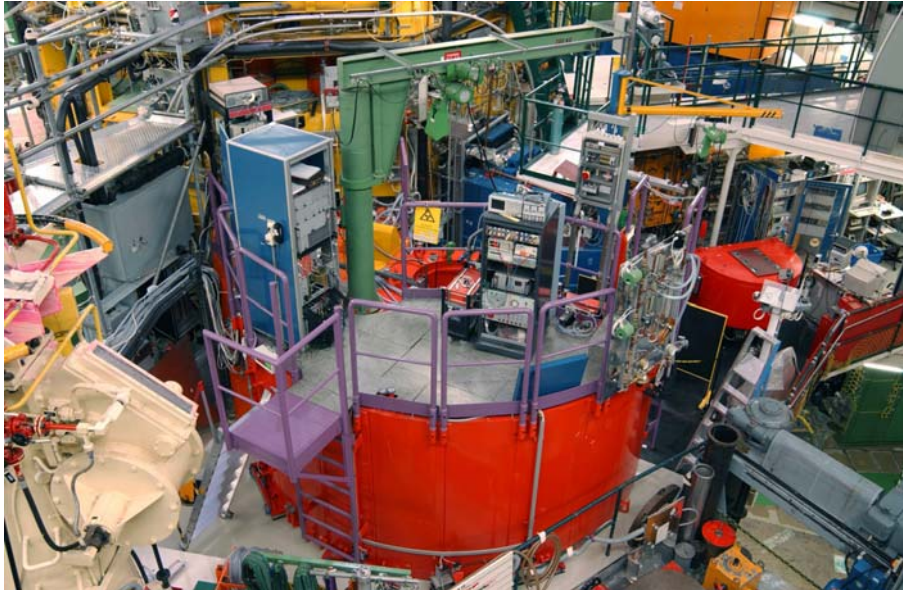


Time-of-Flight Spectrometer (SV29)



Instrument Parameters

Beam line:	4H2 (radial beam tube)
Monochromator:	matrix of 75 PG002/PG004, vertical+horizontal focusing
Incident wavelengths:	$1.0 \leq \lambda \leq 4.0 \text{ \AA}$
Take-off angle:	$35 \leq 2\Phi_M \leq 75^\circ$
Momentum transfer:	$\approx 1 \dots 10 \text{ \AA}^{-1}$
Energy resolution:	$3\% \leq \Delta E/E \leq 8\%$
2 phased choppers:	$\leq 21000 \text{ rpm}$
Collimation:	0.8°
Duty cycle:	4×10^{-3}
Neutron flux at sample:	$\approx 10^5 \text{ n/cm}^2 \text{ s}$
Beam size at sample:	$3 \times 8 \text{ cm}^2$
Flight path:	1.91 m
Detectors:	500 ^3He counters in 90 units
Solid angle covered:	$\approx 0.05 \text{ srad}$
Range of scattering angles:	$10^\circ \leq \Theta_S \leq 130^\circ$
Sample environment:	
- Cryostats:	$1.5 \leq T \leq 310 \text{ K}$
- Top-loading cryofurnace:	$1.5 \leq T \leq 600 \text{ K}$
- Furnaces:	$50 \leq T \leq 1400 \text{ }^\circ\text{C}$
- Low-T pressure cell:	$p \leq 3.5 \text{ kbar at } T \geq 4.5 \text{ K}$

Instrument Responsible

Dr. Michael Prager

Tel. +49-(0)-2461-61-6759

Email: m.prager@fz-juelich.de



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-002		
Experiment title:	Rotational dynamics of methyl groups in the tetracyanoquinodimethane plus hexamethylbenzene complex		
Dates of experiment:	4.3.2005, 9 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Results of this experiment are published in the paper

Titel: Elastic, quasielastic, and inelastic neutron-scattering studies on the charge-transfer hexamethylbenzene-tetracyanoquinodimethane complex

Authors: W. Sawka-Dobrowolska, G. Bator, L. Sobczyk, A. Pawlukoje, H. Ptsiewicz-Bak, H. Rundlöf, J. Krawczyk, M. Nowina-Konopka, P. Jagielski, J.J. Janik, M. Prager, O. Steinsvoll, E. Grech, J. Nowicka-Scheibe

Journal: J. Chem. Phys. 123, 124305(2005)

Abstract: The 1:1 hexamethylbenzene (HMB)-tetracyanoquinodimethane (TCNQ) complex shows a first-order phase transition at 230/218K (heating/cooling) with no change of the space group. The neutron-diffraction studies reveal that this transition is related to a freezing of the rotation of methyl groups. The result for 100K enabled precise determination of configuration of HMB.TCNQ complexes. The planes of HMB and TCNQ molecules form small angle (6°) so that the dicyanomethylene group approaches the HMB molecule to a distance of 3.34Å. The conformation of methyl group was exactly determined. The quasielastic neutron-scattering spectra can be interpreted in terms of 120° jumps with different activation barrier in low and high temperature phases, equal to 3.7 and 1.8 kJ/mol, respectively. These values are lower than that for neat HMB (6kJ/mol). The conclusion can be drawn that the methyl groups can reorient more freely in the complex. This conclusion is in agreement with the results of inelastic neutron-scattering studies of low-frequency modes assigned to torsional vibrations of methyl groups. These frequencies are lower than those in neat HMB. The analysed increase of frequencies of these modes as compared with free molecules can be interpreted as due to formation of unconventional C-H...Y bonds which are more pronounced in crystals of neat HMB than in those of HMB.TCNQ. The low-frequency librational modes can be treated as sensitive measure of unconventional hydrogen bonds formed by the CH_3 groups.

