting medium for thermal radiation with the gray and pararellel surfaces. The finite difference method is used to get the temperature and the heat flux distribution. The method of correction for the thermal radiation component in the measured apparent thermal diffusivity is proposed.

As an example, the apparent thermal diffusivity for a soda glass disk were measured as function of the sample thickness of 2 to 5 mm in the temperature range of 250 to 800 K. The absorption coefficients of the soda glass were subdivided into three ranges in wavelength, namely, the band model was adopted. After correcting the thermal radiation effect on the apparent values, the thermal diffusivity leaded to independent on the sample thickness. The thermal conductivity of the soda glass were calculated from these corrected thermal diffusivity, specific heat capacity and density. These thermal coductivity agree well with the previous data.

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THE PRESSURE DEPENDENCE OF THE DIELECTRIC CONSTANT OF GLASSES

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Measurements of the pressure dependence of the static dielectric constants of a number of tellurite and phosphate glasses at elevated temperatures (295K-380K) are reported. The dielectric constants have been determined from the low frequency impedance spectra of glass discs within a Bridgman opposed anvil cell. The most notable feature is that the pressure dependence of the static dielectric constants are positive in sign: vitreous TeO_2 $dE/dP = 4.3 \times 10^{-11} (Pa^{-1})$, at 293K. This is in agreement with data for vitreous silica but is in contrast with the behaviour of crystalline insulators, for which dE/dP is usually negative. The data has been analysed using the Clausius-Mosotti equation to enable the pressure dependence to be correlated with the temperature dependence. The analysis identifies the compressibility as the determining factor for the pressure dependence of the dielectric constant.

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THERMAL DIFFUSIVITY MEASUREMENTS ON Li_2SiO_3 USING THE MODULATED ELECTRON BEAM TECHNIQUE AND DISCOVERY OF SOME ELECTRICAL PHENOMENA

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Lithium appears to be the only material suitable for breeding tritium in a fusion reactor. Next to liquid lithium several solid lithium compounds are viable tritium breeding materials among which lithium-metasilicate (Li_2SiO_3).

Thermal conductivity-diffusivity are in this matter properties of primordial importance. The data for the lithium compounds are very limited and for Li_2SiO_3 even non-existing in the open literature.

Three kinds of specimens have been measured between approximately 500°C and 1000°C, using the modulated electron beam thermal diffusivity equipment, namely nearly stoichiometric specimens, specimens containing small amounts of lithium-orthosilicate (Li_4SiO_4), and specimens containing 6 % of lithium-disilicate ($Li_2Si_2O_5$). Also these specimens have density values in the range 72 - 95 % T.D.

The diffusivity and the conductivity increase with increasing degree of hypostoichiometry (more disilicate) and presumably also with density. Unfortunately exact values for the hyperstoichiometric (containing orthosilicate) samples cannot be given since in these samples an hysteresis effect occurs which however is only partly reversible.

Above approximately 900°C to 950°C all specimens undergo an irreversible, steep increase of the diffusivity-conductivity. Some parameters affecting the behaviour of the different specimens as a function of temperature are discussed.

An investigation to find out a reason for the unstable results obtained with some specimens led incidentally to the discovery of unlooked-for electrical phenomena. Specimens which had been irradiated by the electron beam in the diffusivity apparatus, and also specimens which were brought in contact with a voltage source, built up a voltage between their surfaces. This voltage depends on a few parameters, as exposed in a preliminary discussion. Perspectives are opened for a new and expedient high temperature battery system.

Partly supported by the Commission of the European Communities.

MEASUREMENT OF THE THERMAL CONDUCTIVITY OF NON-SATURATED POROUS MEDIA

THEORETICAL ANALYSIS AND EXPERIMENTS

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The difficulties encountered to measure "thermal conductivity" of a non-saturated porous material, are mainly linked to :

- the definition of the thermal conductivity
- the modelisation to describe the coupling effects between heat and mass transfer
- the experimental methods.

