NUCLEAR TECHNIQUES IN THE DEVELOPMENT OF ADVANCED CERAMIC TECHNOLOGIES

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Abstract

The importance of research, development and application of advanced materials is well understood by all developed and most developing countries. Amongst advanced materials, ceramics play a prominent role due to their specific chemical and physical properties. According to performance and importance, advanced ceramics can be classified as structural ceramics (mechanical function) and the so-called functional ceramics. In the latter class of materials, special electrical, chemical, thermal, magnetic and optical properties are of interest. The most valauble materials are multifunctional, for example, when structural ceramics combine beneficial mechanical properties with thermal and chemical sensitivity. Multifunctionality is characteristic of many composite materials (organic/inorganic composite). Additionally, properties of material can be changed by reducing its dimension (thin films, nanocrystalline ceramics). Nuclear techniques, found important applications in research and development of advanced ceramics. The use of neutron techniques has increased dramatically in recent years due to the development of advanced neutron sources, instrumentation and improved data analysis. Typical neutron techniques are neutron diffraction, neutron radiography, small angle neutron scattering and very small angle neutron scattering. Neutrons can penetrate deeply into most materials thus sampling their bulk properties. In determination of the crystal structure of HTSC, $YBa_2Cu_2O_7$, XRD located the heavy metal atoms, but failed in finding many of the oxygen atoms, while the neutron diffraction located all atoms equally well in the crystal structure. Neutron diffraction is also unique for the determination of the magnetic structure of materials since the neutrons themselves have a magnetic moment. Application of small angle neutron scattering for the determination of the size of hydrocarbon aggregates within the zeolite channels is illustrated.

1. Introduction

The shift from traditional to high technology-based industries depends on the development of advanced materials. Better functional materials have their impact not only on economic, but also on environmental issues. Products made from high durability materials have a longer life cycle, producing less waste and effecting lower overall energy invenstment.

Similar advantages are gained when using miniaturised systems. Engines made from materials resistant to high temperatures, assure better efficiency of burning, thereby decreasing both fuel output and gas formation. Parasitic heat production will decrease and efficiency increase when electricity can be transferred by superconductors etc.

The importance of development and application of advanced materials is well understood by all developed and most developming countries. The U.S.A. for instance is doubling its expenditure on materials research in the next year. The development as well as the reliable and efficient processing of new materials rely strongly on their characterization.

Many physical, chemical and optical methods are in use, the selection of the technique being dependent on the kind of information to be obtained and on the available equipment. Nuclear methods, and more specifically neutron diffraction and scattering, has proved very fruitful in investigation structural properties of complex materials. The performance of advanced ceramics is dependent on their structural, chemical and electronic configuration. High temperature superconductors for example exhibit wide compositional fluctuations and oxygen disorder effects as a result of aging, method of fabrication and other conditions; these changes, that affect their electrical properties, can be observed by neutron techniques. Apart from superconductor research, the variety of materials studies by neutron diffraction and scattering is equally impressive, inclunding zeolites, fast ionic conductors, permanent magnets, materials with defects, materials undergoing phase transitions, residual stress analysis, ordering and phase separation in alloys and multilayer structures.

Beams of electromagnetic radiation, electrons or other charged particles, which are used as probes, interact primarily with electrons and are therefore confied to the surface. Neutrons can penetrate deeply into most materials thus sampling their bulk properties. As a probe of materials, neutron scattering suffers from a number of limitations: it is expensive, non-portable, cannot be obtained by other means. However, the use of neutron techniques has increased dramatically in recent years due to the develompment of advanced neutron sources, instrumentation, and improved data analysis. For example, the discovery of $YBa_2Cu_3O_7$ was quickly followed by several X-ray determinations of the crystal structure; however, because of twinning problems and relatively weak oxygen stoichiometry and location, X-rays were unable to establish accurately the oxygen stoichiometry and location. This knowledge, which is vital to a proper understanding of this material, cames only as a result of neutron powder diffraction studies.

Material scientists and technologists are finding that the great penetration depth, nondestructive nature of neutrons, their ability to probe materials not only under ambient conditions but also at high and low temperatures and pressures, are also making them indispensable in characterizing real materials using small angle scattering (SANS) techniques. Grain boundary cavitation, whereby small voids develop and accumulate at the grain boundaries of materials subjected to deformation at elevated temperatures, is an important and poorly understood damage mechanism in real high temperature materials. The type of information needed to understand this phenomenon includes the number of densities of the voids and their size distribution. Transformation toughened zirconia represents another example where this kind of knowledge is essential. Another use of neutron scattering in the study of real materials is the measurement of bulk residual stress. Other methods commonly employed, e. g., strain gauges or ultrasonics, are either destructive or strongly affected by texture in the sample. Yet the ability to reliably measure the distribution of internal stress is vital to the safe and effective design of parts made from composite ceramics or metals.

2. Advanced Ceramic Materials: An Overview

Amongst advanced materials, ceramics play a more and more important role due to their specific properties but also in many cases due to availability, low costs and environmental compatibility. According to performance and importance, advanced ceramics can be classified according to their properties, as structural ceramics (mechanical function), and the so-called functional ceramics (Figure 1). In the latter class of materials, special electrical, chemical thermal, magnetic and optical properties are of interest. These materials are expected to become more and more significant as components of intelligent systems composed of sensors (information, cf "senses"), actuators (movement, cf. "legs and hands"), batteries (power, cf. "metabolism") and computers (cf. "brain") (Figure 2). In the field of electroceramics (electric function), high Tc superconductors (e.g. $YBa_2Cu_3O_{6+x}$) play a prominent role in view of many applications such as high performance magnets (Figure 3). Of high potential are ionic conductors such as oxygen, proton, sodium and lithium conductors (e.g. ZrO_2 (Y_2O_3), $SrCeO_3$ (Yb_2O_3), β-Al_2O_3 (Na_2O), LiI:γ-Al_2O_3). They can be used as solid electrolytes for batteries, fuel cells, chemical sensors and electrochemical pumps (Figure 4). Ceramic semiconductors such as $BaTiO_3$, $SrTiO_3$, SnO_2 , TiO_2 , $PbZrO_3$ are used for example as capacitor materials, chemical sensors and actuators (Figure 5). Mixed conducting materials combine both ionic and electronic conductivity, and thus enable neutral components to permeate through, or dissolve or remove them. This is of relevance for advanced electrodes and electrochemical filters e. g. $La_{0.5}Sr_{0.5}CeO_{3+x}(TiS_2)$, for catalysts ($CeO_2$), and for chemical storage of $H_2(NbH_x)$ or $Li(TiS_2)$ as a cathode in Li-batteries. In the latter case accompanying colour changes can be used in electrochromic devices (smart windows) WO_3Li_x) (Figure 6).

