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NONTRADITIONAL AND TRADITIONAL METHODS OF THERMAL TREATMENT AND ANALYSIS IN SOLID-STATE CHEMISTRY AND PHYSICS

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ABSTRACT

The methods of thermal analysis and of experimental physics are compared. Different manners of temperature measurement and regulation are analysed and classified as an electronic control of the furnace temperature or a mechanical control of the sample position in the preheated furnace. Examples of special devices developed for nonconventional thermal treatments are shown for cases of laser-aided microfurnace melting and of a melt quenching by copper tongs and/or by a metallic belt continuously running between two rotating wheels. In contrast to the high-temperature treatment utilized to prepare materials of required properties the low-temperature measurements are stressed as the basis for material state characterization (e.g. classification of the various types of magnetic glasses and oxide high-temperature superconductors and their utilization in metastable state).

PREFACE

Working at the Institute of Physics I should not forget to mention the worldwide reputation of the Czechoslovak school of experimental physics [1,2,3] and also the well known school of thermal analysis [3,4] within which specialized methods of thermophysical measurements were put into practice by various Czechoslovak scientists, such as dielectric (A. Bergstein), emanation (V.Balek), hydrothermal (V.Šatava), periodic (I.Proks), photometric (S.Chromý) and permeability (J.Komrska) methods of thermal analysis [5]. In this review I should also like to delve into my 28 years of experience in solid-state chemistry which have covered different aspects of inorganic compounds as developed in the framework of scientific projects carried out in our Institute (e.g.[6]) having recently matured into three books dealing with material science [7-9]. These achievements would not be possible without the professional basis laid down by distinguished personalities who influenced the early progress of thermal analysis as an art of science, in particular the late Dr.Arnošt Bergstein and Professor Vladimír Šatava, see Fig.1.

<u>Dedication</u>: My invited ICTA 9 plenary lecture in its published form is dedicated to my dear mother Žofie Šesták'ová who died in Prague just after the 9th ICTA on September 5th, 1988 at the age of 83. Her continuous devotion and loving support ensured my early growth into a person.

1988 Bodenheimer Award Lecture of the Israel Group for Thermal Analysis

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Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

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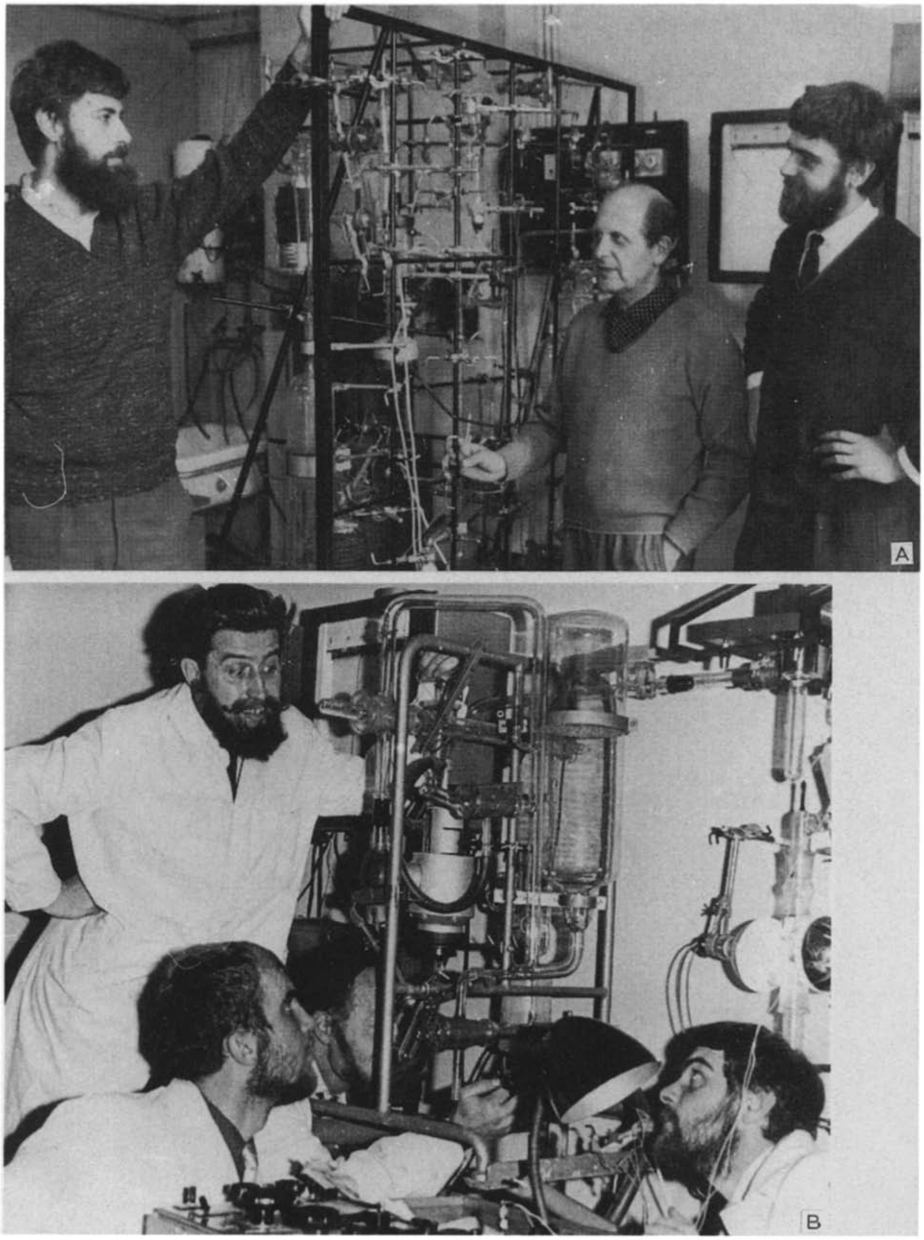


