# Condensed Matter Studies by Neutron Scattering

In the season of 1990-1991 experiments were mainly conducted on eight spectrometers positioned on 6 beam-lines of the IBR-2 reactor. With respect to the method used the experiments can be classified as follows:

- diffraction studies on the spectrometers DN-2, NSVR and SNIM-2;
- SANS studies on the MURN spectrometer;
- polarized neutron reflection studies on the SPN spectrometer;
- neutron spectroscopy measurements on the DIN, KDSOG-M and NERA-PR spectrometers to study inelastic scattering of neutrons.

Investigations of crystal structures with neutron diffraction methods at the IBR-2 reactor are carried out in the directions:

- structure study experiments on single- and polycrystals;
- phase transitions in superconductors, ferroelastics and superionic samples;
- phase transitions in the presence of strong external magnetic fields;
- structure of lipid membranes;
- transition phenomena investigated by diffraction techniques.

They, for the most part, are the traditional directions of research for LNP, where it enjoys well established cooperation with numerous scientific institutions active in the field.

Of structure works a noticeable role belongs to HTSC studies. In experiments on a single crystal A.I.Beskrovnyi and colleagues investigated modulated structure in $Bi_2(Ca, Sr)_3Cu_2O_{8+\gamma}$. Though with a very small single crystal ($1.5\times10\times0.03$ mm$^3$) they have succeeded in measuring (in a wide temperature range) satellite peaks in number sufficient to develope a model. In spite of expectations the structure modulation does not change observably in the temperature range 8 K to 920 K.

With $YBa_2Cu_3O_7$ a detailed study of structure effects connected with the substitution of copper by iron or nickel was undertaken. In order to enhance the substitution effect and thus increase the diffraction data reliability the contrast variation technique was applied with the use of $^{57}$Fe and $^{58}$Ni isotopes (A.M.Balagurov et al.). The results have confirmed an earlier guess that copper substitution by other 3-d metals, which leads to fast degradation of superconductive properties, reflects preferential substitution in the $CuO_2$ plane. It has been shown that both nickel and iron (at concentrations $\geq$10%) penetrate actively into the $Cu_2O$ plane. At that, however, the decrease in T is not so sharp as in the case of Cu by Co substitution, that occurs only in CuO chains. Then the conclusion follows that it is not only the substitution site that is of significance, but also some purely structural characteristics play the important role here, the bond length value, in particular.

With Y123 ceramics a series of experiments were conducted to study oxygen diffusion in samples that were cooled at different cooling rates, annealed at constant temperature or heated slowly. The one-dimensional model of diffusion appeared to be sufficient to describe oxygen diffusion. Estimates of diffusion coefficients were made for each of the above-mentioned regimes of sample treatment.

A comparatively new branch of research at the IBR-2 reactor are the real time experiments. Quite a number of interesting data have been obtained in them. Of recent ones the emphasis should be laid on the study of phase transitions in different compounds, e.g. titanium hydrate, $Cu(Li,V)_{0.4}Fe_{1.6}O_4$ spinel, high pressure heavy ice $D_2O$. The method developed by LNP scientists allows them to carry out these investigations in the second resolution range not achieved

yet at other neutron sources. The measurements were performed on the diffractometer DN-2, currently the most high luminosity and powerful diffractometer in the IBR-2 suit.

The NSVR diffractometer dedicated for texture studies is positioned on the 100 m flight path of the reactor. It has a lower luminosity but a three times higher resolving power that makes it very effective in investigating textures of complex low-symmetry materials. Textures of various geological samples were investigated on this diffractometer (K.Helming, W.Voitus, K.Walther et al.).

On the diffractometer equipped with a pulsed magnet, SNIM-2, there was investigated the kinetics of spin-flop transitions in single crystals of $Cr_2O$ and $\alpha$-$Fe_2O_3$ induced by a pulsed magnetic field of 1 msec duration and 150 KOe amplitude (D.Georgiev, V.V.Nietz et al.).

Works published in the past year reflect also efforts made by the Laboratory staff to upgrade now existing and build new neutron diffractometers. In particular V.L.Aksenov, A.M.Balagurov et al. report on the work being done to put into operation the new Fourier diffractometer with a resolving power at a level of 0.05%.

The Small Angle Neutron Scattering (SANS) spectrometer MURN is a high luminosity instrument built for the investigation of SANS in isotropic systems. It allows one to measure small scattering cross-sections in absolute units in rather a wide range (0.05–0.7 reciprocal Angstroms) of scattering vector lengths. Main activities in the season 90/91 were aimed at a search for new applications of its advantages.