Besides the chemical functions mentioned so far, catalytic properties of ceramic surfaces (external or internal) are also significant (e. g. zeolites or γ-Al_2O_3). Thermal functions are important for appropriate substrate materials, such as AlN or diamond (films) exhibiting

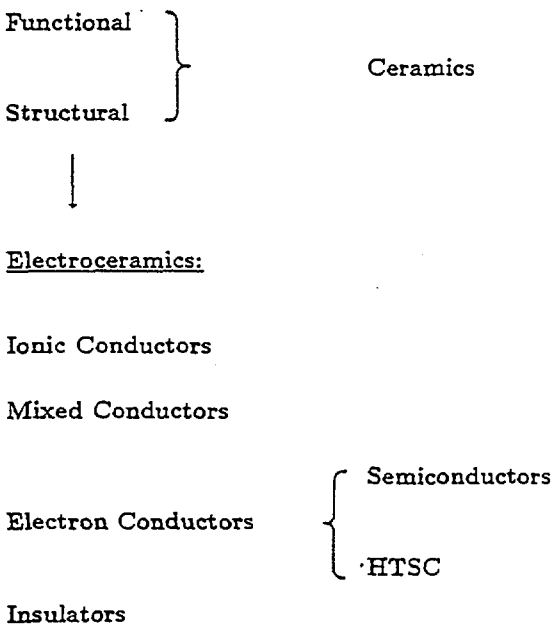
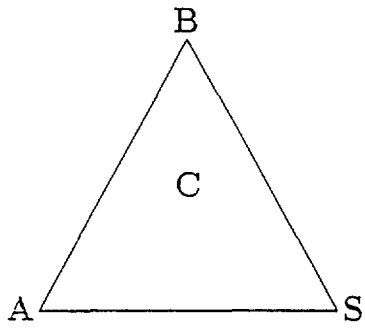


FIG.1. Advanced ceramic materials



A: Actuator ("arms", "legs")

S: Sensor ("senses")

B: Battery ("metabolism")

C: Computer ("brain")

FIG. 2. Intelligent materials

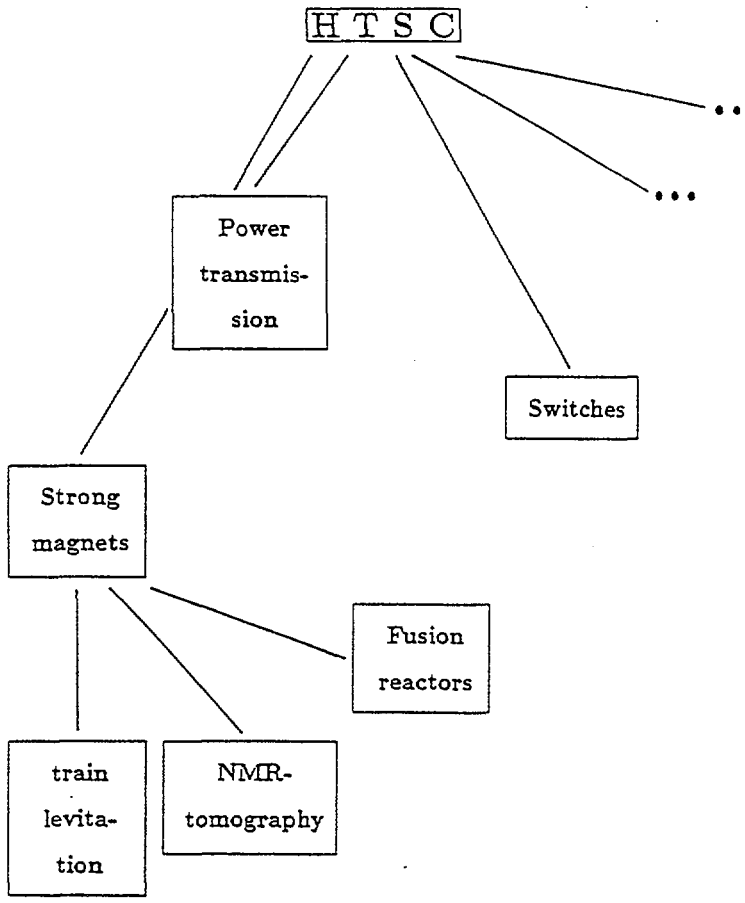


FIG. 3. Possible applications of HTSC.

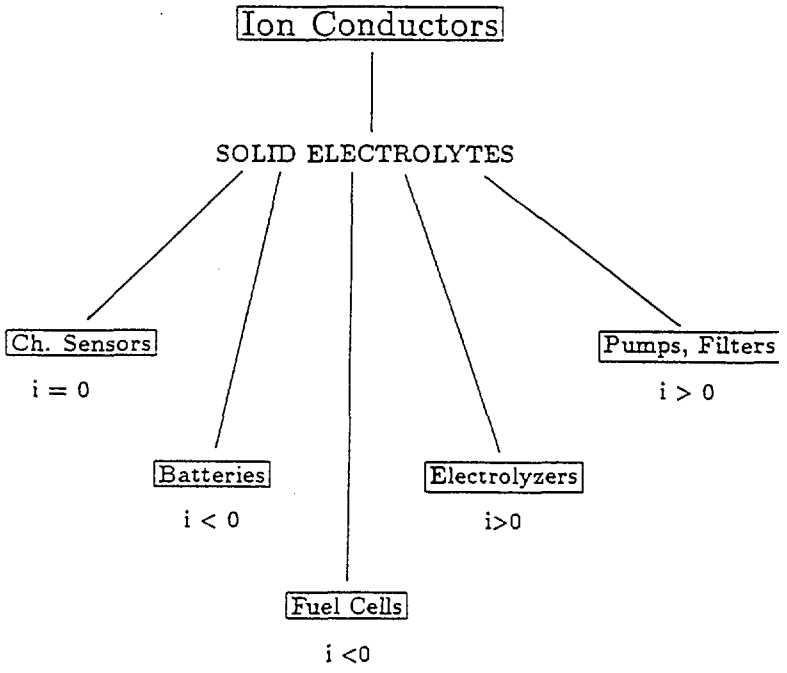


FIG. 4. Possible applications of ion conductors.