Fig.1.: The late Dr.A.Bergstein (middle A) in front of our selfconstructed apparatus for the EMF determination at his laboratory for Chemistry and Technology of Ferrites and Professor V.Šatava (upper left B) with his scientific team investigating different types of cements at the Chair of Silicate Chemistry of the Prague Technical University (both late sixties).

INTRODUCTION

Classification and utilization of thermal methods [3] are matters of tradition and of specialization for individual scientific workers in a given field of science. Among traditional methods, thermoanalysts customarily include those methods which are associated with the detection of **thermal properties** (DTA, DSC) of a sample completed by the detection of the sample mass (TG,EGD,EGA) or size (dilatometry). Determination of **nonthermal properties** ,e.g., thermodynamic (magnetic), flux (conductivity) or structural (XRD) properties is usually considered nontraditional and judged as complementary with regard to the above traditional methods. It, is evident, however, that these nontraditional methods can become superior in other fields of science, e.g., in solid-state chemistry and physics.

For example, crystalchemistry would not exist without XRD nor would physics without electric and magnetic measurements. In the latter case the classical methods of **thermal analysis (TA)** would than serve as a supplementary source of information, often considered of exploratory value only. Current examples are easy to find in the novel field of oxide superconductors, see Fig.2 [6]. However,there arises the problem of how to compare correctly different kinds of static (XRD) and dynamic (DTA) measurements (as TA in general) the latter not even carried out under the temperature change but often at a derivative mode of measurements. An analogous comparison of the rates of oxygen dissociation (p_{O_2}) and the radioactive tracer release (ETA) was shown in our previous communication [14].

Yet another problem lies in the existence of two kinds of observations,which are difficult to correlate. One is based on the averaged measurements of the property of a sample state by a standard thermophysical technique (e.g. DTA, TG, XRD, magnetometry).The other consists of localized measurements at a precise spot on the sample surface such as traditional morphology measurements (e.g.light or electron microscopy). Such a contradiction is particularly important in studies directed to heterogeneous kinetics where the centered data on the degree of reaction and thus derived phenomenological kinetic models are often criticised for the apparent lack of its physical meaning. On the other hand the morphological kinetic information can equally be questioned as based on a very localized surface pattern which represents a negligible part of the sample and is observed under conditions much different from those occuring during the entire reaction.

TEMPERATURE DETECTION AND CONTROL

Knowledge about the sample temperature is a unifying and necessary requirement for all successful temperature treatments or analysis. Moreover the **temperature** is the basic quantity which is naturally involved in all types of physicalchemical measurements regardless of what physical property is chosen to represent the sample state [3]. In TA it is traditional to investigate the **state changes** exhibited by a sample exposed to steady conditions of steady temperature increase or decrease. On the other hand experimental physics studies the **equilibrated state** of the sample under preferably stationary temperature conditions (usually isothermally). Associated measurements at room temperatures, however, require a suitable method of quenching the sample so as to preserve its equilibrated (usually high-temperature) state.

In TA we traditionally employ constant heating. Commercially produced TA regulators control heating upon a mere response signal from a single-pointed temperature sensor placed in a certain thermal contact with the heater surrounding the sample [3]. There, however, a feed-back connection between the required temperature of the sample and the actual controlled temperature of a heater is missing. Such a feed-back response to the entire sample temperature is available only in fine calorimetry apparatuses where, moreover, a heat generator and/or sink is situated in the measuring head to help to maintain the preselected temperature conditions.

The sample can be placed within a homogeneous or gradient **temperature distribution** as produced by the given type of surrounding heater. The sample can be exposed to a conventional continuous or constant temperature programme employing a mutually static arrangement of the sample and furnace, common for most thermophysical measurements or apparatuses (e.g. single crystal growth from fluxes). Stepwise change of the furnace temperature can be altered in such a way that the sample is inserted into the preheated furnace. It complies with the less conventional arrangement of the mutually movable sample and furnace which requires, however, a definite distribution of temperatures along the furnace. Possible continuous temperature control is then carried out mechanically by positioning the sample along the given temperature gradient by moving either the sample or the furnace, see Fig.3. In contrast to the conventional static system it enables one to make a relatively fast change from one temperature to the other as well as to apply relatively low rates of cooling needed for crystal growth experiments (e.g. Bridgemann or floating zone methods).