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Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-003		
Experiment title:	Studies on the crystalline electric field in RE ₂ Ru ₂ O ₇		
Dates of experiment:	15.3.2005-21.3.2005 6.4.2005-10.4.2005	Date of report:	13.6.2006
Experimental team:			
Names:	Addresses:		
J. Voigt L. J. Chang	Forschungszentrum Jülich Nuclear science and Technology Development Center Hsinchu 30013, Taiwan		
Local contact:	M.Prager		

Introduction

Pyrochlore oxides of the chemical formula A₂B₂O₇, where A is a rare-earth ion and B is a transition-metal ion, have the face-centered-cubic structure with space group *Fd3m* and eight molecules of its general formula in a unit cell. In the RE₂Ru₂O₇ (RE= rare earth and Y), Ru has a partially filled 4d shell and possesses a magnetic moment. RE and Ru form two individual networks of corner sharing tetrahedrons^{1,2}. It was reported that all the RE₂Ru₂O₇ show a specific heat jump in the temperature range 75 -160 K, which is correlated with the rare-earth ion size. In Tb₂Ru₂O₇, the specific heat jump was reported at 110 K. An additional magnetic transition was observed at 3.4 K by magnetisation measurement³. This magnetic transition was considered to be associated with the magnetic interaction between Tb³⁺ ions. A former inelastic neutron study showed an intensity shift from a distinct crystal field level into quasielastic scattering between 90 and 120 K.

Experimental

15 g of Tb₂Ru₂O₇ powder were prepared and characterised by powder x-ray diffraction. The sample is single phase within the accuracy limit of a few percent. Experiments have been performed at SV29 between 2.5 K and room temperature, using a closed cycle cryostat. High resolution data was taken using a neutron wavelength of 3.62 Å. For a wider energy range, a neutron wavelength of 1.81 Å was chosen.

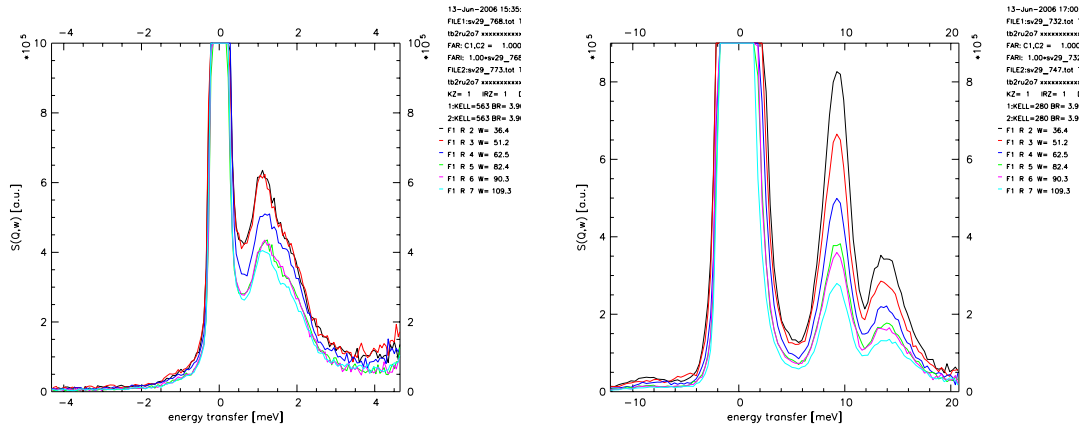


Fig 1: $S(Q, \omega)$ for $T < 10$ K. 16 detectors have been integrated, the average 2θ angle is given in the figures. The background was deduced from a measurement with empty sample container. The detectors were calibrated by a vanadium measurement. **Left)** $E_i = 6.2$ meV, **right)** $E_i = 25$ meV.

Results

In Fig 1 we present low temperature spectra measured with different incoming energy E_i . Distinct energy levels are found at 1.1 meV, 1.9 meV, 9.3 meV and 13.7 meV. The intensity of the observed features decreases with increasing scattering angle 2θ , indicative of magnetic excitations following the magnetic form factor. Fig 2 shows the temperature dependence of the low energy spectra at an averaged scattering angle $2\theta = 36.4^\circ$. The excitation at 1.9 meV decreases strongly with increasing temperature. Between 70 K and 100 K the intensity is shifted from the distinct level at 1.1 meV into quasielastic scattering, which may correspond local fluctuations at the Ru site prior to the phase transition.

References

- ¹ M.Ito et al., J. Phys. Chem. Solids **62**, 337(2001).
- ² C.Bansal et al., Phys. Rev. B **66**, 52406 (2002).
- ³ N. Taira et al., J. Mater. Chem **12**, 1475 (2002).