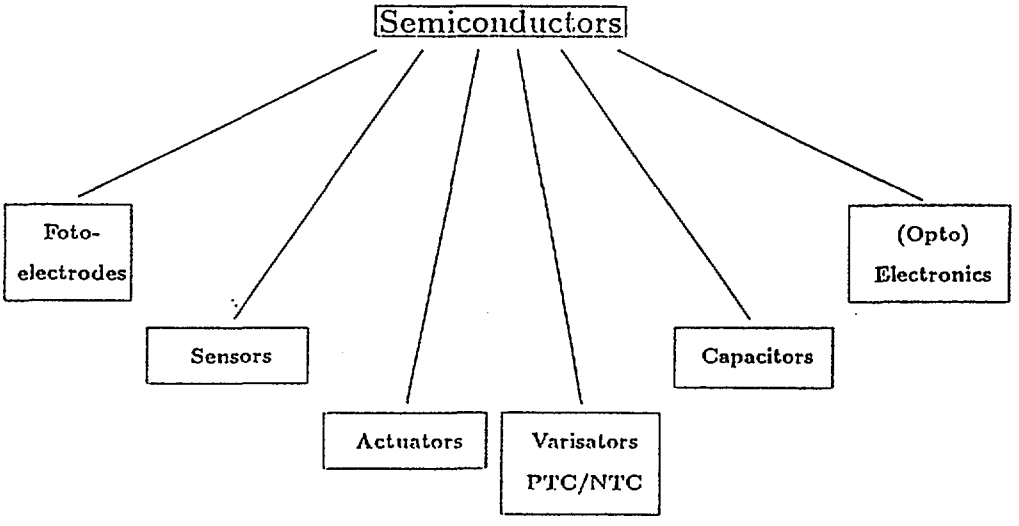


FIG. 5. Possible applications of ceramic superconductors

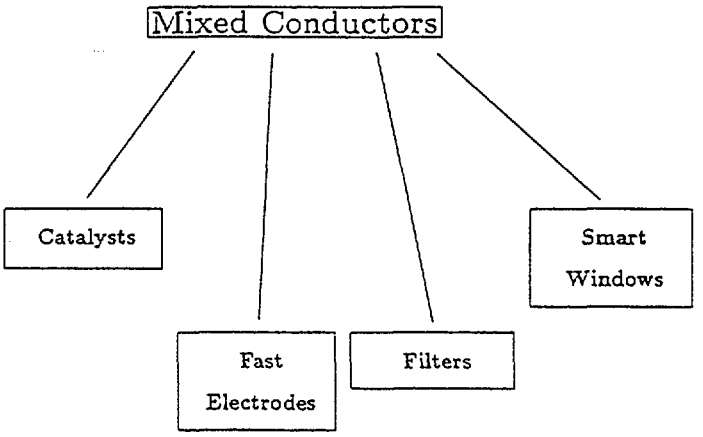


FIG. 6. Possible applications of mixed conductors

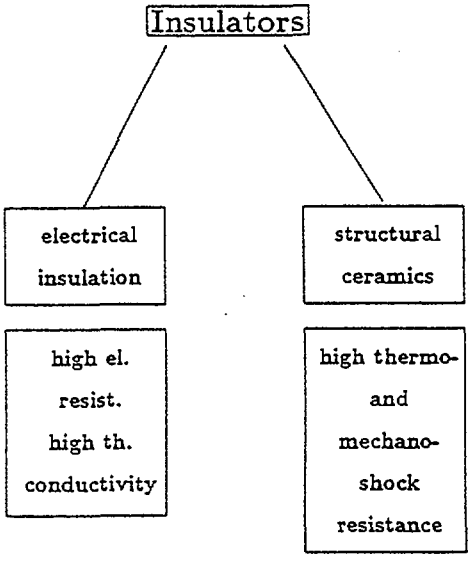


FIG. 7. Possible applications of insulating materials

high thermal conductivity but being nevertheless electrical insulators. Figure 7 indicates important applications of insulating materials. Glass ceramics are examples of composite materials with low (and tunable) thermal expansion. Besides these functions, specific magnetic properties, e.g. ferrites or optical, e. g. laser materials, are also met in ceramic materials. Of course most important materials are multifunctional, e. g. structural ceramics combine beneficial mechanical properties with thermal and chemical resistivity. Multifunctionality can also be achieved by composite materials (e. g. organic/inorganic). Additionaly, properties can be chaned by reducing sample dimensions (thin films, nano-crystalline ceramics (mesoscopic effects).

The main tasks of materials science can be classified as follows:
1) search for new materials
2) understanding and characterization of given materials
3) modification of given materials

Since recommendations will mainly refer to the last two points, the main classes of problems with respect to existing materials may refer to

a) understanding of the kinetics
b) understanding of the structure including the defect structure
c) understanding of the interfacial behavior (outer and inner surfaces, grain boundaries)
d) thermodynamics and kinetics of interactions with neighbouring phases
e) understanding of the interaction of the material with external forces (electrical, magnetic, stress etc. effects) as a function of controlling parameters such as temperature, O_2 partial pressure etc.

Due to the specific weaknesses and strengths of neutron methods the following more specific problems have been selected to be appropriate for neutron investigation:

i) Detection of Impurities in Ceramics-Hydrogenous Impurities in Oxides

This has become a major problem in materials science and is especially important for materials such as Yb-doped $SrCeO_3$, where oxygen vacancies due to the Yb-incorporation provide the possibility for H_2O incorporation and make the material a most prominent proton conductor. (A second problem is detection of oxygen in AlN, where O drastically reduces the thermal conductivity).

ii)Defect-structure

For understanding the properties of functional ceramics, an understanding of the defect structure is especially necessary. With neutron methods the normally low defect concentrations cannot be investigated. A lot of important materials, however, are heavily doped or may exhibit substantial frozen-in intrinsic disorder. Examples are Y_2O_3 doped ZrO_2 a most important ion conductor (solid electrolyte in electrochemical O_2 sensors, or in high temperature fuel cells) where high Y-concentrations (typically 10 %) are present, Yb doped $SrCeO_3$ as mentioned above, Sr doped $LaCoO_3$ used as an advanced anode in high temperature fuel cells; as well as Sr-doped La_2CuO_4 or oxygen and cation disorder in $YBa_2Cu_3O_{6+x}$). In all these cases the influence of small defect concentrations is sufficiently well understood but the effect of the large defect concentration (typically 10 % and more) is still an open and very relevant problem with respect to the properties.

iii) Mesoscopic Effects

In general trend in materials science to reduce the dimensions of the samples, be it by producing thin films or be it by producing ceramics of very fine grain size, gives rise to the question of the dependence of properties and especially of structural changes upon size reduction. Consequences may be changes of transport properties in ionic conductors (e.g. β-Al_2O_3) or the transition temperature in high Tc superconductors.

iv) Interfaces

An overwhelming number of materials problems are connected with interfacial problems (e. g. grain bounderies and interfaces reducing critical currents in superconductors, enhancing or decreasing overall conduction in ionic conductors). With neutrons, however, only materials with high interfacial densities as in zeolites (catalysis), γ-Al_2O_3 (catalysis, composite electrolytes) and nano-nano composites can be studied.

v) Mechanical Failure

The occurrence of stress effects especially in view of cracking of the material is of crucial significance for structural ceramics (cracking is often induced by macroscopic inclusions), e. g. used as engine parts or turbines where high (thermo-) mechanical demands have to be fulfilled. In the same way e. g. the sodium conductor, β-$Al_2O_3(Na_2O)$, used as a solid electrolyte in high performance Na/S cells (electrovechicles) shows a tendency to crack at 300 °C in contact with liquid sodium on one side, and with liquid sulfur on the other side, after a certain number of de- and reloading cycles.

vi (Ideal) Structure

Although the (ideal) structure of most advanced materials has been clarified, studies of this type are nevertheless important to elucidate the average local structure in non-crystalline systems such as glasses or gels. This is particularly true for characterizing multiphase mixtures (e. g. during the preparation) porous materials or composite materials in general.

vii) Kinetics

The above points essentially refer to static experiments. A field which has not been tackled so much but which is of substantial interest for understanding and optimizing materials in view of preparation, modification and also durability (aging effects!) is the investigation of transistent phenomena. Examples would be preparation and kinetic stability of high Tc superconductors which are thermodinamically unstable under real conditions.

viii) Materials Modification by Neutrons

A completely different neutron application from using them as a tool of characterization, is their use in the preparation or modification of a given material. Successfull examples are the increase of the critical current density in HTSC materials ($YBa_2Cu_3O_{6+x}$) due to flux pinning by the introduction of defects, and P-doping of Si by inducing nuclear reactions.

3. Neutron Scattering in Materials Science

As a tool for the charcterization of materials thermal neutrons offer several well-known but unique advantages over other common probes such as protons, electrons or X-rays. Carrying no electrical charge, they are weakly interacting and therfore deeply penetrating. Because of their low energy they are non-destructive. Their low energy also makes them ideal for inelastic scattering studies-extremely important for the detailed fundamental understanding of all classes of materials. However, inelastic scattering cross-sections are invariably very low and such studies are best left to high flux reactor facilities. By contrast in neutron transmission and elastic scattering experiments a substantial fraction of the incident neutron flux is actually measured, and these studies can be successfully carried out at reactors with very modest fluxes. Furthermore-and this is a key point-several of these techniques are particularly powerful in attacking the important ceramic materials problems discussed below on a level likely to lead to practical progress which can be rapidly passed on to the technological sector.