In the ternary system AOT–Water–Benzene an alternative approach to the well-known contrast variation technique was approved. It is found, that variation of a so-called internal contrast (isotopic composition of the water nucleus in inverse micelles) do lead to the same results as external contrast variation, if measurements are done well inside the micelle stability gap on the phase diagram. However, near the gap's borders isotopic substitution affects strongly the structural properties of solutions and different ways of contrast variation reveal largely different structures. This observation seems to be very important for the safe interpretation of SANS data. Besides of this, investigation of the inverse micelle friability phenomenon, observed previously at lowest water contents, was continued with other solvents and in a widened range of water contents.

Properties of water solutions of small organic molecules is another new field of SANS application. This year we have tried to find SANS evidence of the existence of a long range repulsive interaction between solute molecules at very high dilutions (mole fraction as small as 0.001), recently proposed on the basis of calorimetric experiments. Though the SANS experiments were rather accurate, no important signs of the assumed repulsion were observed.

The third micellar system investigated recently was the (oxyethylene-oxypropylene-oxyethylene) block copolymer in water. Very detailed experiments in a wide range of temperatures and concentrations allowed one to determine experimentally a number of characteristics of this system, with the degree of swelling of a hydrophobic micellar nucleus among them.

A rather unexpected field of SANS application is connected with an attempt to investigate the Porod region of the scattering cross-section from components of cement (the clinker minerals) and from cement pastes at different steps of their aging. Results, obtained to-date, show, that in chemical transformations which are the essence of cement pastes hardening, there occur very important changes in spatial arrangement of phase boundaries, responsible for small angle scattering observed. Important changes are also detected in scattering curves during the aging of a cement paste to the age of up to 241 days.

The whole host of results obtained are in many relations new and their interpretation in

terms of the physical chemistry of solutions and solids requires some efforts to be made.

The time-of-flight spectrometer of polarized neutrons SPN was found to be a very effective instrument for the investigation of magnetic properties of surfaces of thin films in the reflectometry mode. Among the results obtained during the season 90/91, the most interesting, perhaps, is the observation of the dependence of the magnetic field penetration depth in superconducting niobium on the thickness of the niobium film. The dependence was discovered to be rather strong (the penetration depths of 43 nm, 90 nm and 145 nm in a massive sample and in films 700 nm and 255 nm thick, respectively, are quoted). However, up-to-date there is no satisfactory theoretical explanation of this phenomenon.

An interesting and important step was done towards the realization of the "non-reflecting mirror", an important component of ideal neutron mirror-polarizer. The reflection of unwanted spin from known constructions of polarizing mirrors is the important factor that sets limit on the application of these otherwise nice devices. First experiments with absorbing sub-layers made of thin films of titanium and vanadium borides have shown that in this way the properties of polarizing mirrors can be improved drastically.

Another interesting possibility opens with the reflectometric observation of aging of a thin (163 nm) titanium film. It was found that on the surface of metallic titanium at normal conditions during first two weeks the titanium oxide layer 9 nm thick appeared, while during the following two years this oxide layer has thickened to 12 nm.

Two direct geometry spectrometers, DIN-2PI and DIN-2PR for double analysis of neutron energy by time-of-flight act in parallel on one neutron beam-line at a distance of 20 m and 95 m from the reactor core, respectively. On the higher luminosity one, DIN-2PI, experiments on inelastic and quasielastic scattering of neutrons on samples of liquid helium, liquid metals and adsorbed water continued. Measurements of phonon spectra of V-O, V-N, $TaV_xN_y$ continue the investigation of nitrogen and oxygen solid solutions in metals. For $ThO_2$, $VO_2$ and $ZrH_xU_{0.32}$ (x=16 and 1.84) dependences of the phonon density of states on room temperatures up to about 1300 K were measured. On the DIN-2PR a first series of experiments on the scattering of neutrons with an incident energy of 200 meV from liquid helium at T=4.2 K and 1.4 K has been conducted in continuation of the study of Bose condensate and elementary excitations in liquid helium at large momentum transfers and good energy resolution.