The sample thermal treatment associated with any temperature change intentionally introduced directly to the sample or to its surroundings can be carried out at lower or higher temperatures, at spontaneous or constant heating/cooling rates at a standard ($10^{-2} < \beta < 10^{1}$ K/s) or slow (10^{-4} K/s, for single crystal growth) or high (10^{3} K/s, for **nonequilibriated** materials such as glasses) regime. Slow cooling is more easily accessible by standard TA equipment than high cooling which requires a special set up (e.g. cooling by high velocity flowing gas against a sample having one very small dimension such as ribbons). Such a thermal treatment can be thus easily localised to the sample surface (e.g. by laser glazing).

As already stressed above, the basic task of all thermal measurements is to obtain reliable knowledge of the sample temperature, which can be detected directly (if a suitable contact between the sample and a temperature sensor can be made) or indirectly (if a temperature of a reference point is measured and related to the true sample temperature by e.g. calibration). Single point measurements of the so-called **centered temperature** assumes gradient averaging by high enough thermal conductivity of the sample and/or its holder. Multipoint measurements make it possible either to scan temperature gradients or to localize the reaction (macro)surface or to read the mean surface temperature (such as in the case of Calvet calorimetry). Contactless measurements are not conventional as yet and can be only realised by detecting the emitted sample radiation pyrometry) or from thermal behaviour of a reference material held under similar temperature conditions.

Popular **twin arrangements** which includes the measurements of the difference between the sample and a geometrically and

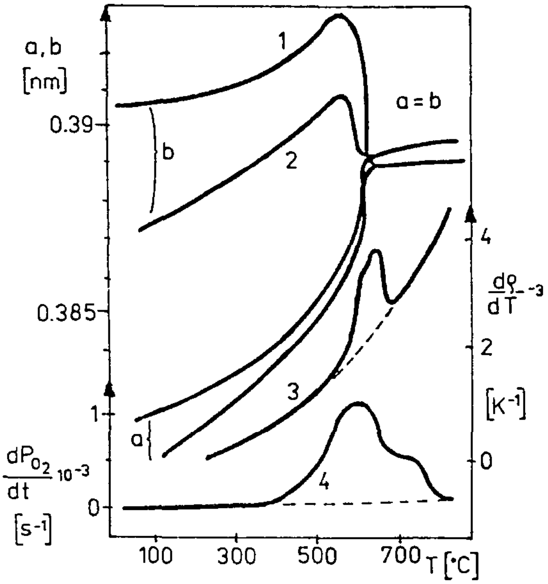


FIG.2: The XRD measurements of lattice parameters (a and b) from two different laboratories [10,11] showing not only a very good agreement but also localising the region of ortho-rhombic-to-tetragonal transition for $YBa_2Cu_3O_{7-y}$ (a=b when y>0.5). The transition region is confirmed by two independent measurements of the changes of electric resitivity 3: ($d\varrho/dT$) [12] and oxygen pressure 4: (dP_{O2}/dt) [13].

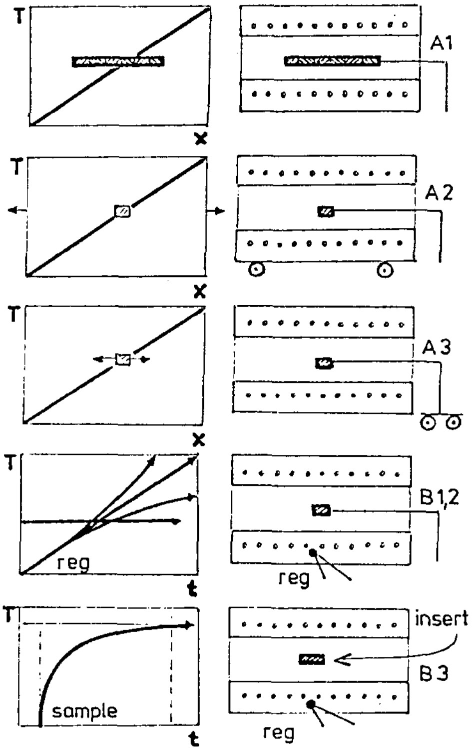


FIG. 3: Illustrative classification of the sample temperature control for either (A): a fixed temperature gradient: 1) long enough or multiple stationary sample(s) placed along the furnace temperature gradient, 2) stationary sample placed inside the movable furnace and 3) movable sample placed in the stationary furnace, or (B): a controlled temperature gradient which in combination with (A) is usually applied to technological processes under computer control. (C) shows the programmed temperature control of a stationary furnace employing (1) isothermal, (2) nonisothermal (TA) and (3) spontaneous heating (as drop-in calorimetry or computer simulated reference in direct TA).

physically similar reference specimen requires, however, increased attention so as to avoid sudden changes in the preselected experimental regime (e.g. in constant heating or gas flow). In specialised methods of TA the sample temperature serves at the same time as a measured quantity to indicate a thermal property of the test material (e.g. heating and cooling curves, DTA). In particular DTA is the only method where the entire course of the sample temperature is monitored it thus being of use for a more detailed analysis. Behaviour of the reference specimen can, however, be simulated by a computer which analyses the course of the temperature increase if the sample would behave as a reference (inert) material. Consequent superposition of the actual (including changes caused by reactions involved) and idealised curves makes it possible to calculate differences in any desired forms (e.g. as a DTA-like trace with peaks). This method, moreover, does not require traditional constant heating as it works with any type of constant temperature change (e.g. exponential exhibited by the normal sample insertion into a preheated furnace [15], cf. Fig. 3.-B3).