The thermal conductivity of wet porous media (beyond the problem of the determination of the conductivity of heterogeneous media) is strongly influenced by evaporation-condensation effects.

To describe these coupling effects between the heat and mass transfer, it is necessary to develop physical model. This model enables us to define the parameters which can be really measured by experiment.

Among the measurement methods, the heat pulse method is particularly convenient to implement.

Moreover the numerical simulation of the experiment shows that these methods are very well suited to this kind of situation.

Experimental results obtained with beads of glass and light concrete are shown for a wide range of temperature. The interpretation of these results remains very open even if it confirms partly classical analysis such as those from KRISCHER or DE VRIES.

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THERMAL DIFFUSIVITY AND CONDUCTIVITY OF POWDER COMPACTS AND SINTERED SPECIMENS OF CEMENTED CARBIDE

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A study was conducted of the thermal diffusivity and thermal conductivity of several grades of cemented carbide. Measurements were made as function of the temperature on compacted powder samples with or without lubricant as well as on high-density, sintered specimens.

The thermal diffusivity was measured by the hot-strip method (THS-method) in the lower temperature range and by the laser flash method over the whole range up to approximately 1200°C. The thermal conductivity was measured at a steady-state heat flow by the comparative method up to 450°C.

The specific heat capacity was determined by differential scanning calorimetry from room temperature up to 700°C on both powder compacts (with or without lubricant) and sintered specimens. From the data a function has been evaluated which gives the relation between the composition, temperature and specific heat capacity.

At high temperatures an influence of the Curie temperature transition has been noticed on the specific heat capacity as well as on the thermal diffusivity, but as expected not on the thermal conductivity.

THERMOPHYSICAL MEASUREMENTS UNDER PRESSURE BY THE HOT-WIRE PROCEDURE

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The transient hot-wire method has frequently been used for determining thermal conductivities of gases and liquids under elevated pressure. In our laboratory it has been used for measurements on solids as well as liquids up to 2.5 GPa. Here we present a new and simplified version of the circuitry which makes use of the best instruments commercially available at the present time. The circuitry provides a wide range of current to enable the probe wire diameter to be changed in order to match the thermal properties of the specimen to be investigated. The analysis of the temperature increase during the heat pulse is based on the exact solution for a heated wire immersed in a medium. Data are corrected for varying power. The alkali halides are of special interest and importance in the study of the thermal conductivity (λ) of crystals under pressure, because of the relatively simple crystal structures involved. We have investigated the temperature and pressure dependence of λ for RbF and LiBr, using the new method. Although most alkali halides already have been investigated, no thermal conductivity data exist for these substances. What makes them especially interesting is the high values of the mass ratio, 4.5 for RbF and 11.5 for LiBr. As is well known, the mass ratio affects the separation in energy of the acoustic and optic modes in a crystal of diatomic basis, and it is assumed that this in turn should influence the relative influence of acoustic and optic phonons in the heat transport process. This study enables further analysis of this problem.

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TRANSPORT PROPERTIES OF GADOLINIUM FROM 40 - 340 K.

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The thermal diffusivity a, electrical resistivity ρ, and Seebeck coefficient S, of polycrystalline gadolinium have been measured in the temperature range 40-340 K. From experimental data the thermal conductivity λ, and Lorenz function L, have been calculated. The results are compared to earlier experimental results and also to theoretical predictions of ρ and S in the critical region of Tc, (292K).

TEMPERATURE DEPENDENCE OF OPTICAL CHARACTERISTICS OF SEMITRANSPARENT POROUS MEDIA

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In a previous paper, (presented at the 10 th ECTP, Rome, 22-25 September, 1986) we computed absorptions, $\sigma_{a\lambda}$ and diffusion, $\sigma_{d\lambda}$, coefficients of fibrous layers of pure vitreous silica, using KERKER-MIE model, at ambient temperature. Refined infrared optical measurements of spectral bidirectionnal transmittances had shown a good agreement between experimental results and theoretical predictions.