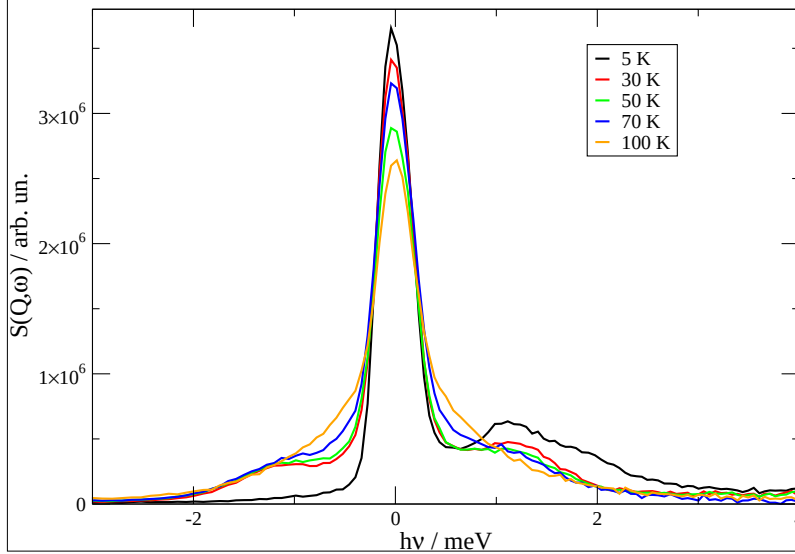


Fig 2: $S(Q, \omega)$ as a function of temperature. $E_i = 6.2$ meV, $2\theta = 36.4^\circ$.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-004		
Experiment title:	The isotope effect in acetone clathrates		
Dates of experiment:	14 days after 02.03.2005	Date of report:	02.06.2006
Experimental team: Names	Addresses		
M. Prager	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Acetone clathrate could be prepared according to ref [1] with an ingot where some KOH had been added to the stoichiometric mixture of acetone and water. The formation of clathrate requires an annealing step after a first cooling. The clathrate structure has been confirmed earlier by neutron diffraction [2] but the crystal structure – likely of cubic II structure - is not yet fully solved.

All possible isomers were investigated: h-acetone in H₂O, h-acetone in D₂O, d-acetone in H₂O and d-acetone in D₂O. All samples were annealed after cooling first to 5K at an annealing temperature $t=240\text{K}$ for more than 30min. While the spectra of samples with the protonated matrices changed significantly with annealing indicating clearly the transformation in the clathrate structure, those with the deuterated matrix changed little. These samples, however, allow to test a phase change by diffraction. There is even little change of the elastic intensities too, however. Thus it is unclear whether the deuterated host samples are one-phase materials with the expected structure.

The fig. shows the measured spectra of all samples at large scattering angles averaged over 32 of the 125 detectors. The project is going on.

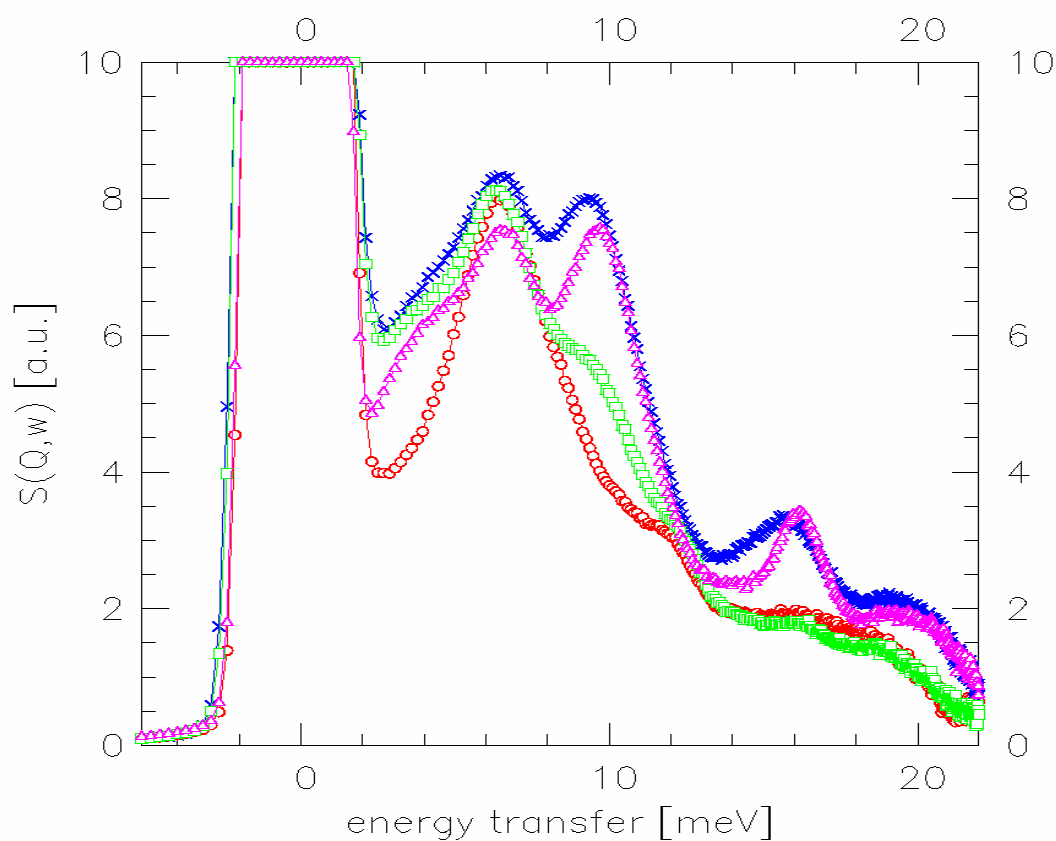


Fig. 1 Spectra of stoichiometric acetone-water mixtures. Sample temperatures $T=2.5\text{K}$. All samples annealed. oooo: h-acetone: $^{17}\text{D}_2\text{O}$; xxxx: d-acetone: $^{17}\text{H}_2\text{O}$; square: d-acetone: $^{17}\text{D}_2\text{O}$; Triangle: h-acetone: $^{17}\text{H}_2\text{O}$. $\lambda=1.76\text{\AA}$.

