GRANTS:

1. *Dr Z.T. Lalowicz*,

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2. *Assoc. Prof. A. Jasiński*,

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4. *Dr Z. Olejniczak*,

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5. *Prof. K. Parliński and Dr M. Sternik*,

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"The Mechanisms of Structural Phase Transitions".

OVERVIEW:

Research at the Department of Nuclear Radiospectroscopy of the H. Niewodniczański Institute of Nuclear Physics concerns various problems of nuclear magnetic resonance (NMR) and its applications in different areas of science, with molecular dynamics in the first place. The Department is equipped with a 1.5 T, 6cm-gap electromagnet, a 6.4 T superconducting magnet, an XP4-100 Bruker spectrometer, a home-made 270 MHz MR microscope system and a home-made Zero-Field NMR spectrometer of unique design permitting work at helium temperatures. The Department cooperates closely with the NMR group of Prof. J.S. Blicharski at the Department of Physics of the Jagellonian University in Cracow.

Current research programme covers three areas: magnetic resonance, magnetic resonance imaging, and solid state physics by computer simulations.

MAGNETIC RESONANCE LABORATORY

We apply magnetic resonance methods in studies of molecular rotations in solids. We can distinguish two ways of rotations: tunnelling through the potential barriers and random jumps between distinct orientations. The former is responsible for orientational delocalisation at liquid helium temperatures, causing so-called tunnelling splitting of the ground torsional energy level and therefore strongly influencing the NMR spectrum. Random jumps are possible at higher temperatures since the molecule needs a sufficient amount of energy to overcome the potential barrier. This type of motion can be treated classically. This also influences the NMR spectrum but in a manner quite different from that of tunnelling. In particular, the deuteron NMR spectra provide explicit evidence of the type of motion. Moreover, measurements of tunnelling frequency and reorientation rate are possible. Both supply data on height and symmetry of the potential. Theoretical fits to deuteron NMR spectra of $(ND_4)_2SnBr_6$ at 4.2 K gave the ground torsional level structure and estimates of splittings within it. Ammonium ions perform tunnelling rotation at relatively low frequences in a low-symmetry potential.

In the case of ammonium tetrachloroplatinate, combined analysis of powder and single crystal samples as well as, proton and deuteron relaxation, guided us among several possible motional

models. The current interpretation involves existence of domains of differently ordered ions and exceptional mobility of ions within domain walls.

Deuteron NMR spectra of tunnelling CD_3 groups in the single cristal of aspirin were measured and analysed. Tunnelling frequency temperature dependence was established and explained by jumps between all torsional levels within the potential well.

Studies of deuteron NMR spectra and spin-lattice relaxation were continued for partially deuterated rotors CH_3D and NH_3D^+.

MAGNETIC RESONANCE IMAGING LABORATORY

Work on the construction of a MR microscope based on a 6.3 T superconducting magnet was completed. Each part of the system was tested. Software written in the Laboratory was used for the MR microscope testing, optimization and running the experiment. Multi-slice multi-echo with pilot scan sequence was implemented. A special probe with integrated, actively shielded gradients coils, a set of custom-designed rf coils and a temperature control system were built. MR images of phantoms with in-plane resolution of 15 μm x 15 μm with slice thickness of 100 μm were obtained.

The MR microscope was used for small-plant imaging (e.g. *Dactylis glomerata*) to study water distribution and water transport by applying diffusion-weighted imaging sequences. MR microscope was also used for visualisation of internal structure of the honeybee *in vivo*. Most of the organs have been identified. Reproductive organs of honeybee queen and drone were imaged and their size measured noninvasively for the first time. Our results show that MR microscopy is a very promising tool for research in insect biology.

In collaboration with the FORENAP Foundation in Rouffach, France, new 3-dimensional T_1 weighted FLASH and Magnetisation Transfer FLASH sequences were implemented and tested on 3 T whole-body system.