Following the same approach the authors have studied the influence of temperature, first on the complexe index of refraction n^*_λ, and then on $\sigma_{a\lambda}$ and $\sigma_{d\lambda}$ coefficients. Spectral reflexion, R_λ, ans transmission, T_λ measurements have been made, using a Perkin-Elmer 983 spectrophotometer equipped with special accessories, on pieces of pure silica heated up to 500°C. From these measurements it has been possible to derive the complex index of refraction of silica as a function of temperature and then to compute $\sigma_{a\lambda}$ and $\sigma_{d\lambda}$ for a fibrous layer.

These results have been used to predict the thermal resistance of a fibrous silica sample as a function of temperature, the radiation heat transfer equation beeing solved with the SCHUSTER- SCHWARTZSCHILD approximations.

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THERMOPHYSICAL PROPERTIES MEASUREMENTS OF STRUCTURAL MATERIALS IN LABORATORY AND IN SITU: METHODS AND INSTRUMENTATIONS

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Thermal stresses arising in massive structures in non-steady state conditions can be computed provided the thermal properties of the materials are well known.

Structural materials, such as concrete, rocks and soil are heterogeneous, damp and porous so that measurements of their thermal properties by conventional methods are subject to large errors. In order to overcome this limitation, the Hydraulic and Structural Research Centre (CRIS) of the Italian National Electricity Board (ENEL), in cooperation with CISE S.p.A., has developed methods and devices for the measurements of thermal conductivity, thermal diffusivity and thermal expansion coefficient of such materials.

Two different transient methods for thermal conductivity and diffusivity measurements have been set up: the first (namely the two linear and parallel probe method) is based on the linear heat source theory while the second relies on the plane heat source theory. Moreover, in order to study the effects of the temperature and the moisture content, the measurements can be performed in samples conditioned inside a closely controlled climatic cell where the temperature and the moisture can range from -30°C up to 190°C and from 0 to 100%, respectively.

The linear thermal expansion coefficient is evaluated by a properly designed dilatometer. Samples of 160 mm in diameter and 200 mm in height can be tested between -10°C and 100°C.

For in situ thermal conductivity and diffusivity measurements two different apparatuses have been set up: the first is a particular version of the two linear and parallel probe method device used in laboratory, the second, with a cylindrical massive conductive probe (40 mm in diameter and 1200 mm in length), is based on an analytical model proposed by Blackwell.

The instrumentation is throroughly described and test results are reported.

HEAT CAPACITY, ENTHALPY AND CRYSTALLINITY OF LPE, LLDPE AND VLDPE AS A FUNCTION OF TEMPERATURE BY A CONTINUOUS DSC METHOD

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Although semi-crystalline linear polyethylene has long been an object of study, until now hardly any quantitative DSC measurements have been performed in the interval from room temperature all through the melting range. The present calorimetric studies for the greater part relate to precisely this interval, where C_p and crystallinity markedly change.

By means of computer controlled differential scanning calorimetry (DSC), dynamic, continuous (single-run) heat capacity measurements were performed between -70 and 250 °C, in heating as well as in cooling. The reference states for purely amorphous and purely crystalline polyethylene within the two-phase model were used to determine the crystallinity as a function of temperature across the range mentioned [1].

The method turns out to be extremely useful even for semi-crystalline ethylene-octene copolymers with a high degree of branching, like linear low density polyethylene (LLDPE) and very low density polyethylene (VLDPE) [2]. The classical, stepwise method, involving relatively small temperature increments, is hardly feasible with these copolymers, because the crystallization and melting processes in these materials proceed as a function of time at any point of an extremely wide temperature range, viz. between -60 and 130 °C.

The usefulness of the continuous C_p method in combination with the dynamic DSC technique will be illustrated by results for a number of samples and by a comparison of crystallinity data obtained by the continuous DSC method with those from a density measurement (as usual performed at a single temperature, 23 °C).