- [1] O. Yamamuro, M. Oguni, T. Matsuo, H. Suga, Solid state commun. **62**,289(1987)
- [2] O. Yamamuro, T. Matsuo, H. Suga, W.I.F. David, R.M. Ibberson, A.J. Leadbetter, Physica **B213&214**,405(1995)



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-005		
Experiment title:	Investigation of choline and acetylcholine neurotransmitter		
Dates of experiment:	24.6.2005, 12 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Acetylcholine is synthesized in certain neurons by enzyme choline acetyltransferase from the compounds choline and acetyl-CoA. Organic mercurial compounds have a high affinity for sulfhydryl groups, which attributes to its effect on enzyme dysfunction of choline acetyl transferase. This inhibition may lead to acetylcholine deficiency, contributing to the signs and symptoms of motor dysfunction.

Normally, the acetylcholine is quickly removed after having performed its action, this is done by the enzyme acetylcholinesterase which converts acetylcholine into choline and acetate. The devastating effects of nerve agents are due to their inhibition of this enzyme, resulting in continuing stimulation of the muscles, glands and central nervous system.

Acetylcholine and choline were studied as cations in the salts with Cl, Br and I anions. Since the spectra are dominated by the proton dynamics we observe in choline mainly the dynamics of the $N^+(CH_3)_3$ group. In acetylcholine the methyl group rotation of the acetyl group will modify the spectrum. Here we observe the superposition of methyl group torsional vibrations of the trimethyl ammonium and the acetyl group. While strong rotational potentials have so far been found for tetramethyl ammonium ions, acetates show low rotational barriers [1].

The TOF spectrometer was used with wavelengths $\lambda=1.76\text{\AA}$ and $\lambda=1.17\text{\AA}$. This gives access to the lattice modes and low lying internal vibrations. Two typical spectra are shown in the figures. Fig. 1 compares the acetylated sample with the pure choline. Chlorine forms the anion. In fig. 2 we compare two acetylcholine ions with different anions, chlorine and bromine. (Similar spectra are obtained with the iodide compound.)

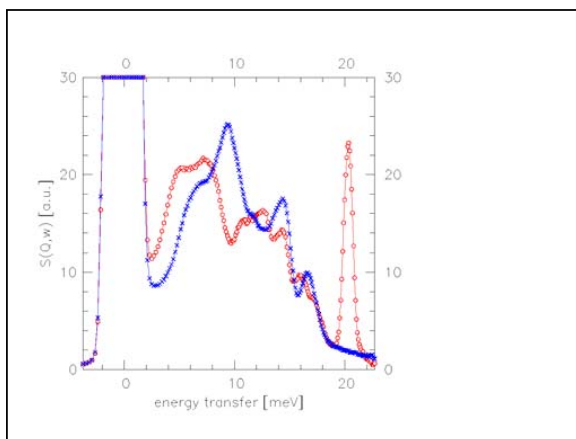


Fig. 1: Acetylcholin chloride (ooo) vs Cholin chloride. T=2.5K.

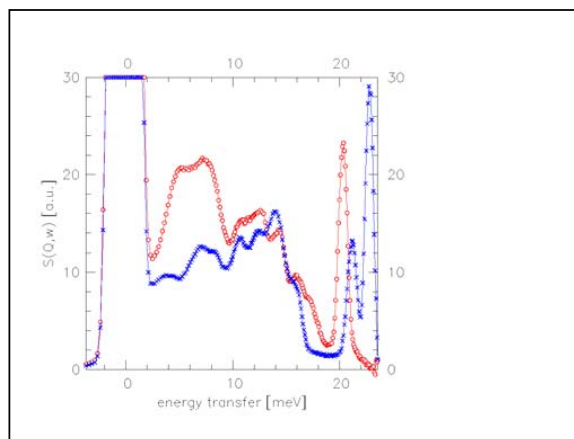


Fig. 2: Acetylcholin chloride (ooo) vs Acetylcholin bromide (xxx). T=2.4K.

In fig. 1 the band at 20meV is obviously related to the acetyl group and represents the librational mode of the methyl group. Its splitting in acetylcholin bromide (fig. 2) must most likely be caused by a symmetry reduction which leads to the presence of inequivalent acetyl environments in this compound. The bands of the trimethyl ammonium group are not such clear. According to the general experience they are more likely found at higher energy transfers. To identify these modes ab-initio calculations at the DFT level using the GAUSSIAN98 program will be well suited. Furthermore the CLIMAX program shall be well used to model the scattering from the different eigenmodes. This program is under way.

Finally, future IR and Raman experiments shall complete the inelastic neutron experiment. Selection rules are expected to contribute to an identification of the character of individual modes.

[1] M. Prager, A. Heidemann, Chem. Rev. **97**,2993(1997)



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-006		
Experiment title:	Influence of isomerism/substitution on the internal and external modes of various xanthenes		
Dates of experiment:	20.9.2005, 17 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

The methylxanthenes represent a biologically most important class of molecules. These rather simple double ring molecules include the natural drugs caffeine, theobromine and theophylline which are used in daily live and medical application.

Caffeine is an alkaloid found in such foods as coffee fruit, tea etc. Its main pharmacological properties are a stimulant action on the central nervous system with psychotropic effects and stimulation of respiration, a stimulation of the heart rate. By oxidative demethylation caffeine is metabolized in the liver to the dimethylxanthenes theobromine, theophylline and paraxanthine. In a second step demethylation leads to monomethylxanthenes. Other metabolic steps follow.