LABORATORY OF SOLID STATE PHYSICS AND COMPUTER SIMULATIONS

In the Laboratory of Solid State Physics and Computer Simulations the work was concentrated around the following topics:

Consequences of tetragonal-orthorhombic phase transition, experimentally observed in high-T_c superconducting material $YBa_2Cu_3O_{7-\delta}$, have been studied extensively on a 2d model by molecular-dynamics simulation. The model has been supplemented with a term of external field which could be coupled to oxygen concentration, and with the second nearest neighbour interaction. That allows one to establish temperature-oxygen concentration phase diagram with the tetragonal - orthorhombic phase boundary, and with new incommensurate phase, known as a OII phase. The corresponding microstructure pattern shows a tiny grid of domains in this case. A MD simulation of the same model with substitutional impurities in place of copper showed influence of these atoms on the microstructure pattern. The impurity atoms pin the domain walls, and therefore hinder formation of a single domain.

The ground state of our hexagonal model contains one-dimensional $1q$ and two-dimensional $3q$ modulations. That model has been extensively simulated by the MD method in order to elucidate phase transition mechanisms between different types of modulated phases. The simulations have shown that: (i) The $1q$ commensurate $\frac{1}{4} \rightarrow 1q$ incommensurate phase transition is driven by stripple mechanism, with stripples built up from four discommensuration planes. (ii) At the $3q \rightarrow 1q$ phase transition, the columns of $3q$ phase merge together to form a stripe of $1q$ incommensurate phase.

Another activity in the simulation of incommensurate phases was related to the question of coupling of the order parameter to the crystal strain. A simple three-dimensional model

specially constructed for this purpose showed that elastic domain walls can serve as a source of nucleation of discommensurations. Moreover, the modulated phase induces some modulation also in the crystal strain. We have also proved the existence of stripples with a complicated structure consisting of six discommensuration planes. Such defects are responsible for driving the phase transition from commensurate phase $k = \frac{1}{3}$ to the incommensurate one.

The domain patterns are consequences of the phase transition. The microstructure in the molecular crystal of KSCN has been studied along this line. This crystal undergoes an order-disorder phase transition, which has been simulated by the molecular-dynamics technique. Evolution during the annealing process shows that ferroelastic domain walls keep fixed orientation of matching lattice directions, while antiphase domain walls are oriented arbitrarily.

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REPORTS ON RESEARCH:

Deuteron NMR of Methyl Groups in Tunneling Regime. Single-Crystal Study of Aspirin-CD_3

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We report the first single-crystal deuteron NMR spectra of CD_3 groups which display the so-called $\pm\beta$, $\pm(|\alpha| \pm \beta)$ and $\pm(2|\alpha| \pm \beta)$ lines characteristic of rotational tunnelling in a higher sufficiently clear to allow a quantitative comparison with theory developed in 1988 by the group of W. Müller-Warmuth. The molecular system we study is aspirin-CD_3. We recorded spectra for differently oriented single crystals and we measured spin-lattice relaxation times T_1 in a wide temperature range. At 12.5 K we used dependence of the $\pm(|\alpha| \pm \beta)$ and $\pm(2|\alpha| \pm \beta)$ lines on the orientation of applied field $\mathbf{B_0}$ for determining the equilibrium orientation of the CD_3 group in the crystal lattice. The spectra display features which by comparison with simulated spectra allow to measure of tunnel frequency ν_t. Its low temperature limit is (2.7 ± 0.1) MHz. It allows one to infer height V_3 of potential $V(\varphi)$ in which the CD_3 group moves, provided that this potential is purely threefold. We get $V_3 = (47.2 \pm 0.5)$ meV. Transition from the tunnelling to the classical, fast reorienting regime occurs in the 15 K$\lesssim$ T$\lesssim$ 35 K temperature range. In this range we observe broadening, merging and eventually narrowing of the $\pm|\alpha|$ and $\pm 2|\alpha|$ lines in very much the way predicted by Heuer. His theory, however, must be extended by taking into account all librational levels. The behaviour of the $\pm\beta$ lines in the transition temperature range signalizes reduction of the *observable* tunnel frequency with increasing temperature. This reduction allows an independent measurement of the potential height and represents a test of the assumption of a purely threefold potential. From the T_1-data we derive temperature dependence of correlation time τ_c of the reorientational jumps. The plot of $\log \tau_c$ vs $1/T$ follows a straight line for more than five decades. From its slope we get yet another independent number for the potential height. It agrees well with the other ones, confirming the assumption of essentially threefold potential $V(\varphi)$ in aspirin CD_3.

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