Generally, the techniques that we feel are particularly well-suited to modest research reactor facilities fall into three broad catagories depending upon the magnitude of the angle, Q_S , by which the neutron beam is refracted or scattered-

1) $Q_S = 0$, neutron transmission or radiography which reveal microscopic features (e.g. cracks) of charcteristic size $1\mu = 10\text{-}3$ cm.
2) .001 -<Q_S-<1o, small angle neutron scattering (SANS) which probe homogeneity (e.g., granularity, pores) of mesoscopic dimensions, 100 Å - 1μ.
3) Q_S-> 10^o, powder diffraction which explores structure on the interatomic length scale (10 Å - 1 Å).

Note that the length scale examined is inverse to the scattering angle. Each of these techniques require different instrumentation which will be briefly described later, but in each case the instrumentation is (a) comparatively simple, robust and inexpensive and (b) requires a minimum degree of sophistication to operate. Both of these characteristics are important for developing countries.

It must be clearly understood that thermal neutron techniques are not a sufficiently broad base upon which to build a successful program of advanced ceramic materials characterization. Other traditional methods (electrical, optical, electron microscopy, x-ray scattering, etc.) are also indispensable tools which can and must be used as appropriate. But, as we hope to make clear, the development of home-grown neutron capabilities of the type discussed here would be a substantial benefit to any well-conceived program in ceramic synthesis and processing. Furthermore, such facilities already exist, at least at a rudimentary level, in many developing countries or could be developed at existing low flux reactors at minimal incremental cost. (Suitable reactors exist in many countries.). Of course, such facilities, once developed, are useful in the context of other industrially significant, materials studies (metals, polymers, etc.).

4. Neutron Materials Science Techniques at Small Reactors

Neutrons are a very capable tool for investigating new advanced materials and modifying their properties by irradiation to produce defects. At small and medium flux reactors it is necessary to choose problems appropriate to the manpower and beam hole resources. Often simple techniques can be used to investgate properties of new materials which are of basic technological interest - for example, formation of cracks, aging effects, fatigue effects and structural changes. Neutron radiography, neutron small angle and very small angle scattering are examples of suitably simple techniques.

Neutron Radiograpy

This is one of the most typical application of small reactors and is a first step for materials orianted neutron work. Neutron radiography can be devoted to applied as well as to more fundamental research. One can investigate metalurgical problems such as the diffusion of hydrogen in various ceramic materials, and changes in atomic diffusion and exchange rates for hydrogen at the surface with different atmospheric conditions. For example, one can study the distribution and aggregation of 3He produced by the decay of tritium in such ceramics. Extreme internal strains and the formation of bubbles with very high He-pressure occur, and contribute to the embrittlement of such materials. This can be a limitting factor in future fusion devices. Long term investigations can deal with the aging process and with the increasing embrittlement stage of the materials. Sensitivities for hydrogen detection to the order of 1 %, for oxygen to the order of 3 %, and for metallic composites to 5 % are feasible. A typical radiography installation is shown in Figure 8.

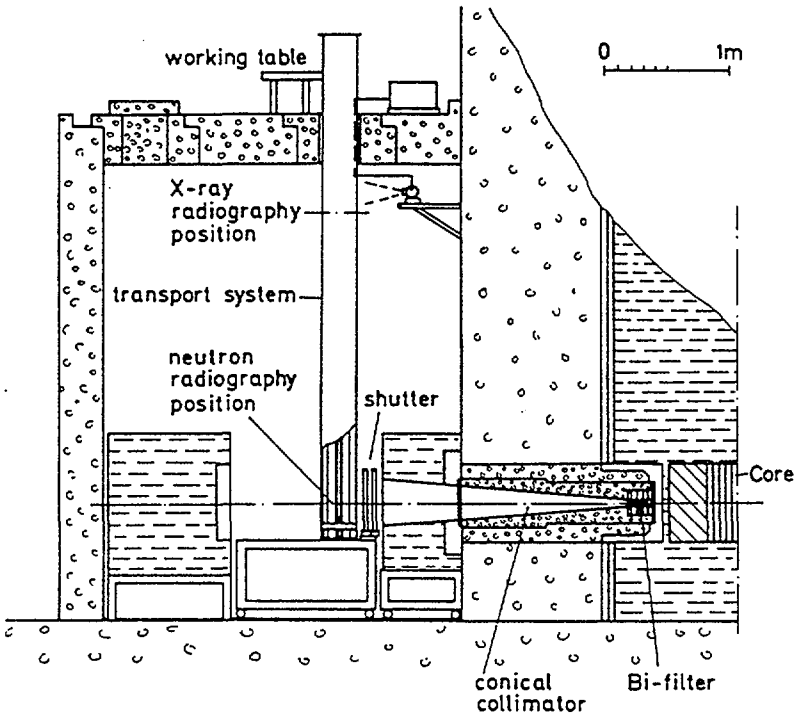


FIG. 8. An installation for neutron radiography at the Vienna University reactor.

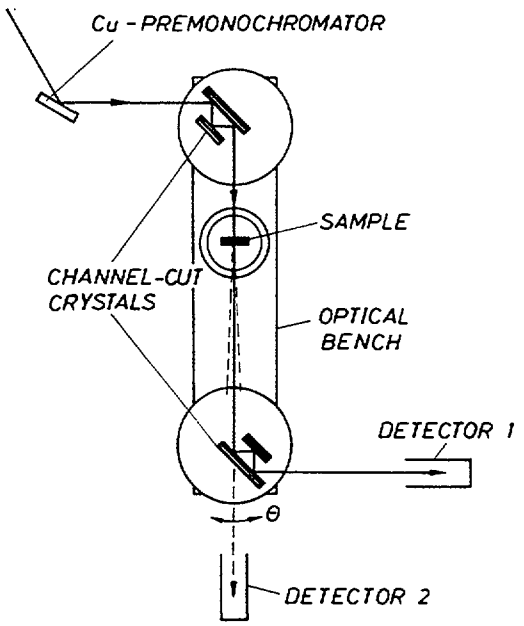


FIG. 9. The perfect crystal small angle scattering camera at the Vienna University reactor.

Neutron Small Angle Scattering

We recommended the use of the perfect crystal small angle scattering camera because it is especially sensitive to large inhomogeneities and ckracs, which are serious problems related to the performance of new ceramic materials. This kind of small angle camera (Figure 9) is based on the non-dispersive arrangement of two perfect crystals, and operates with thermal neutrons, avoiding the need for a cold neutron source. Such an instrument is equipped with monolithic channel crystals increasing the angular resolution, which is of the order of several seconds of arc - i.e. two orders of magnitude better than for standard small angle scattering instruments. Because the resolution is decoupled from the divergence of the incident beam, a rather divergent beam can be used, providing sufficient intensity at small and medium flux reactors. Due to the compactness of this kind of camera, real time experiments can be performed to investigate aging and fatigue effects. The formation of precipitates or other inhomogeneities can be investigated. Even the forward transmitted intensity contains valuable information of the bulk properties of the sample. Cracks and other inhomogeneities with spatial dimension in the order of 1mm can be detected very easily. Measurements at different temperatures, different surrounding atmospheres and different strain conditions can help to develop these new materials in a form applicable for routine use. In future such materials will also be used in filament form. In such cases this kind of very small angle scattering can contribute substantially to testing such materials before industrial use.

