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Recent neutron scattering research and development in India

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Abstract. A national facility for neutron beam research is operated at the research reactor Dhruva at Trombay in India. The research activities involve various nanoscale structural, dynamical and magnetic investigations on materials of scientific interest and technological importance. Thermal neutron has certain special properties that enable, e.g., selective viewing of parts of an organic molecule, hydrogen or water in materials, investigations on minerals and ceramics, and microscopic and mesoscopic characterization of bulk samples. The national facility comprises of eight neutron-scattering spectrometers in the reactor hall, and another four spectrometers in the neutron-guide laboratory. In addition, a neutron radiography facility and a detector development laboratory are located at APSARA reactor. All the instruments including the detectors and electronics have been developed within BARC. A new powder diffractometer (PD-3) is being developed by UGC-DAE-CSR. The national facility is utilized in collaboration with various universities and other institutions.

Keywords. Neutron scattering; national facility; structure; dynamics; magnetism.

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1. Introduction

The research activities at the Dhruva reactor involve various nanoscale structural, dynamical and magnetic investigations on materials of scientific interest and technological importance. The main advantages of using neutrons over much brighter photon beams are that the former provide (i) a sharp contrast between isotopes or between neighbouring atoms in the periodic table, (ii) high energy resolution of sub-meV, (iii) intense magnetic probe and (iv) characterization of bulk samples. These enable, e.g., selective viewing of parts of an organic molecule, hydrogen or water in materials, investigations on minerals and ceramics, and microscopic and mesoscopic characterization of bulk samples.

A national facility for neutron beam research is operated at the research reactor Dhruva (figure 1). It includes single-crystal and powder diffractometers, a polarization analysis spectrometer, inelastic and quasi-elastic scattering spectrometers in the reactor hall, and small-angle scattering instruments, a polarized neutron reflectometer and a spin-echo cum polarized-neutron small-angle spectrometer

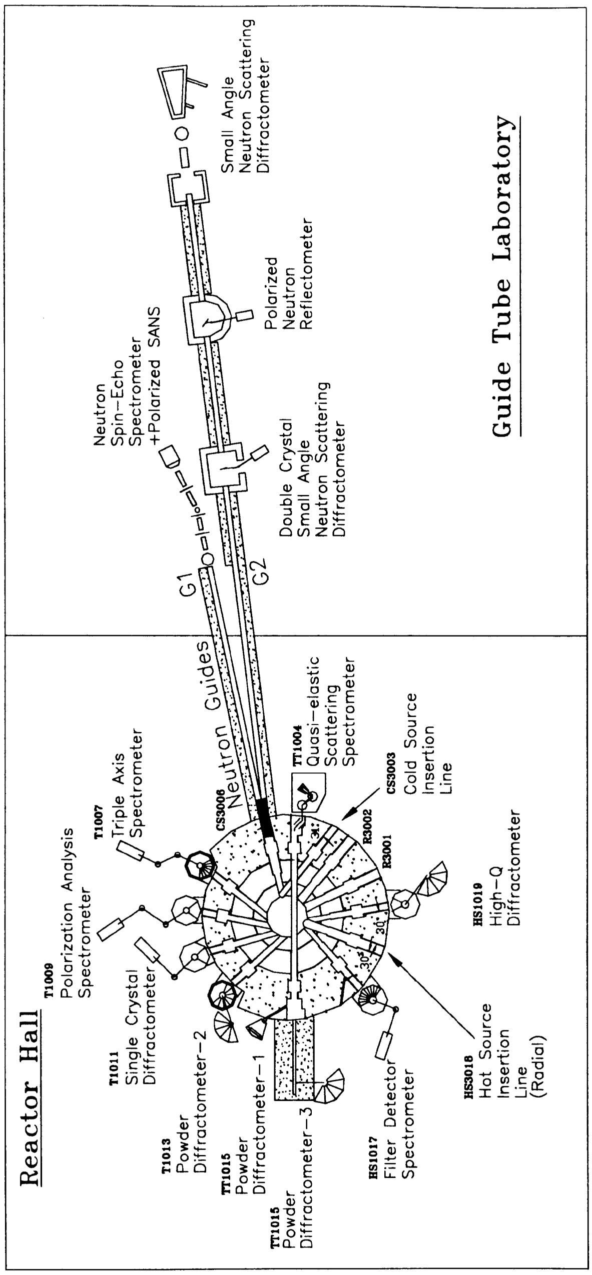

Figure 1. Neutron scattering facilities at Dhruva reactor at Trombay.

in the neutron-guide laboratory. The last two instruments have been added in recent years. In addition, a neutron radiography facility and a detector development laboratory are located at APSARA reactor. All the instruments including the detectors and electronics have been developed within BARC. A new powder diffractometer (PD-3) is being developed by UGC-DAE-CSR. The national facility is utilized in collaboration with various universities and other institutions.