Theobromine is an alkaloid found in cocoa and chocolate. Theobromine has an antitussive effect superior to codeine by suppressing vagus nerve activity.

Theophylline is a drug, a phosphodiesterase inhibitor, that is widely used in therapy for respiratory diseases. It is naturally found in black tea and green tea. The main actions of theophylline are relaxation of bronchial smooth muscle, positive inotropic (increases heart muscle contractility and efficiency) and positive chronotropic (increases heart rate) impact. It lowers blood pressure, increases renal blood flow and has some anti-inflammatory effect.

While caffeine, theobromine and theophylline are biologically active, paraxanthin, interestingly, is almost completely inactive and therefore also non toxic.

Theobromine, theophylline and 1,7-dimethylxanthin (paraxanthin) are isomeric molecules. The molecules differ by the positions of the 2 methyl groups on the double ring. The figure shows theophylline as an example

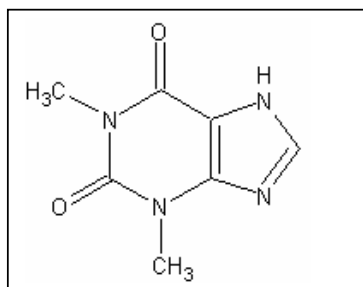


Fig. 1 Molecular structure of theophylline

In theobromine the methyl group between the two oxygens is moved to the upper nitrogen on the 5-ring. In 1,7-dimethylxanthin the bottom CH_3 is moved to this position. In caffeine with its third methyl group all three nitrogen atoms bound by single bonds in the double ring carry a methyl group. This structure allows no isomeric form.

From the spectra measured on SV29 with wavelengths $\lambda=1.76\text{\AA}$ and $\lambda=1.17\text{\AA}$ the biologically active theophylline (right) and the inactive 1,7-xanthine (left) are compared in the figures 2 and 3.

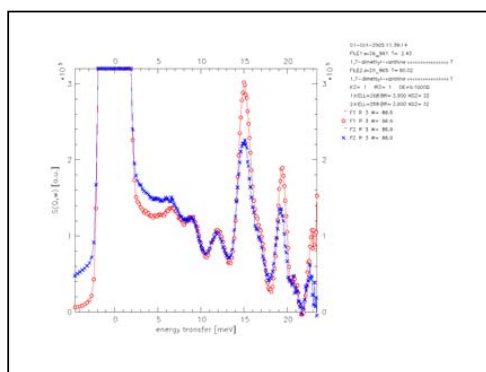


Fig. 2 spectra of 1,7-dimethyl-xanthine at Sample temperatures $T=2\text{K}$ and $T=60\text{K}$

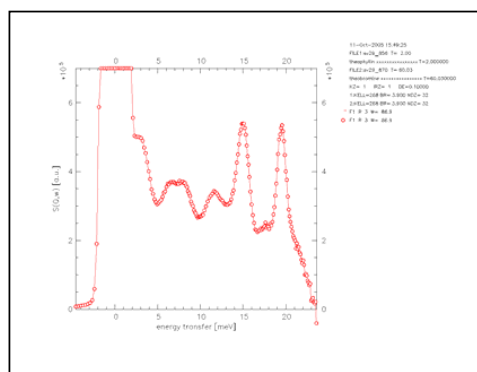


Fig. 3 spectrum of theophylline. sample temperature $T=2\text{K}$

Despite of close similarities – for example finding the two dominant bands at the same energies - there are clear differences especially in the regime of lattice modes. The mode at 3meV in theophylline has possibly to do with the methyl tunnelling mode observed at high energy resolution [1]. It is well known from the halomesitylenes and their derivatives that the hindering potential can strongly and often unexpectedly change with the methyl group position and neighborhood on the ring [2].

The data analysis is under progress. DFT and lattice dynamical calculations are planned.

[1] Experimental Reports FRJ2 2005, Report BSS-05-021

[2] A. del Rio, A. Boucekine, J. Meinel, J. Comp. Chem. 24,2093(2003)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S29-05-007		
Experiment title:	Magnetic Excitations in nanocrystalline terbium		
Dates of experiment:	May 2005	Date of report:	May 2006
Experimental team: Names	Addresses		
A. Hoser O. Moze, C. Vecchini A. Michels J. Weissmueller	Institut fuer Festkoerperforschung, Forschungszentrum Juelich, D-52425 Juelich, Germany Università di Modena e Reggio Emilia, Via Campi 213/a, 41100 Modena, Italy Technische Physik, Universitaet des Saarlandes, Saarbrueken, Germany Institut fuer Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany and Technische Physik, Universitaet des Saarlandes, Saarbrueken, Germany		
Local Contact:	M. Prager / A. Hoser		

Experimental report text body

Nanocrystalline composites are attracting attention because of the very different properties they show when compared to their coarse counterparts. Recent neutron diffraction measurements on a nanocrystalline sample of pure Terbium, with average grain size of 12 nm, gave evidence for the suppression of the antiferromagnetic phase that occurs in the coarse material at 216 K and vanishes at 229 K in the paramagnetic phase. Single crystal Terbium has been widely studied in the past showing the presence of a high energy excitation gap (which correspond to an optical zone center magnon mode) in zero applied field and a lower energy one which corresponds to the acoustic magnon mode¹. No previously reported neutron scattering experiments with the aim to determine the magnetic excitations on this nanocrystalline Rare Earth are known to us. We performed a neutron inelastic scattering experiment on the Time Of Flight Spectrometer SV-29 in order to determine the spin-wave energy gap. A first attempt was done on the Triple Axis Spectrometer UNIDAS and a small inelastic signal was observed at about 8.8 meV at 200K (Fig. 1). Here we report the continuation of this experiment on the TOF SV-29 Spectrometer. These results of these measurements have been just published in J. Appl. Phys².