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INFLUENCE OF THE CONTACT HEAT RESISTANCE BETWEEN GRAIN AND MATRIX ON THE THERMAL CONDUCTIVITY OF A COMPOSITE

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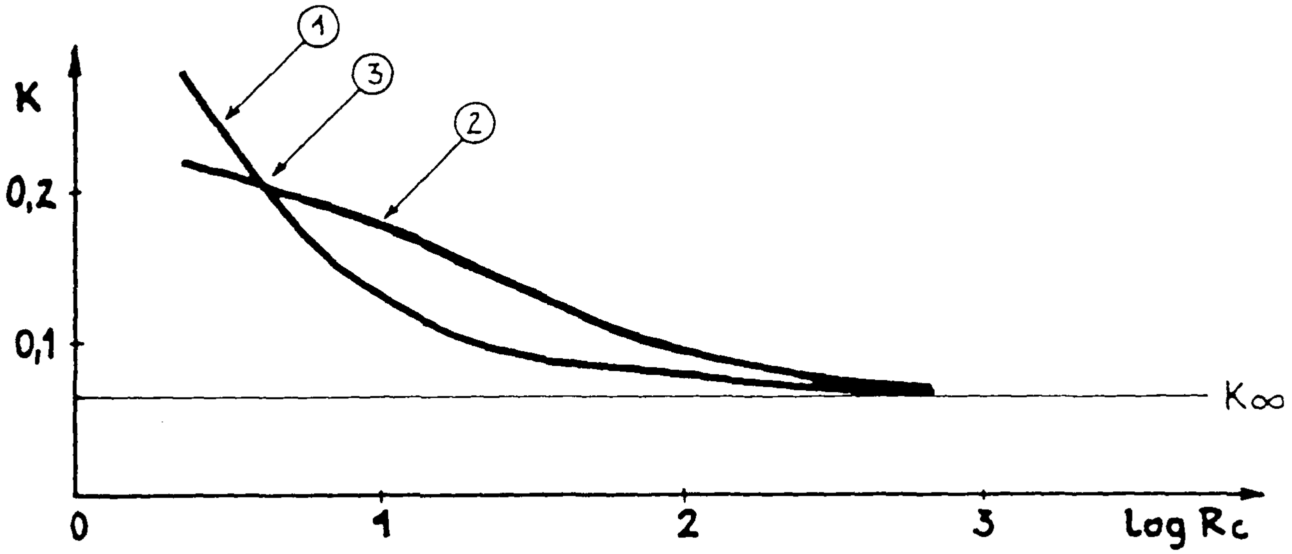
It is difficult to estimate in an experiment the share of the contact heat resistance on grains boundary in the total value of thermal conductivity of a composite.

To examine that problem, a computer model of the composite was used. The thermal conductivity coefficients of the matrix and a filler and the percentage were constant. Changing the contact heat resistance from very high values, through zero /for ideal Maxwell contact/ to the condition when the properties of matrix in the contact area undergo such a modification, that the thermal conductivity increases, there is possible to observe the caused changes in properties of the whole sample. Tests were realized for different degrees of dissipation of the filler.

One of the obtained graphs is shown in Figure:



Figure

R_c = the heat resistivity of a volume element in the contact area of grain and matrix, K = thermal conductivity coefficient of the composite, 1 - fine-grained material, 2 - coarse-grained material, 3 - Maxwell contact

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Thermal conductivity of liquid UO_2

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Measurements of the thermal conductivity of molten UO_2 on self-contained partially molten samples (High Temp.- High Pressures 15 419-431 (1983)) gave results that differ grossly from data taken on quasi-isothermal encapsulated samples. These measurements are presently being corroborated, with particular emphasis on the quality of the input data, i.e. the evolution of the surface temperature profiles with time. The quasi-stationary situation of the partially molten sample yields the thermal conductivity, whereas dynamic data from the heating period provide additional evidence on the thermal diffusivity between 1800°C and the melting point. First results obtained on UO_2 are presented.