When seeking a gradientless experimental set up, the sample size has to be miniaturized (which consequently brings problems of the sample correct starting weights), or the sample should be placed in the form of thin layers onto well conductive sample holders, e.g., in the form of multistory (ribbon) crucible invented by us for thermogravimetry [16]. Such an approach, however, can conflict with common requirements of sufficiently sensitive measurements of the sample`s extensive properties (e.g. heats of reactions). Hence the development of TA apparatuses designed to indicate either intensive or extensive properties may not follow the same path.

SPECIAL DEVICES DEVELOPED FOR NONCONVENTIONAL THERMAL TREATMENTS AND ANALYSIS IN OUR LABORATORY

The most difficult regions of working temperatures applied to study processes are very high temperatures ($T > 1800^{\circ}C$) or those a little above room temperatures ($0 < T < 100^{\circ}C$, where the ordinary temperature control of most TA apparatuses is not sufficiently effective). Herewith I would like to mention a few examples of selfconstructed apparatuses developed for this purpose under my supervision in our laboratory profiting from some nonconventional ideas.

For TG study of dehydration of sulphates around $100^{\circ}C$ we developed infrared heating [17] realised by two opposing infrared lamps. Sufficiently sensitive control was achieved by power oscillation around a preselected temperature increase which was realised mechanically. Temperature was indicated indirectly by means of two geometrically similar cells. The sample suspension in a suitable liquid was dried out onto the inner surface of the cell (i.e. unirradiated walls) where it formed a thin layer [18]. An overview of the apparatus can also be seen on the right side of Fig. 1B, including an obsolete vacuum accessory (middle) and an old but precise manual compensation temperature measurer (bottom).

For a **high-temperature treatment** of refractory oxides (e.g. CeO_2, UO_2 or ZrO_2 investigated during my scientific visit to the Swedish nuclear center in Studsvik 1969) we constructed a high-vacuum furnace [19] resistively heated by tungsten tin formed into a tube-like element, see Fig. 4. Temperature concentration was aided by concentric radiation shields making it possible to achieve temperatures as high as $2700^{\circ}C$. For the temperature in-