The inelastic neutron scattering measurements were performed on the SV-29 Time of Flight Spectrometer at different temperatures, from 2.5 K to 250 K ($T_c=229$ K) on a nanocrystalline 1 gm sample of rare earth Terbium. The incident wavelength used was 1.81 Å for determining the high energy magnon mode, and a longer wavelength was used of 2.4 Å. in order to determine the lower energy magnon. A different sample holder has been used with respect to UNIDAS in order to maximize the scattering intensity vs absorption ratio. It is known that the coarse material shows two inelastic excitations at about 1.5 meV and 9 meV at 90 K. The spectra were collected for long measuring times due to the intrinsic low scattering intensity of the nanosized crystalline sample. The data were corrected for detector sensitivity and for the empty beam. The measurement revealed the presence of two magnetic excitations, one at approximately 10 meV at 2.5 K that decreases with increasing temperature and a very weak one at lower energy at about 2.5 meV.

We think that they correspond respectively to the optical and acoustic magnon modes similar to the magnon modes observed in a single crystal sample. More measurements with the purpose to determine the temperature dependance of the low energy excitation with more accuracy are highly desirable.

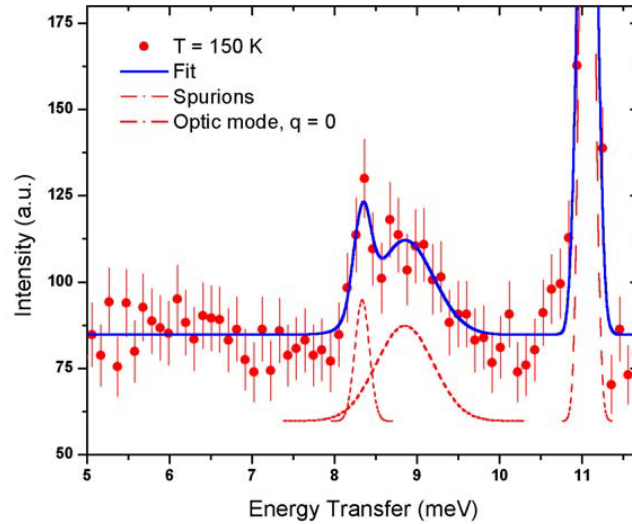


Fig. 1 – Inelastic neutron scattering spectrum for nc Tb at 150 K collected on the triple-axis-spectrometer UNIDAS. The peak at approximately 9 meV is the magnetic excitation that has been attributed to intrinsic optic zone center ($q=0$) magnon mode. The other two narrow peaks are due to instrumental effects.

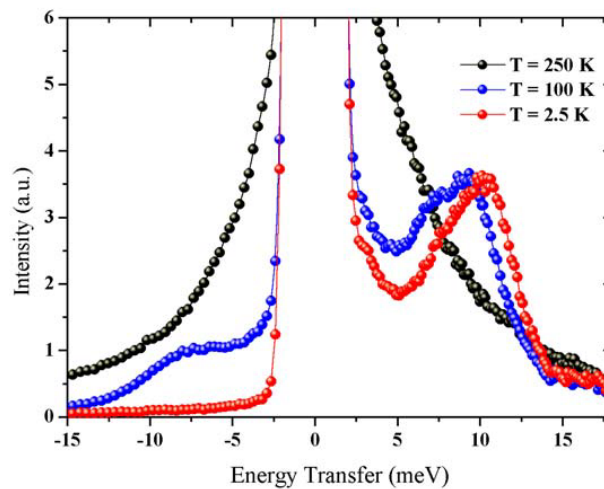


Fig. 2 – Magnetic scattering for nc Tb at 250, 100 and 2.5 K as measured with the TOF spectrometer SV-29. The peak at 10 meV moves with temperature and disappears at 250 K in the paramagnetic state.

Reference:

- 1) Moeller et al., Phys. Rev. Lett., **16**, 737 (1966.)
- 2) Vecchini et al., J. Appl. Phys., **99**, 08F502 (2006.)



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-008		
Experiment title:	Methyl group dynamics in methyl fluoride clathrate: the isotope effect		
Dates of experiment:	19.5.2004, 10 days	Date of report:	22.2.2006
Experimental team:			
Names	Addresses		
M. Prager	Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Molecular guest molecules included in water clathrate cages have been recently intensively studied. On the one hand there is the methane clathrate [1,2]. Beside its supposed role as one of the major future fossile energy resources it represents the prototype non polar guest molecule. On the other hand there are the methyl halide guest molecules [3,4] with a strong dipolar moment, varying size and therewith different crystal structures and also varying tendency to form hydrogen bonds with the cage protons. Du to this variability different systems illuminate different aspects of the interaction with the cage in different way. The work on the protonated methyl fluoride clathrate is published [4]. The abstract summarizes:

Neutron spectroscopy in the meV and μeV regime and quasielastic scattering is applied to characterize the dynamics of methyl groups of methyl fluoride guest molecules in cubic I CH_3F -water clathrate. Only above $T \sim 60\text{K}$ quasielastic spectra are unaffected by quantum effects. They are well described by two Lorentzians representing the CH_3F species in the small and large cages of the structure. The intensities show that both cages are completely filled. Linear broadenings with temperature follow the model of rotational diffusion. Two clearly separated tunneling bands were observed at $T=4.2\text{K}$ and are also assigned to the two types of water cages. Disorder of the environment (H-bonds) is reflected in the shape of the bands. For the less hindered species housing the large cages the tunneling band can be quantitatively converted into a potential distribution function within the model of single particle rotation. Transitions to excited rotational states show the dominance of a sixfold potential term $V_6=13\text{meV}$ modified by a weak threefold term distributed around a characteristic value $V_3=0.9\text{meV}$. The potential distribution of V_3 influences the barrier for classical reorientation only weakly in agreement with the results from quasielastic data. Adsorption sites with the guest molecules oriented towards a hydrogen bond along one of twelve local twofold axes of the cage are proposed. Such sites are consistent with the sixfold rotational potential and earlier results from methyl iodide clathrate [3]. Rotation-translation coupling as alternative dynamical process is excluded.

The work is now extended towards the deuterated methyl fluoride clathrate. Diffraction data have been taken on D20 of the ILL, Grenoble, the tunnelling spectrum was measured on IN5 and reproduces a similar broad distribution of tunnelling transitions shifted by the isotope effect of roughly a factor 2. The vibrational density of states of $\text{CD}_3\text{F} \cdot 5.75\text{D}_2\text{O}$ measured on SV29 is compared to that of the fully protonated material in Fig. 1. Here too a strong isotopic shift is obvious for the peak at $\sim 10\text{meV}$.

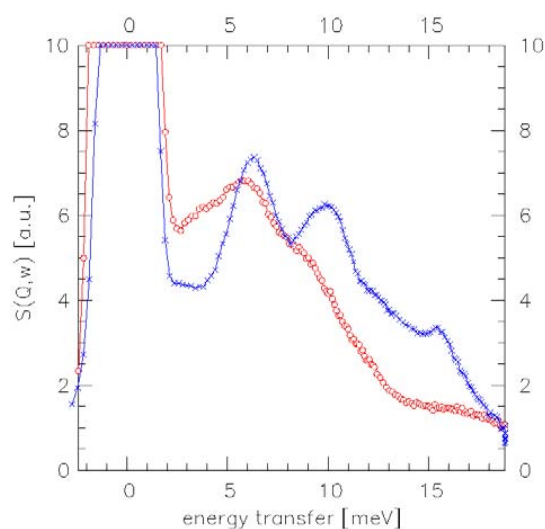


Fig. 1: Spectrum of methyl fluoride clathrate $\text{CD}_3\text{F} \cdot 5.75\text{D}_2\text{O}$ (ooo). $T=4.2\text{K}$, $\lambda=1.81\text{\AA}$. $\text{CH}_3\text{F} \cdot \text{H}_2\text{O}$ (xxx) for comparison.

For clarity the cage housing 75% of the molecules is reproduced as fig. 2 below.

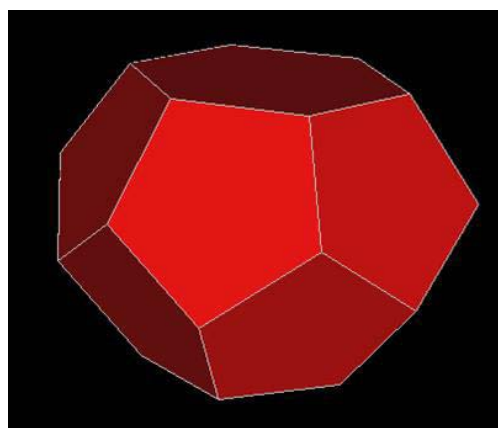


Fig. 2: The large $5^{12}6^2$ cage of the methyl fluoride clathrate $\text{CD}_3\text{F} \cdot 5.75\text{D}_2\text{O}$, which contains 3/4 of the CD_3F guest molecules. Each corner represent an oxygen of the water shell, each edge a hydrogen bond. There are inequivalent hydrogen bonds: 12 edges connect a pentagon with a hexagon, 12 connect 2 pentagons with a pentagon on each side of the edge, 12 connect 2 pentagons with a pentagon on one and a hexagon on the other side of the edge.

- [1] C. Gutt, B. Asmussen, W. Press, M.R. Johnson, Y.P. Handa, J.S. Tse, J. Chem. Phys. **113**,4713(2000)
- [2] C. Gutt, W. Press, A. Hüller, J. Tse, H. Casalta, J. Chem. Phys. **114**,4160(2001)
- [3] M. Prager, J. Pieper, A. Buchsteiner, A. Desmedt, J. Phys. Condens. Matter **16**,7045(2004)
- [4] M. Prager, J. Baumert, W. Press, M. Plazanet, J.S. Tse, D.D. Klug, PCCP **7**,1228(2005)



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-009		
Experiment title:	A systematic search for correlation of hydrogen bonding and lattice dynamics in methyl pyrazines		
Dates of experiment:	13.6.2005, 11 days	Date of report:	23.2.2006
Experimental team:			
Names	Addresses		
O. Kirstein M. Prager	ANSTO, Menai, Australien Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