Ceramics Irradiation

Semiconductor and superconducting properties can be effectively influenced by neutron irradiation. In many cases the critical current, which for presently available HTC-superconductors is a weak point, can be increased by more than one order of magnitude. Several kinds of neutron irradiation at different temperatures can produce different pinning centres causing various changes in the superconducting properties, which can be stable as well as unstable. Such investigations can help in the basic understanding of ceramic superconductors, but are also of importance for increasing their performance.

5. The Microstructure of Ceramics Investigated by SANS

Ceramics are currently made from a wide variety of raw materials, and come in a wide variety of forms, which range from glasses to conglomerates of small crystals and combinations of the two. The consequence of such diversity of forms and compositions is the wide range of their applications.

Ceramics are complex materials. A material that is a mixture of two or more component substances, my consist of two or more phases - homogeneous, physically distinct and mechanically separable portions. Under ideal conditions the phases are in equilibrium. However, in practice the material is manipulated under non ideal conditions. When a material is heated, worked and cooled, it may pass through various nonequilibrium states. Indeed, it has been primarily by the processing of materials far from equilibrium that a range of truly new structures have been obtained, exhibiting new properties and performing in new vays. It is common knowledge that the coupling of a materials bulk properties to its microscopic structure is essential to drive advances in the development of new materials and new processing technology. Namely, information is required on relations among structure, properties and performance and how those mutual interactions are affected by processing.
In all their applications ceramics are valuable for their ability to withstand heat and chemical attack. These properties stem directly from the strong bonds (ionic and covalent) which hold their constituent atoms together but, on the other hand, this also leads to brittleness. Indeed,

ceramic materials under load have a propensity to crack and break instead of to deform. They are thus particularly sensitive to the presence of imperfections in the microstructure that migt serve as starting points for cracks. Ceramics can be made more crack-resistant if such defects as voids or chemical impurities segregated between the materials grains, could be eliminated.
A ceramics microstructure on a scale of the order of 100 Å can be investigated by conventional Small Angle Neutron Scattering (SANS) techniques, using a neutron beam produced at a medium flux reactor. Basically it requires a well collimated beam of roughly monochromatic neutrons around the transmitted beam axis. The restriction to small angles eliminates "Bragg" scattering from individual atoms, which occurs at larger angles. Thus, as far as the SANS technique is concerned, the material presents itself as a continuum with a certain average scattering power for neutrons. SANS occurs whenever there are significant changes from this average value in the material due, for example, to voids or precipitates in the matrix. Material homogenity, on the 100 A scale, can therefore be examined by SANS [1, 2].
Microstructure modifications caused by thermal, mechanical and other specific treatments can be detected by comparing SANS spectra measured before and after treatment [3, 4]. The stability of the microstructure can be checked as a function of time. For example, aging effects can be followed by SANS measurements at different times. This is particularly relevant for technologically important materials, which are used in a "metastable" state [5]. Microstructure dependence on the processing parameters can be investigated by performing systematic SANS measurements as each parameter is changed. Ultimately, the optimum processing conditions can be found. This is also an important aspect since the microstructure of ceramic samples obtained, for example from oxide powders by sintering, strongly depends upon such parameters as the powders grain size, applied pressure, temperature and sintering time [6].
SANS intensities, adequately treated and analysed, can provide quantitative information on the volume fraction, average size and even shape of inhomogeneities present in the matrix and responsible for the scattering. To this end, experimental results should be compared with the predictions of analytical and/or numerical models [7]. It should be noted that, for most technical materials, this type of information can only be obtained using neutrons. As for any neutron method, SANS provides information (on the material's microstructure) averaged over the whole volume sampled by the beam (a few cm^3); it is a non-destructive technique which means that a given piece of material can be examined repeatedly at different times and/or under different conditions; it does not require any special preparation of the sample, unlike transmission electron microscopy (TEM), for example. For these and other reasons, conventional SANS instruments are currently the neutron scattering facilities subject to the heaviest demand by materials scientists and engineers all over the world. It is fortunate that such an instrument can be a useful tool for materials R&D even when installed at low flux reactor [8]. The reason for this is that only rough monochromatization is required for the incident beam, so that a relatively large slice of the thermal neutron spectrum can be used. It has therfore been considered one of the first-choice instruments for low flux reactors [9]. The small angular spread of the incident beam, which is required in order for small scattering angles to be measured, is the main factor reducing the neutron intensity at the sample. Recently, however, it has been shown that the intensity can be substantially increased if the instrument is large enough to use the full neutron source area [10]. Several SANS instrument designs have been described in the literature [7]. Under certain circumstances it is advisable to opt for a SANS facility that uses a collimation assembly without movable guide segments [11]. Its implementation is simpler and less expensive than that of an instrument using quides in the collimation path [12], and this can be a valuable asset when it comes to the implementation of a performing instrument at a lower flux reactor.
A SANS instrument can be partially constructed locally but there are a few parts that, because of their intrinsic complexity, should be purchased-the mechanical velocity selector for rough

monochromatization, and the position sensitive detector for neutron detection and angular positioning. The remaining components are the beam-plug and shutter, the collimator with a set of diaphragms, the sample chamber, and the detector chamber, which can all be constructed at a normally equipped mechanical workshop. Some basic vacuum equipment will be needed since the whole beam line should be in rough vacuum, to avoid neutron intensity losses due to air scattering. Microstructure investigation by SANS, including data analysis at different levels of complexity, as well adapted to the training requirements of both undergraduate and graduate students engaged in the preparation of thesis to obtain a University degree. Cooperation between research group using small reactors with similar capabilities in different countries should be promoted. The same applies to the collaboration between groups that do complementary work by investigating different properties of the same material. Finally, groups that work at low flux reactors should have access to neutron scattering instruments at higher flux reactors whenever necessary to complement measurements carried out at their home facilities, and to perform more detailed studies of particularly interesting (or samples).

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6. Characterization of Materials by Neutron Diffraction

Defects and Structure of Materials

One of the most basic measurements of a material that can be performed with neutrons is to determine its crystalline structure. Of course, X-rays are normally used for this purpose, but neutrons have unique adventages. For example, classical X-ray diffraction requires the growth of a small single crystal of the material. In some cases this is not possible, or perhaps undesirable since crystal growth is a "purification" process that may change the properties of the material. Neutron powder diffraction provides a method of obtaining the crystal structure from the ceramic material itself, without the need for growing a single crystal. This powder method using Rietveld refinement is less successful with X-rays because then scattering is from very small volumes of sample, and the "texture" of these small samples introduces important systematic errors. The much greater penetrating power of neutrons means that large samples can be used, eliminating most systematic errors. As well, X-rays are scattered mainly by heavy atoms, while neutrons are scattered equally well by oxygen, nitrogen and other light atomic constituents of ceramics. Finally the penetrating power of neutrons means that samples can more easily be examined under extremes of temperature and pressure, when their structure often changes. The structure of the 90 K superconductor $YBa_2Cu_2O_7$ is perhaps the most well known example of the success of neutrons compared to X-rays, but is typical of many of the structural problems that must be tackled for ceramics. The most concerted efforts at X-ray analysis have ever performed were of course applied to this material as soon as it was discovered, yet the structure was not understood until neutron measurements were made. Figure 10a shows the structure obtained with X-rays, in this case at Bell Labs [1], but typical of the results obtained at other large laboratories. Figure 10b shows the apparently quite different structure obtained by neutrons, in the case at ILL Grenoble [2] but typical of results obtained at other neutron centres. The X-ray structure located the heavy metal atoms, but failed to find many of the oxygen atoms, while the neutron structure located all atoms equally well. This was particularly important in the case of the ceramic oxide superconductors, because the oxidation state of these materials drastically changes their superconducting properties.