The new spectrometer, NERA-PR, that exploits the inverted geometry principle for inelastic and quasielastic neutron scattering studies was positioned at a distance of 109 m from the reactor core and began operations. Energy analysis of scattered neutrons by their reflection to an angle of 175° from a single crystal of Cu(111) allows one to investigate neutron quasielastic scattering with a resolution of $\Delta E = 0.05$ meV in rather a wide momentum transfer range from 0.5 to 5Å. Experiments were initiated to investigate stochastic reorientations of molecules in liquid crystals. The beryllium filter used in the spectrometer for energy analysis provides for high luminosity and good resolution at large momentum transfers ($50 \leq \Delta E \leq 500$) meV. Partial vibrational densities of copper and oxygen atoms in $YBa_2Cu_3^*O_{6+x}$ (x = 0.95, 0.25) were determined by measuring neutron inelastic scattering spectra with copper isotopes ($^{65}Cu$ and $^{63}Cu$) having different cross sections for neutron scattering. Measurements of phonon spectra of $NH_4Cl$ and $H_2O$ at T = 290 K and 80 K at pressures up to 10 Kbar have proved the beryllium filter method on the NERA-PR spectrometer to have high enough luminosity and resolution for investigating phonon spectra on pressure dependences.

On the KDSOG-M spectrometer, that also exploits the inverted geometry principle, the energy analysis of scattered neutrons is performed with the help of pyrolytic graphite plates

installed behind the beryllium filter. High luminosity and a relatively good resolution in the energy transfer range up to 200 meV allows effective study of inelastic scattering from hydrogen-free samples or samples with low hydrogen content that are the usual case in the spectroscopy of adsorbed molecules. A comparative study has been undertaken of vibrational spectra of a number of dispersed silicas (silicagel, aerogel, aerosil, silochrom). The data analysis has allowed identification of adsorbed or retained water in investigated samples. These spectra are much different and thus point to different configurations of adsorbing centers in investigated silica samples. Experimental data are compared with quantum mechanical calculations in the framework of a selfconsistent cluster approach to allow the conclusion about the polymorphism of dispersed silicas being in dependence on the sample manufacturing technology (see works by E.F.Sheka, V.Khavryutchenko, I.Natkaniec et al.).

In the past years the chief object of research on the KDSOG-M spectrometer were the crystal field excitations in rare-earths containing compounds and alloys. In the reported period there continued investigations of magnetic excitations in heavy fermion systems like $CeCu_4Al$, $CeCu_4Ga$ and $CeCu_2Si_2$. In them it was important to carefully take into account the phonon spectra that affect essentially the neutron inelastic scattering spectra. For that there were measured simultaneously spectra from stoichiometric lanthanum samples of $LaCu_4Al$, $LaCu_4Si_2$ showing no magnetic scattering. The characteristic feature of the magnetic scattering spectra of cerium containing heavy fermion compounds is the only one Lorentzian-like crystal field transition having a rather broad energy distribution and an intense contribution from quasielastic neutron scattering also with a broad energy distribution of the Lorentzian type (see works by E.A.Goremychkin et al.).

Study of the crystal electric field parameters continued with the metallic rare-earth compounds of the isostructural family $Re_{0.05}Y_{0.95}Ni_2$ (where R = Nd, Pr, Tb, Tm, Er, Dy, Ho). Rare-earth metals in this family are diluted strongly with nonmagnetic yttrium atoms and the 4-f shell interaction with crystal electric field can be studied in a most pure form.

By investigating crystal electric field transitions in $Nd_2CuO_4$ in dependence on temperature (from 10 to 300 K) it appeared possible to identify transitions from excited states. Data interpretation with account for the mixing between the ground and first excited state has for the first time yielded a satisfactory description of neutron inelastic scattering data as well as the qualitative description of the magnetic susceptibility measurement data.

In 1990-1991 the LNP scientists took part in joint experiments at the ISIS of RAL, UK. On the inelastic scattering spectrometers HET and MARI the temperature dependence of the widths of the crystal field transitions in $Y_{0.9}Tm_{0.1}Ba_2Cu_3O_{6+x}$ (x = 0.1 and 0.9) was measured. Results point to the formation of a gap in a spin excitation spectrum at temperatures about 20 K above $T_c$.

The HET record resolution at high energy transfer allowed investigation of intermultiplet transitions in a heavy fermion system $CeAl_3$. Splitting of the first excited CF multiplet was found to be three times stronger than that of the main one, in evidence of a considerable contribution of conductivity electrons into the CF potential.

On the quasielastic scattering spectrometer IRIS there was investigated the dynamics of $NH_4$ groups reorientations in the process of dipole glass formation in the system $K_{1-x}(NH_4)_xH_2PO_4$ (x = 0.4 and 0.9).

Domain structure formation following phase transitions in a ferroelectric crystal of $LiKSO_4$ was investigated on the SXD diffractometer.