Important examples of recent work include studies of structures in triglycine family of hydrogen-bonded ferroelectrics, manganites showing CMR behaviour, cobaltates showing coexistence of ferro- and antiferromagnetism, phosphate and oxide glasses, cluster formation in hydrogen-bonded liquid methyl alcohol, pore morphology in sintered ZrO_2–Y_2O_3 ceramic, pore surface roughening in rocks, multiple scattering due to very large inhomogeneities, micellar formation using Gemini surfactants and multi-head group surfactants under various conditions, structure and magnetic properties of ultra-thin multilayer of Fe–Ge, lattice vibrations in materials having negative thermal expansion and minerals of geophysical interest, alkyl chain dynamics in monolayer protected metal nanoclusters, and diffusivity of various guest molecules in zeolite cages.

The following sections provide a brief overview of recent developments and research involving neutron scattering.

2. Neutron detectors and radiography

Linear position-sensitive detectors using He^3 gas have been developed and extensively used in several neutron spectrometers at BARC during the past decade. Two powder diffractometers in the reactor hall have been upgraded recently leading to a substantial increase in their throughput. Now a diffraction pattern can be recorded within a few minutes time. Neutron and X-ray detectors, developed in BARC, not only meet all the in-house requirements but also cater to the needs of various users outside BARC. Recently 2-D PSD [1] and microstrip [2,3] based neutron detectors have also been developed and these would further enhance the data acquisition efficiency. Neutron radiography facility [4] is available at APSARA, which has provided a useful non-destructive technique to characterize materials, particularly for nuclear and space applications.

3. Structure and magnetism studies

Neutron diffraction with unpolarized and polarized neutrons is used [5–10] routinely to identify various magnetic phases of materials as a function of temperature. In addition, neutron depolarization studies with polarized neutrons provide the magnetic domain size at mesoscopic length scales (∼5 microns). Figure 2 shows an example of diffraction patterns from $La_{0.5}Ca_{0.5}MnO_3$ [10] that shows additional peaks indicating a magnetic supercell ($2a \times b \times 2c$) of a charge ordered antiferromagnetic structure at 16 K. A variety of samples of CMR materials with various atomic substitutions, alloys, analogs of Prussian Blue-A$[B(CN)_6]$ molecular magnets, nanoparticles of γ-Fe_2O_3, etc. have been investigated.

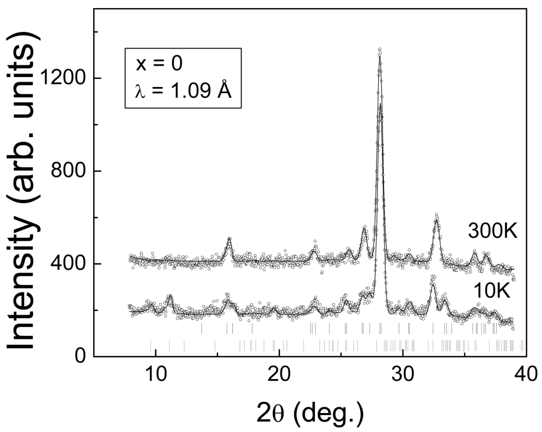

Figure 2. Neutron powder diffraction patterns from $La_{0.5}Ca_{0.5}MnO_3$ [10]. The upper and lower patterns are at 300 K and 10 K respectively. The 10 K pattern shows additional peaks indicating a magnetic supercell ($2a \times b \times 2c$) of a charge ordered antiferromagnetic structure.

Neutron diffraction studies were carried out to understand the short-range order in rare-earth doped phosphate glasses [11] and liquids [12]. Single crystal diffraction studies have been performed on several organic crystals where hydrogen bonding plays an important role [13].

4. Structural studies at mesoscopic length scale

Small-angle neutron scattering provides mesoscopic (1–1000 nm) structural information. Three small-angle neutron scattering facilities are operated at Dhruva. One instrument based on pin-hole collimation geometry has been extensively used [14–23] for research in the area of soft condensed matter, such as polymers, colloids, surfactants, biopolymers, gels, liquid crystals, foams and emulsions. A polarized neutron small-angle facility is also available recently on the spin-echo spectrometer [24].

Another instrument based on double perfect-silicon-crystal collimation geometry has been used [25–32] extensively for the characterization of naturally occurring materials including advanced ceramics, hydrated cement composites and engineering materials like special steels (figure 3). These materials typically possess structures at mesoscopic length scale, which determines their macroscopic physical properties. Our efforts are to probe this relationship.