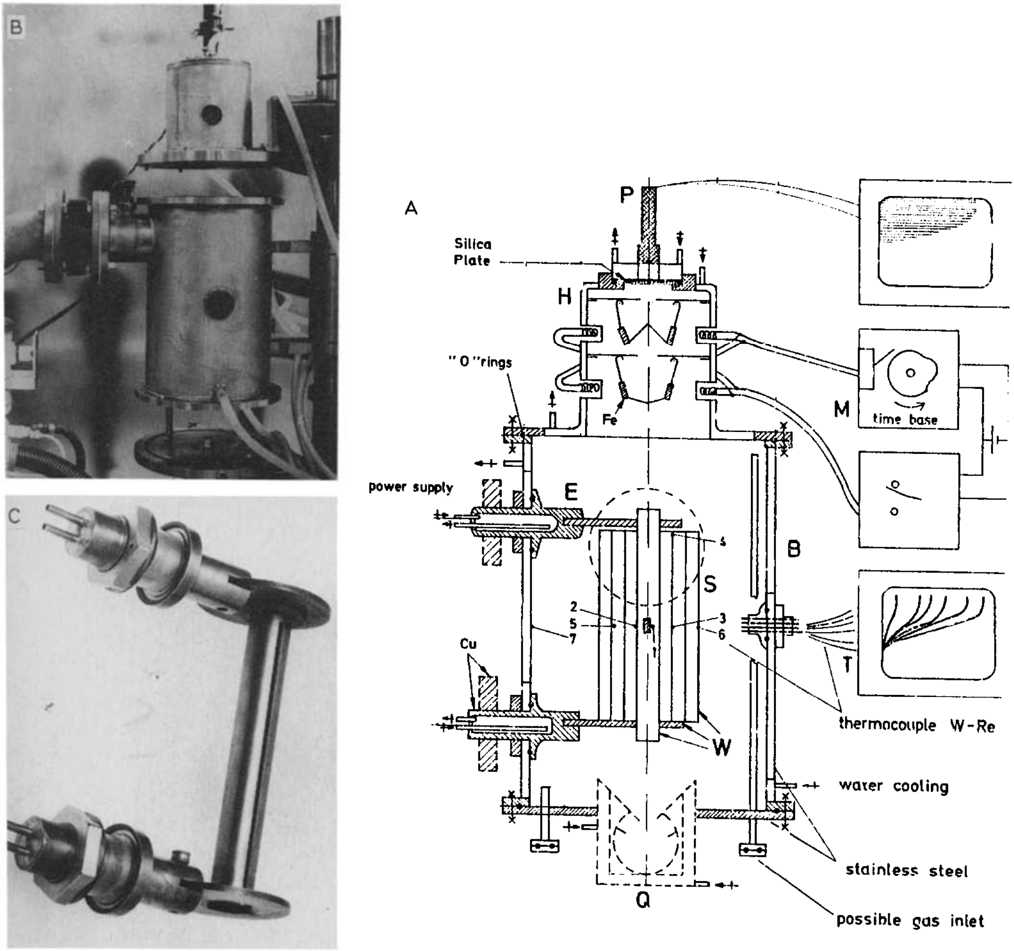
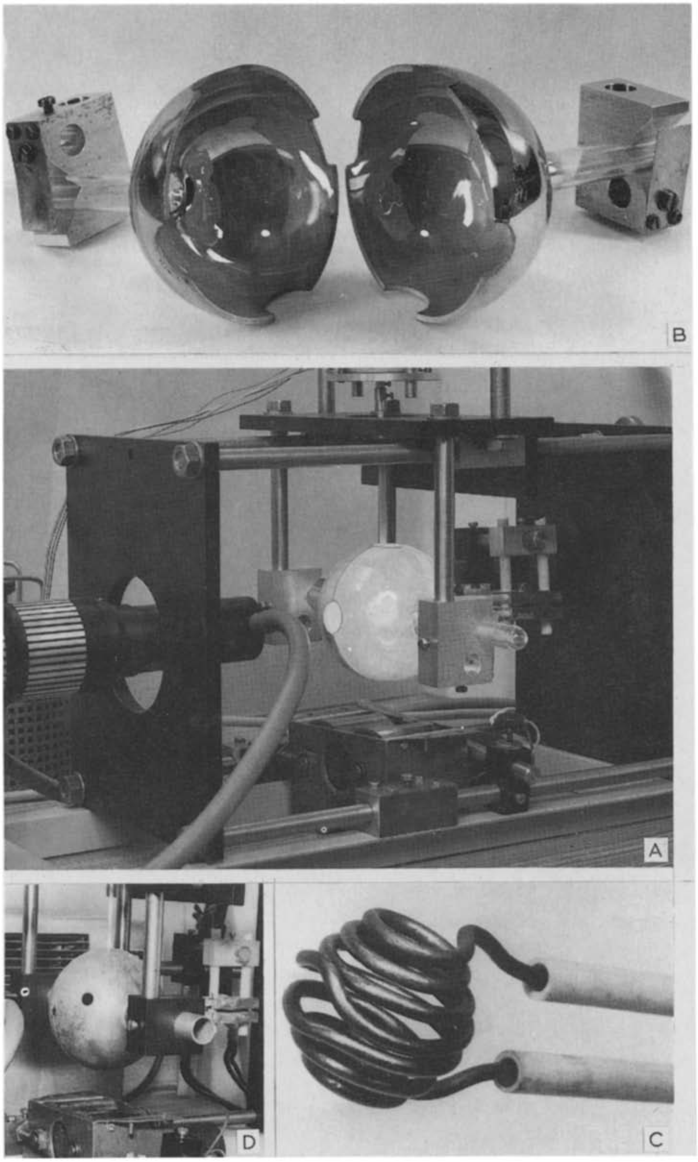


FIG. 4: High-temperature vaccuum furnace for multipurpose utilization where the schema (A) shows the following parts:
B- twofold wall made from stainless steel (B) watercooled,
H- furnace lid with two magnetically controlled openers (Fe), pyrometer (P) and look-through windows (K),
M- electric regulation system,
Q- furnace floor with a quenching accessory (dashed),
T- thermal readings of W-Re thermocouples positioned in the points 1 to 7 with vaccuum tight lead-out (N),
E- electrodes with the tungsten heating element (see C),
S- concentric radiation shields,
C- watercooled power supply holders.