Magnetic Structures-Hard Permanent Magnets

Neutron diffraction is of course unique for the determination of the magnetic structure of materials, since the neutrons themselves have a magnetic moment.
In the early 1980's a Nd-Fe-B alloy was found to have remarkably good magnetic properties up to 585 K, with an energy product up to 360 J/m^3. Since these new materials are also cheaper than rare-earth-cobalt magnets such as $SmCo_5$, they are of interest for many applications. Initially, even the chemical formula of this new phase, $Nd_2Fe_{14}B$, was not known until the crystal and magnetic structures were established [3]. The Nd and B atoms were found to occupy layers (Figure 11), separated by Fe-layers. The strong anisotropic magnetic properties of these materials up to room temperature and above, due to the rare earth ions, and the relatively large proportions of common iron compared to an expensive rare earth element, make these materials particulary attractive.

Interfaces and Catalysis e.g. Zeolites

The active surface of a catalyst makes up a large part of its volume, so neutron scattering from the bulk material can provide information about the catalytic interface. For example, zeolites are important for hydrocarbon production, as molecular sieves, etc.. They consist of a silicate skeleton containing channels of various sizes that can accommodate

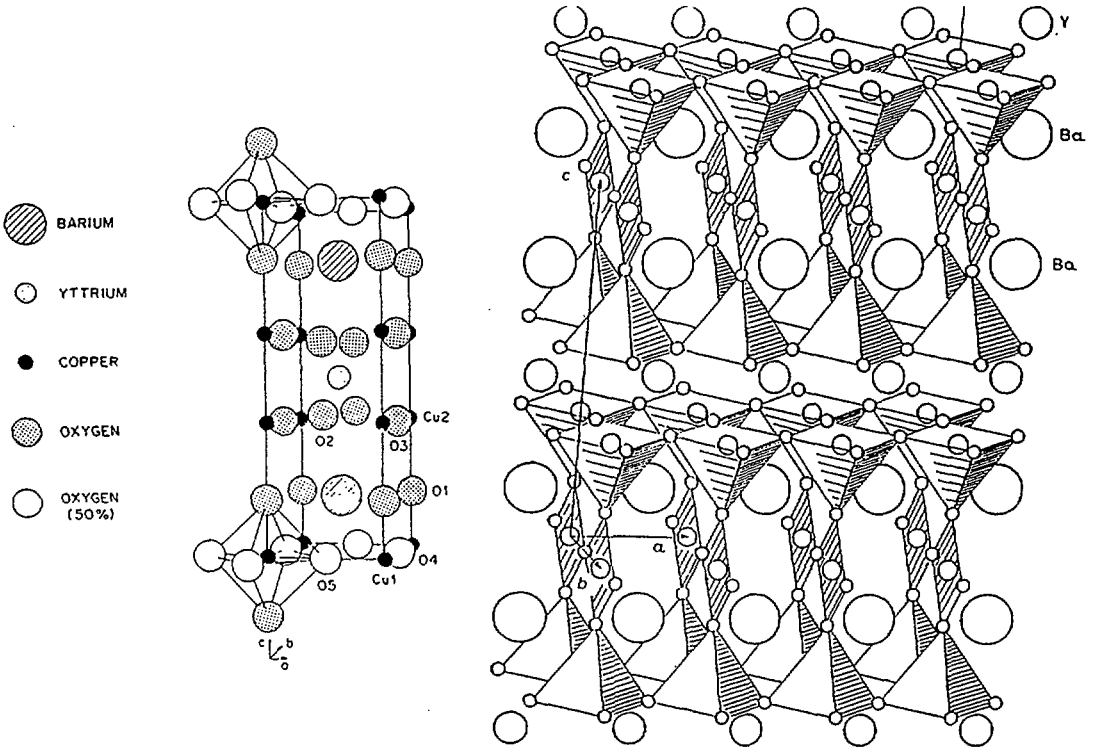

FIG 10. The structure of the 90 K superconductor $YBa_2Cu_3O_7$ as obtained by a) X-rays [1] and b) neutrons [2].

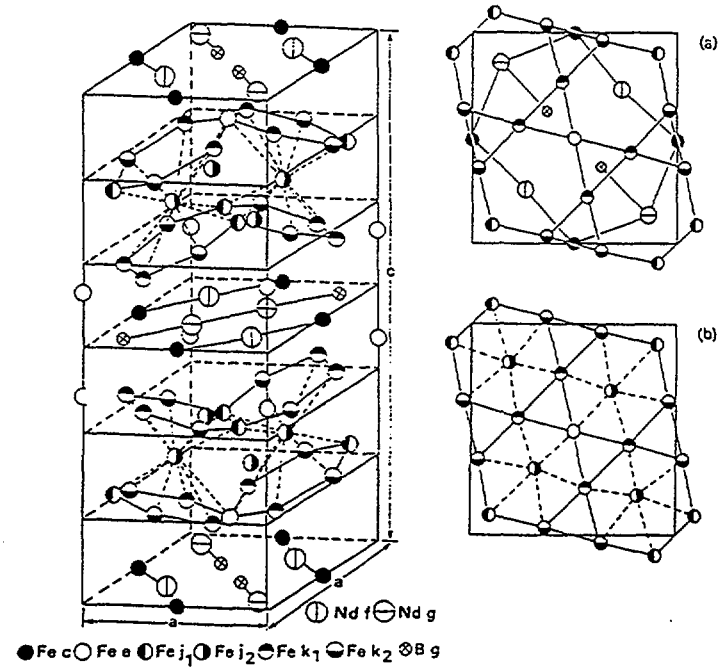

FIG. 11. Tetragonal layer structure of the hard permanent magnet $Nd_2Fe_{14}B$ obtained by neutron powder diffraction: notice that the (Nd,B)-layers are separated by layers of Fe, the inexpensive major constituent of the material. These Fe-layers are shown more clearly in projections (a) and (b) [3].

different hydrocarbon molecules; it is important to understand how these molecules interact with the zeolite interface and with each other. The basic zeolite structure can of course be obtained with X-rays, but neutrons are much better for seeing the light atoms of the hydrocarbon. Hydrogen itself has a large negative scattering length, and even greater contrast can be obtained by comparison with deuterated materials, since the deuterium hydrogen isotope has a large positive scattering length. The experiment is simply to collect the neutron diffraction pattern from a powdered sample of anhydrous zeolite, and to compare it with the pattern from the same sample containing hydrocarbon. The difference between the two can be used to construct a "Fourier" map of the location of the hydrocarbon in the channels. In this way one can identify which atoms of the hydrocarbon interact with which atoms in the zeolite channels. Figure 12a shows a simple example of such a difference Fourier map, showing benzene in sodium Y-zeolite [4]. In Figure 12b this information has been used to show schematically how the benzene molecules pack into the zeolites channels. Since these channels