Predictions of non-linear theories for new phase formation for the hydration of calcium silicates with light water and heavy water has been investigated [28] using USANS facility at ILL, France. A monochromatic neutron beam with the sharpest angular profile, limited only by theoretical Darwin width, has been produced [33] by multiple Bragg reflections from channel-cut single crystals at HMI, Berlin. By placing a magnetic air prism between such a monochromator–analyser pair, the

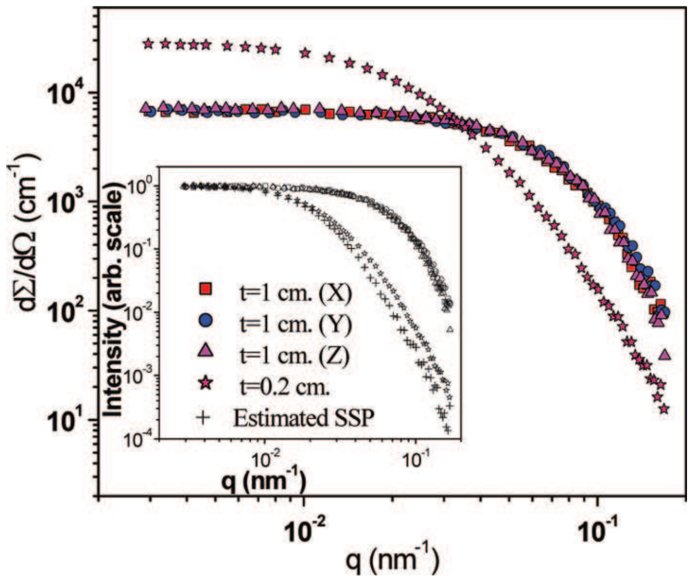

Figure 3. Small-angle neutron scattering pattern due to carbide precipitates in solution quenched PH 13-8 Mo stainless steel samples of various thickness [26].

first polarized SUSANS (super ultra small angle neutron scattering) instrument has been operated.

5. Reflectometry for thin film structure, interface magnetism and surface morphology

Neutron as well as X-ray reflectometry are important nondestructive tools for elucidating the structure of thin films and multilayer systems. Polarized neutron reflectometry can also provide magnetic depth profile in thin film samples. The polarized neutron reflectometer at Dhruva is designed [34] to perform specular and off-specular or diffuse reflectivity runs, since the data are collected on a position-sensitive detector. Such data can provide height–height correlation on a surface or an interface. Multilayers of magnetic materials and semiconductors are prospective candidates for spin-polarized electron transfer from a metal to a semiconductor. Studies on a Fe–Ge ultra-thin multilayer sample (thickness of layers ∼2 nm) by polarized neutron reflectometry (figure 4) showed [35] that the Fe atoms had a magnetic moment of 1.43 μ_B. In multilayers of Ni–Cu, signature of alloying at the interfaces was found as well as a reduction of Ni magnetic moment towards the interface [36]. Recent polarized diffuse-reflectivity studies yielded magnetic height–height correlation function at the interfaces of a magnetic–nonmagnetic multilayer.

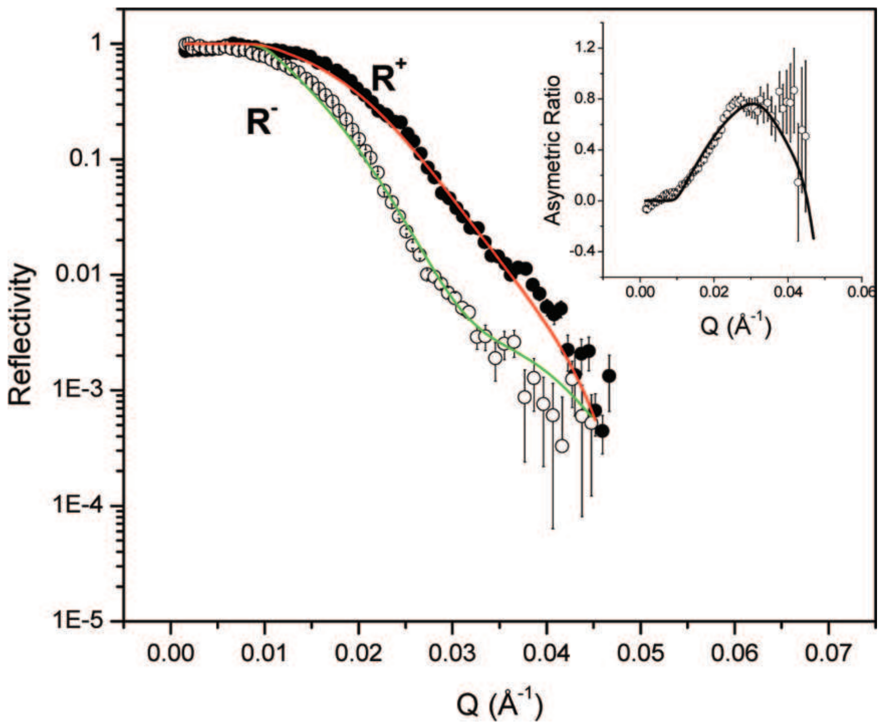

Figure 4. Polarized neutron reflectivity measurements from Fe–Ge multilayers [35].