B
A
D
C

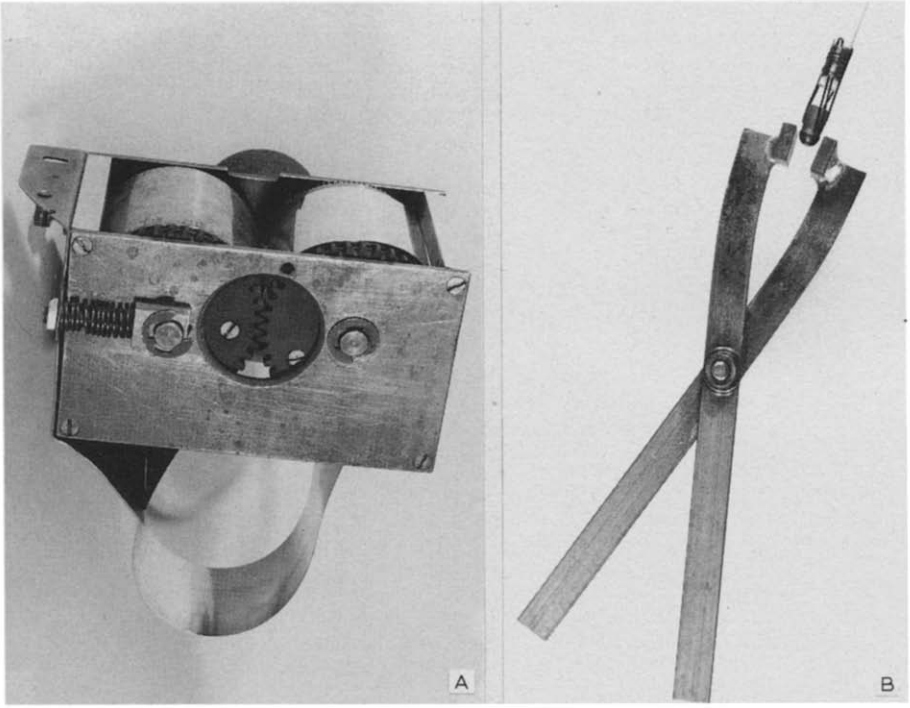


Fig. 6: (A) Apparatus for quenching melts by continuously running belt method being an invented variant of the less effective but conventional method of two rotating wheels. (B) Method of ultrafast cooling of a pendant melted drop by pressing it in-between two Cu-plates using modified tongs applicable directly during laser heating of the rod-like sample mounted at the end of a ceramic sample-holder.

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FIG. 5: Laser-aided microfurnace (A) with two concentric shields of radiation made from Ag+Pd plated silica glass (B) situated on a tridimensionally movable car also enabling the rod-like sample rotation necessary to average the temperature gradient created by one-sided laser heating. The Rh-wired microheating element (see C) surrounding the sample made it possible to achieve the ground temperature of about 1800°C by ordinary resistivity heating. A look-through window is visible in (D) showing a modified variant with Au-plated Cu-reflectors equipped with a temperature readout.

dication several W-Re thermocouples were used and for possible DTA measurements a high-sensitivity pyrometer was used to scan periodically the mutual temperatures of the sample and reference. In order to maintain constant transparency of the look-through window, it was found necessary to shield the window against evaporated oxide deposition, a common trouble of high-temperature treatments in general.

For a contactless melting of mixtures of transition metal and rare earth oxides we developed a laser-aided microfurnace [20]. A resistivity rhodium-wired microheater, see Fig.5., was placed inside a globular reflector made from gold-plated silica glass and/or copper. The sample in the form of presintered rods was mounted inside the heater where we were able to control its rotation and vertical position. The whole globular furnace was movable horizontally in order to optimally focus the laser beam aimed at the sample edge. With Rh-microheater background temperature around 1800°C it was possible to reach about 2600°C by the action of 50W CO_2 laser (powerful enough to melt a few cubic millimeters of an oxide sample [21]). Although the temperature control was possible only exploratorily the arrangement showed utilization in single crystal growth by floating zone and was particularly useful to produce glasses by ultrafast cooling of a pendant melted drop by pressing it in-between Cu-tongs, cf.Fig.6. A special look-through window enabled us to measure temperatures either by a pyrometer or by Re-W thermocouples to indicate at least a rough type of cooling curves.

The need to prepare larger specimens of frozen melts compeled us to invent a unique quenching technique called the continuously running belt method, see Fig.6., derived from a routine method using two rotating wheels [3]. The latter, in fact, did not make it possible to achieve prolonged quenching as the effective cooling was realised for a very short time only along their linear contact often letting the as-quenched sample to recrystallize after leaving the wheel contact. Insertion of an infinite metallic ribbon (made from Ag+13%Pd alloy) allowed us to maintain a melt layer to cool intensively along the prolonged one-sided ribbon contact similarly to the melt spinning method [22] convenient for metallic glass preparation. We found it impossible, however, to measure such ultra-fast temperature changes and we estimated a quenching rate as high as about 10^5 K/s.

It was possible to carry out a more precise temperature measurement during another ultra-fast method of so-called flash heating and cooling of thin ribbons of preformed metallic glasses. For such a glass annealing we employed a discontinuous method of resistivity heating by very short electric pulses introduced directly into the metallic ribbon immersed in various cooling media [20]. Using oscilloscope measurements we could estimate heating rates of about 10^4 K/s while immediate cooling was dependent on the type of cooling liquids, the least effective liquid nitrogen, the deionised (electric resistant) water, and the best oil, making possible cooling at rates as high as 10^3 K/s. Pulling a ribbon through a resistively preheated furnace followed by immediate cooling by a both-sided contact in-between the well polished Cu surfaces was found to be a good and effective method for alternative continuous annealing procedures [20,23].