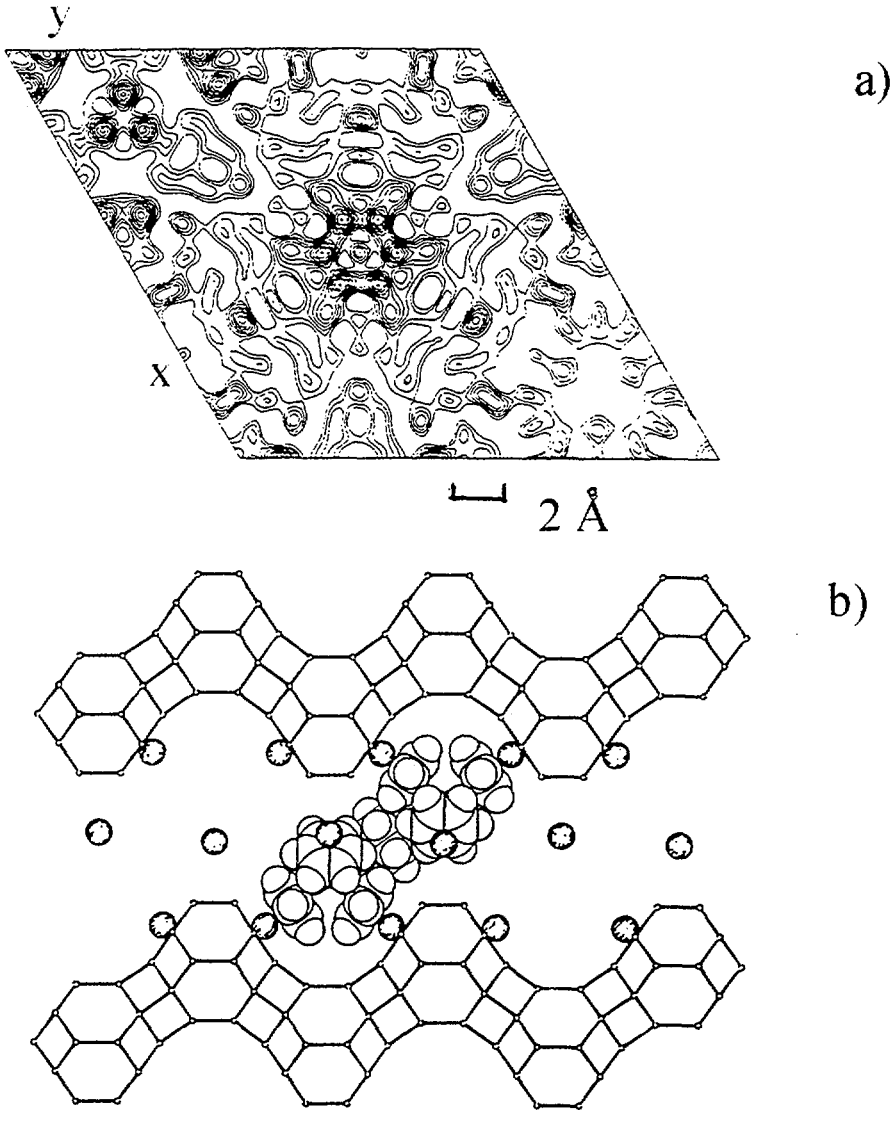

FIG. 12. a) A Fourier difference map showing the location of a benzene molecule in Y-zeolite
b) Small angle neutron scattering showed that the benzene molecules clump together in the zeolite channels

and molecules are of a size that can be investigated by neutron small angle scattering, a further simple experiment can be performed. Neutron small angle scattering patterns are collected, again for the anhydrous and the loaded zeolite. In this case, the difference gives a direct measure of the size of hydrocarbon aggregates within the zeolite channels. For benzene in sodium Y-zeolite it was found that the molecules are not uniformly dispresed, but clump together in small groups. This information is of interest for understanding how the zeolite may catalyse interactions between the hydrocarbon molecules.

Chemical Kinetics

Because neutrons are highly penetrating, it is possible to study physical and chemical reactions in large volumes in real time. For example, when $YBa_2Cu_3O_7$ is heated, it loses oxygen and its superconductivity as it transform to $YBa_2Cu_3O_6$. These structural changes can be monitored directly because of the changes on the neutron diffraction pattern [5] and the strong neutron scattering power of oxygen: with X-rays, scattering is instead dominated by the heavy metals. It is possible to study the effect of oxydising and reducing atmospheres, of quenching from different temperatures, and of aging the resulting material at room temperature. Another example is provided by hydration of Portland cement (a mixture of calcium silicates and aluminates), resulting in solidification. Christensen et al. [6] used neutron diffraction to investigate the reactions between water and the constituent oxides of cement. They showed that the hardening process for Ca_3SiO_5 consists of three stages: initialisation, induction and reaction. During the first stage there is a rapid dissolution of Ca_3SiO_5. The induction period may be due to the formation of a protective layer surrounding the grains until it too is dissolved. Precipitation of $Ca(OH)_2$, the only crystalline product, marks the beginning of the final reaction stage, where all dissolved silicon goes into producing an amorphous gel, with a neutron diffraction pattern quite different from the crystalline phase. Since both hydrogen and oxygen scattering neutrons strongly, the detection of water is relatively easy. Chemical reactions which proceed through hydrated (or hydroxylated) precursors are then ideal for study by neutron diffraction. For example, Figure 13 illustrates the thermal dehydration of $Fe_2F_{5.2}H_2O$ [7]. At low temperature (160 °C) the high background level is due to incoherent scattering from water : as the temperature is increased, the decrease in water content can be measured directly from the decrease in the background, which is accompanied by the transformation of the peaks due to crystalline $F_2F_{5.2}H_2O$ into the different set of peaks due to the anhydrous product. Other examples of chemical reactions then can be followed with kinetic neutron diffraction including solid state reactions where the reactants are strongly mixed and pressed, and then heated while observing the changes on the neutron diffraction pattern. Crystallisation processes can be easily observed with kinetic neutron diffraction. For example when a quasi-crystalline material such as the quenched Al-Mn alloy $Al_{85}SiMn_{14}$ is heated to 630 K it transforms into orthorhombic Al_6Mn with the silicon producing an α-AlMnSi phase at 710 K. Amorphous materials and quasi-crystals have recently excited interests because of their unique electronic and other properties. Kinetic neutron diffraction can help us understand the relations between amorphous and crystalline phases. For example, when $Al_{65}Cu_{20}Fe_{15}$ is cooled from the melt at 1235 K to the solid at 1040 K, neutron diffraction showed that the amorphous phase is not produced directly, but rather via intermediate Al-Fe phases which finally dissolve in the remaining Cu-rich liquid. Complex phase diagrams can be mapped out.