BEHAVIOUR OF $\left(\frac{\partial T}{\partial P}\right)_S$ NEAR $\gamma - \alpha$ TRANSFORMATION OF CERIUM

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The T-P dependencies of $\left(\frac{\partial T}{\partial P}\right)_S$ near $\gamma - \alpha$ transformation of cerium was determined in region $0 < P < 3.0$ GPa and 300 K-700 K. On basis of these data the heat capacity, the entropy and the thermal expansion was calculated as functnons of T and P using temperature dependence of heat capacity at normal pressure.

The volume changes along the line of transition was estimated by "thermo-baric" analise.

The behaviour of thermodynamic functions near $\gamma - \alpha$ transformation are discussed.

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TEMPERATURE MEASUREMENTS ON BOTH SIDES OF A FLAT SAMPLE ILLUMINATED WITH A FLASH, LEADING TO THE DETERMINATION OF THERMAL CONDUCTIVITY AND HEAT CAPACITY

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An experimental set-up has been built to determine thermophysical constants of samples (2 inches in diameter) of metals, plastic, and compound materials at room temperature.

A specimen under investigation is illuminated by a high power flash lamp (2 ms duration, energy ranging from 100 to 3200 joules) and a nitrogen-cooled infrared detector (Hg Cd Te) is used to measure the surface temperature evolution versus time of that sample. Spectral sensitivity of the detector is limited between 8 and 12 microns. Data are recorded with a digital oscilloscope connected to a micro-computer and processing time does not exceeed 5 minutes, including printing results and curve.

Temperature variations on the front surface of the material give indications of its thermal effusivity, diffusivity and conductivity. Back surface observation provides informations on thermal diffusivity and makes a comparison possible with results obtained on the front side.

The theoretical calculations of these phenomena are in good agreement with experimentalk results, taking into account thermal losses, flash lamp efficiency and detector performance.

The same experimental equipment is used to evaluate the joint thermal resistance of a two-layer sample. A theoretical model based on analytical equations has been studied. Applied to different configurations, an air-equivalent wedge of the boundary layer is proposed. Experimental thermograms present a profile that can confirm theoretical calculations.

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METHODS OF STUDYING THERMAL PHENOMENA USING UNSTEADY FREQUENCY METHODS

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The essence of unsteady frequency methods consists of using the objectively existing effects of the unsteady frequency shift both of continuous waves which originate from wave propogation in a medium with time-varying properties and of continuous electric circuit oscillations with time-varying parameters. These methods are highly informative and enable one to considerably improve the measuring accuracy of different physical (electric and non-electric) quantities compared with traditional amplitude, phase and resonance frequency measurement methods. During measurements with unsteady frequency methods, the frequency shift of the output signal carries information about the rate of change of some controlled physical parameter and the time integral of the frequency shift correspondingly carries information about the value or increment of the parameter. Our measuring system which uses these ideas employs a reference frequency of 1 MHz. The system enables us to distinguish frequency shifts at a level of 10^{-7} Hz and a change in the phase difference between measuring and reference signals of $2\pi \cdot 10^{-6}$.

Thus, when unsteady frequency measurements are made, the information obtained at the output of the primary measuring converter is stored in the frequency shift, whose value is uniquely related to the rate of change of a controlled physical parameter, for example a temperature.

If account is taken of the fact that the derivatives of many special functions are the elementary functions, then it becomes clear that it is considerably easier to analyze, approximate and use the solutions for the fields of the rates of varying temperatures as against their time integrals.

A number of problems for semi-infinite and finite bodies with boundary conditions of the first and second kind have been considered. The mathematical solutions for fields of the rates of the time temperature variation and the expressions for the thermophysical characteristics obtained using these solutions are rather simple and precise. Calculations show that the time at which confident measurements of $\partial T/\partial t$ (T = temperature, t = time) can begin by unsteady frequency methods is an order of magnitude less than that for temperature (T) itself using amplitude methods.

AUTHOR INDEX

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