LOW TEMPERATURE CHARACTERISATION OF MATERIALS

Thermally controlled preparation of materials of desired properties is the necessary basis to have a sample for further

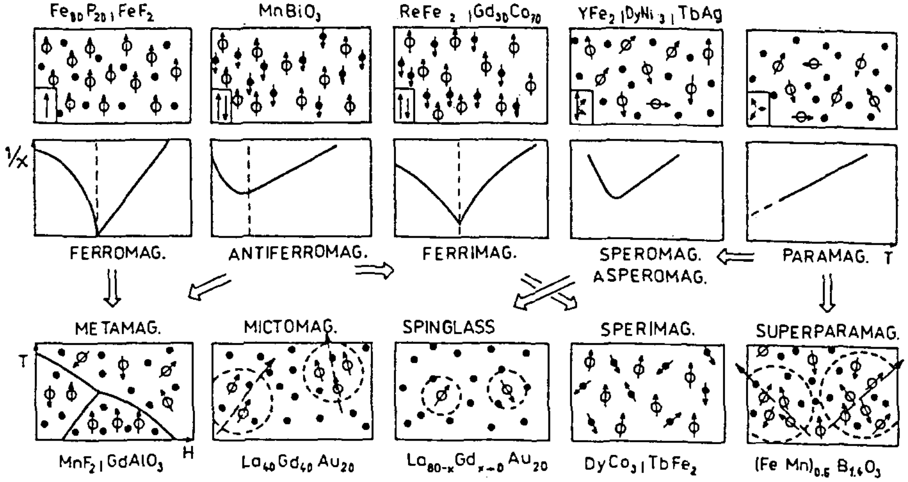

FIG. 7 : The major (upper) and minor (lower row) magnetic behaviour of noncrystalline structures illustrated by a twodimensional representation of magnetic spin orientations (arrows) of individual species (empty and solid circles). Beside thermally free moving (para-) and below Curie temperature magnetically fixed (ferro-, antiferro- and ferri-) orientations (see spin characteristic positioning and size in the left cornered oblongs) the recently investigated spero- and aspero- magnetism display partly rotative spins making it possible to follow the externally applied magnetic field. In contrast to the well established thermal dependence of the reciprocal magnetic suceptibility [24,25] $1/\chi$ of ferro-, antiferro- [26] and ferri- magnetics (see middle row) the dependences of spero- and aspero- magnetics exhibit a more rounded curve. Doubled arrows show possible interconnections, e.g., sperimagnetism can be derived from ferrimagnetism introducing canted spins [21]. Superparamagnetism [27] is analoguous to paramagnetism when the whole clusters (dashed circles) display a cooperative spin behaviour similarly to mictomagnetism where several spins act together in the same momentum. This is in contradiction to the single-behaved species of spin glasses. Metamagnetism is a combined, field induced, effect which can be best exhibited on the temperature (T) versus magnetic field (H) phase diagram where antiferro- (left), ferri-(bottom) and speri- (upper) magnetic phases can transfer from each to other in response to the externally applied experimental conditions.

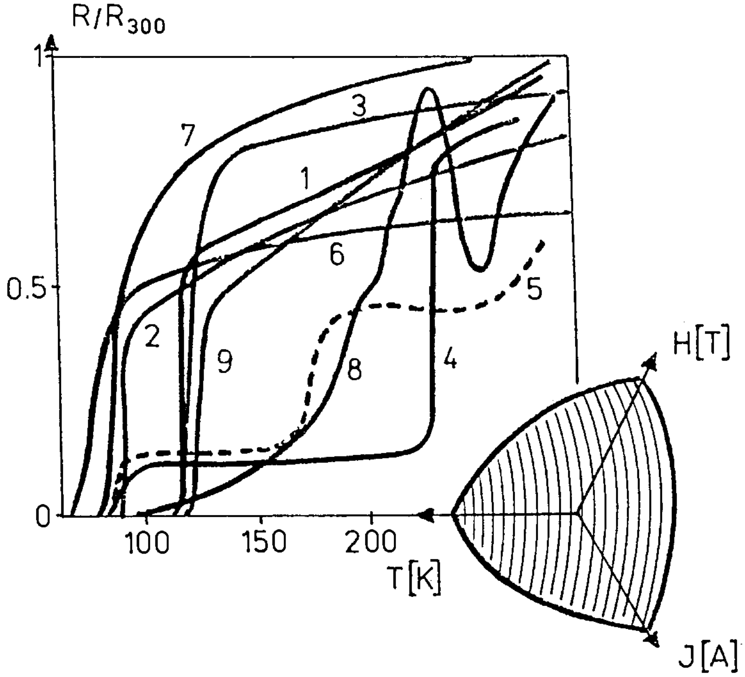

FIG. 8: The temperature dependence of the reduced value of electric resistivity ($R/R_{300\,K}$) for some samples selected to show superconductivity of various oxide materials:

-- Ceramics $YBa_2Cu_3O_x$ prepared either (1) by sintering of an oxalate precursor [28] with T_c= 107 K or (2) by annealing (at 1230 K) of solidified melts on stepwise cooling [31] with T_c= 86 K.

-- (3) Sulphur doped $YBa_2Cu_3O_x$ prepared by conventional sintering of oxide mixture with CuS [32] having T_c= 108 K.

-- Metastable phases probably presented in the $Y_4Ba_9Cu_7O_x$ system [33] exhibiting beside T_c= 83 K another steep drop at T`=170 K for original (4) or recycled (5) samples.

-- Glassceramics [34] prepared by recrystallization and annealing of quenched glasses of the composition (6) $Bi_{1.5}Ca_{1.5}SrCu_2O_x$ with T_c= 65 K and (7) $BiAl_{0.3}CaSrCu_2O_x$ with T_c= 78 K.