Stress and Texture

The mechanical properties of materials are in part determined by internal stresses and "texture" i. e. the preferred orientation of the constituent crystallites. Neutrons are

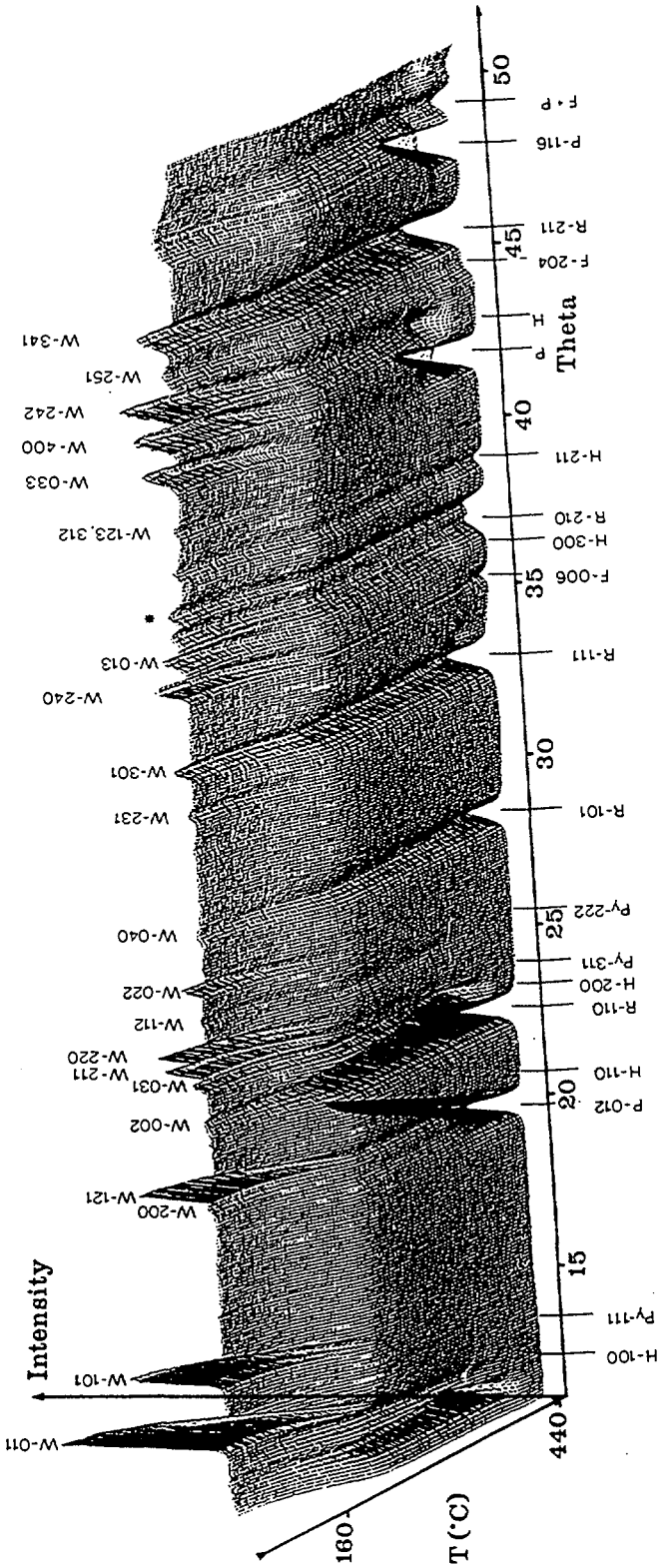

FIG. 13. The thermal dehydration of $Fe_2F_5.2H_2O$ studied by kinetic neutron diffraction, with powder patterns collected at many different temperatures. Note the high background due to scattering from water at low temperature, and the disappearance of some lines and the appearance of others with the crystalline phase change.

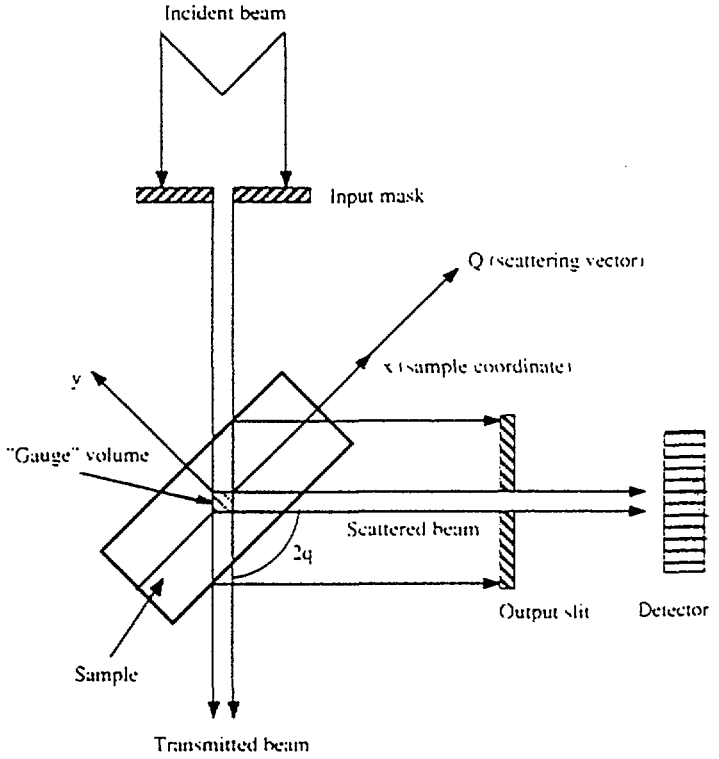

FIG. 14. Simple neutron scattering geometry used to study stresses in materials by measuring small shifts in the positions of the diffraction lines (10). Neutrons see inside the bulk material, while X-rays see only the stresses at the surfaces, which may be quite different

particularly suited to the study of such problems because they can penetrate large objects, while X-rays are scattered mainly by surface. For example, alumina can be strengthened by sintering Al_2O_3 powder with SiC fibres at high temperature. When cooled to room temperature, strong internal stresses are induced in the resulting composite because of differences in thermal contraction of the two materials [8]. Clearly, the mechanical properties also depend on the relative orientation of the SiC fibres (texture). It is important to understand the physical reasons that make this material one of the most successful ceramic-ceramic composites. A second well known example of the use of internal stress to toughen materials is provided by partially stabilised zirconia. The zirconia is toughened zirconia ceramics can exist as cubic, tetragonal, orthorhombic and monoclinic phases. The martensitic tetragonal-monoclinic transformation is accompanied by a volume increase of almost 5 %, and induces strong stresses in the resulting composite material which depend on the relative volume fractions of the different phases. Neutrons cannot only probe the internal stress in the bulk material, but also measure with precision the amounts of the different phases [9]. X-rays are also used to measure the relative phase abundance, but only on the surfaces, and phase transformation on surfaces, which can be altered by grinding for example, may not be typical at the bulk material. These different experiments, to measure internal stress, "texture" and phase abundance can be performed on the same simple neutron diffraction equipment. Figure 14 shows a collimated beam at monochromatic neutrons incident on a large ceramic sample. Simply by measuring the diffraction pattern, the relative abundance of the different phases can be determined from the relative intensities of the peaks characteristic of these phases. If the sample is heated in situ, changes in the relative abundance of the different phases can be monitored. If the orientation of the sample is changed, the intensities of some of the peaks also change when the crystallites are aligned in preffered directions. Such "texture" can then be

investigated by measuring the intensity of a few peaks for a variety of sample orientations. Finally, the changes in internal stress can be monitored by measuring small changes in a peak positions, which reflect changes in the crystal lattice dimensions due to stress. The material then acts as its own strain gauge. This method has been applied with great commercial success to look at stresses in oil pipe-line welds, railway lines [10] etc.

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