6. Dynamics studies: Deterministic and stochastic

The study of dynamics of atoms and molecules in solids is important for the investigation of various thermodynamic properties, electron–phonon interactions etc., and involves the use of a combination of experimental and theoretical approaches. Inelastic neutron scattering experiments are used either for periodic motions like vibrations or thermally activated single particle motions. Periodic motions lead to characteristic frequency whereas stochastic motion shows up as Doppler-broadened elastic lines known as quasielastic scattering.

Lattice dynamical properties of a wide variety of technologically important solids like negative thermal expansion materials, nuclear waste management materials, geophysically important minerals, high-temperature ceramics, ferroelectrics, etc. have been studied [37–44]. The measurements on single crystals and powder samples provide phonon dispersion relations and density of states respectively. Figure 5 shows an example of recent data. The experiments validate theoretical models which in turn provide microscopic insights into a variety of phenomena like structural phase transitions, anomalous thermal expansion, pressure-induced changes in atomic coordination, elastic properties, seismic wave velocities, and other thermodynamic properties. Lattice dynamics calculations have played a key role in the analysis and interpretation of inelastic neutron scattering experiments in these

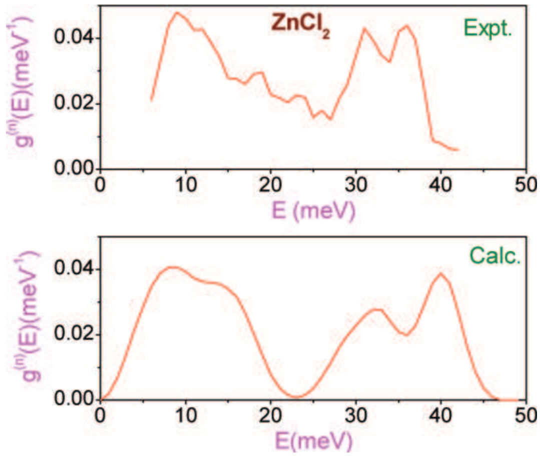

Figure 5. Inelastic neutron scattering measurement of phonon density of states suitably weighted with neutron cross-section, and lattice dynamical calculation of the same in $ZnCl_2$ [44].

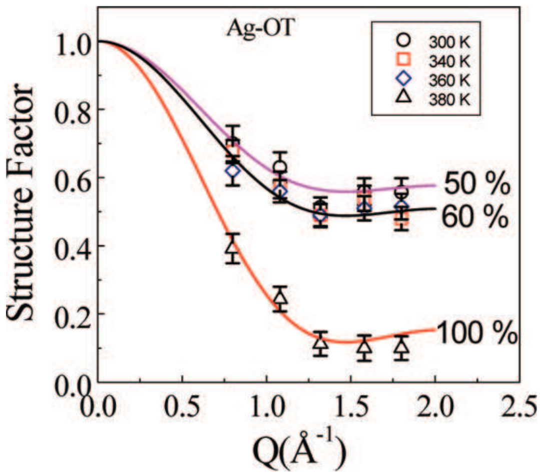

Figure 6. Quasi-elastic neutron scattering data of elastic-incoherent structure factors of octanethiol-capped silver cluster (Ag-SC_8H_{17}) indicating various proportions of interdigitated/non-interdigitated chains [45].

structurally complex solids. Molecular dynamics simulations have helped one to understand the mechanism of atomic diffusion and high-temperature superionic conductivity in nuclear materials.

Various systems have been studied pertaining to the diffusive motion of the atoms or molecules [45–48]. The systems studied include simple molecular solids, liquid crystals, plastic crystals, molecules adsorbed in confined medium like porous materials (gels, clay etc.) or zeolites, polymers, biological systems, metal nanoclusters (figure 6), etc. Molecular motion in confined media *vis-à-vis* bulk is of immense interest, as it exists in large variety of physical situations. Recent study of the dynamics in monolayer protected nanometal clusters has lead to interesting results relating phase transitions and alkyl chain dynamics.

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