--The system $LaSrNb_yO_x$ [35] prepared by sputtering Nb-layers onto the $LaSrCuO_4$ targets in vacuum (assuming reduction of Nb^{5+} to Nb^{4+}) followed by annealing at 990 K (to allow Nb substitution for Cu), with T_c= 80 K and T`= 270 K (8).

--The $Tl_2Sr_{1.5}BaCu_3O_x$ system [36] prepared by conventional sintering reveals so far the highest T_c= 127 K (9).

When analysing the T_c values it is indispensable to consider the interdependence surface of the other critical values boundering superconductivity [37], i.e., magnetic field H_c and electric current J_c as illustrated at the right bottom corner of the Figure.

investigation. Samples prepared by one of the above mentioned high-temperature treatments are first subjected to conventional thermal and structural analysis, cf.Fig.2. Consequently the state characteristics are usually dealt with in more detail by low temperature measurements. Thermoanalytically nonconventional thermophysical measurements of material specific properties at temperatures even below the boiling point of nitrogen were shown to be a useful tool in revealing e.g. the different types of magnetic ordering [24,25]. From the determination of thermal dependence of the reciprocal magnetic susceptibility ($1/\chi$) various types of **glassy magnetic materials** can be classified as illustrated in Fig.7.

The ballistic method based on the relative mechanical movement of either the sample and the measuring coil or the vibrational magnetometers are common in the determination of magnetic susceptibility but nonconventional with respect to different types of the balance-based methods [3]. These techniques were utilized in the study of properties of oxide [21,25-27], chalcogenide [24] and particularly metallic [22-24] glasses containing transition metal ions.A straight measurement of magnetization directly related to increasing mode of temperature is nonconventional in experimental physics although used as a common method of TA called magnetometry [28].

Another requirement for low-temperature characterization of **superconducting oxide ceramics** [29] came just recently. The traditional measure of resistance versus temperature has become a very convenient method for the determination of superconducting critical temperatures [37] where the resitivity vanishes to zero, see Fig.8. However, a new sort of experimental problem arose. As for the interpretation one should be careful as magnetic ordering, ferroelectric and piezoelectric effects, etc., can produce a similar drop in resistivity by several orders of magnitude as well as various experimental artifacts to appear often in multicomponent samples of sintered oxide ceramics with an inherent degree of heterogeneity (e.g. due to poor contacts, unusual current loops, grain surfaces different from the bulk). A more definite proof of superconductivity can thus be obtained by the other nonconventional but complementary low-temperature measurements of e.g. Seebeck or Hall coefficient or Josephson junction. Most frequent, however, is the determination of sample diamagnetism arising from magnetic flux expulsion from the sample bulk superconductor. This so called Meissner effect can be detected only if the percolation threshold of a superconductive phase is about 2/3 while that for the positive resistivity indication is only about 1/3. However, if a superconducting phase would completely surround the nonsuperconductive core the magnetic loop would not indicate the existence of a second phase hidden inside unless this parasite phase would have penetrated outwards. A continuous superconductivity path would be a satisfactory condition for successful conductivity measurements which, however, is easy to disturb by applying external pressure breaking the grain connection necks [38].

Both types of above discussed materials bear some common features. From the moment of their introduction we have been required to find some novel ways not only for their nonconventional preparation but also for their nontraditional application capable to treat such metastable materials in long-term practical utilization. We may equally be unable to prepare superconducting oxide glasses similarly to the previous unsuccessful search for a convenient sort of soft and/or hard magnetism in oxide glasses. On the other hand, we can mention the satisfactory tailoring of metallic glasses with desired magnetic properties (glassy alloy $Mo_{64}Re_{16}P_{10}B_{20}$ also exhibiting superconductivity below $T_c=8.7$ K). Further study of oxide superconducting materials can be again directed to special thermal treatments [23,25], particularly when such procedures of ultrafast [39] or stepwise [31] cooling become capable of direct engineering utilization. Recalling the recent advancement of oxide fiber-glass technology of wave guides we cannot exclude the possibility that superconducting magnetooptics may also become actual in near future. In such a case the drawn and/or deposited filaments will probably consist of a superconducting core (or mantle) in (or on) glassy fibers. Supporting oxide material should then exhibit special properties regarding both the decreased reactivity towards superconducting core (assured, e.g., by increased content of BaO in glass to prevent parasitic reactions with $YBa_2Cu_3O_{7-y}$ [20]) and the sufficient oxygen activity (to assure an appropriate adjustment of oxygen stoichiometry y [40]) at increased temperatures. Nonconventional thermal treatment and analysis would again play an important role as to achieve well balanced composite materials. The resulting need for a more extensive discussion [6,29,31,41] falls, however, beyond the framework of this rather illustrative presentation.

CONCLUSION

Modern research on progressive materials requires a conformable use of thermal treatments and analysis over a wide region of temperatures. There certainly is no room for possible contradictions between individual techniques of thermophysical measurements even though they are employed by thermoanalysts or experimental physicists who can possibly have a contradictory viewpoint of what experimental conditions are more or less suitable for a given type of sample characterisation and investigation.

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