The fundamental quantities that determine the spatial arrangement of the atoms of a molecule and their dynamics are the intermolecular interaction potentials. There are different levels of approximation. In the most fundamental approach the dynamics of molecular crystals is modelled using either ab-initio/molecular mechanics programs e.g. [1,2]. Somewhat more heuristic is the use of semi-empirical interaction potentials. The latter potentials are also known as pair potentials (PP). The most important property of PP's is their transferability, which reduces the number of adjustable parameters and simplifies the theoretical description of atomic interactions within complex molecular systems significantly and would allow in the ideal case to calculate the crystal structure as well as the lattice dynamics of any molecular system. Actually calculations of the properties of molecular crystals using transferable pair potentials (TPP) are essentially limited to systems where accurate crystal structures are known. Transferability is the better the closer the systems are chemically related. Along these lines the interest in the weak hydrogen bond [3] has lanced the systematic X-ray diffraction study of the structures of all methyl pyrazines [4]. Methyl pyrazines are available with 1, 2, 3 and 4 methyl groups. The presence of 2 methyl groups allows the arrangement in 3 isomers. Most materials crystallize in the monoclinic space groups $P2_1/n$ or $P2_1/c$. Only 2-methyl pyrazine assumes a tetragonal lattice with space group $I4$. The number of molecules in the unit cell varies from 2 to 16. The materials are characterized and classified by their C-H...N hydrogen bonds.

The figure 1 shows the density of states as measured for the so far not investigated 2-methyl-pyridine for energies up to 22 meV. The calculation of the density of states was done *before* the experiment was performed using the local program DYNCAL. The calculation is based on the crystal structure [4] and as in former studies [5] universal force field parameters [6]. The similarity of theoretical and experimental spectra is surprisingly good (fig. 1 bottom). The data evaluation is in progress.

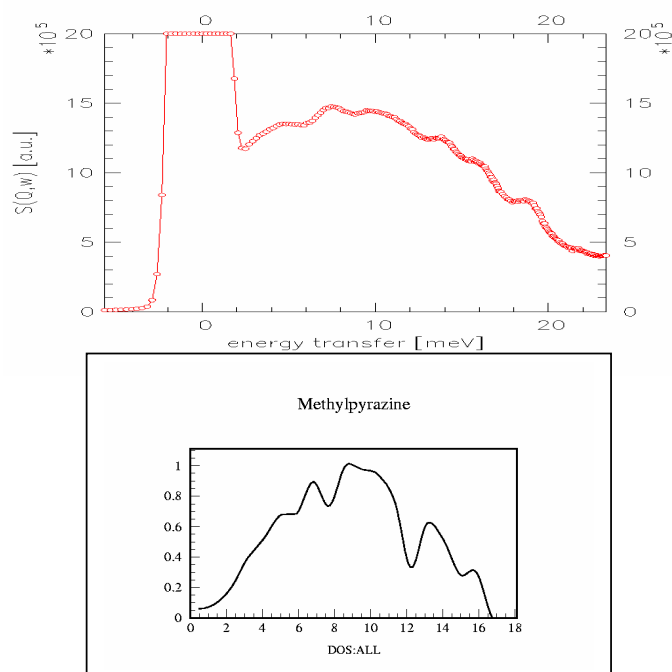


Fig. 1: Comparison of measured spectrum (top) and calculated density of states (bottom).

References

- [1] M.R. Johnson, M. Prager, H. Grimm, M.A. Neumann, G.J. Kearley, C.C. Wilson, Chem. Phys. 244 (1999) 49-66
- [2] B. Nicolai, E. Kaiser, F. Fillaux, G.J. Kearley, A. Cousson, W. Paulus, Chem. Phys. 226 (1998) 1-13
- [3] G.R. Desiraju, T. Steiner, 'The weak hydrogen bond in structural chemistry and biology', Oxford university press, Oxford, 1999
- [4] V.R. Thalladi, A. Gehrke, R. Boese, NJC 24,463(2000)
- [5] O. Kirstein, M. Prager, R.M. Dimeo, A. Desmedt, J Chem Phys 122,14502(2005)
- [6] A.K. Rappe et al, J. Am. Phys. Soc., Vol 114 No 25, 1992
- [7] M.R. Johnson, M. Prager, H. Grimm, M.A. Neumann, G.J. Kearley, C.C. Wilson, Chem. Phys. 244,49(1998)



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-010		
Experiment title:	INS studies of rotational potentials of methyl groups in complexes of methyl derivatives of pyrazines with chloranilic acid		
Dates of experiment:	07.03.2006, 3 days	Date of report:	02.06.2006
Experimental team:			
Names	Addresses		
E. Grech A. Pawlukoje M. Prager	Institut of Chemistry, University of Szczecin, Poland Institute of Nuclear Chemistry and Technology, Warsaw, Poland Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

The present experiment is part of a broader access to charge transfer compounds. Results from a first system studied, tetramethyl pyrazine with chloranilic acid was published recently [1].

In the framework of this project a new 1:1 charge transfer complex, tetramethylpyrazine (TMP) with squaric acid (SA) is investigated. The complex was synthesized in Szczecin.

Fig. 1 shows the spectrum in the regime of lattice modes at two temperatures. The damping of the strongest lattice mode at an energy of 13 meV is taken as fingerprint of its methyl librational origin. The identification of the other bands needs either a lattice dynamical calculation or cross verifications.

The observation of tunnel splittings can help to characterize more convincingly the librational character of a mode of the density of states. Fig. 2 shows the tunnelling spectra of the TMP:SA complex. Two bands at energies 1.55 μ eV and 4.2 μ eV are clearly seen. They show equal intensities. The total tunnelling intensity is a factor ~ 2 lower than expected from the scattering function. This means that 2 tunneling transitions are not resolved. For the crystal structure this means that either there is no symmetry at the site of the TMP molecule or there may be 2 inequivalent TMP molecules in the unit cell with say a mirror plane or a 2-fold axis connecting the two halves of the TMP molecule.

The 2 measured transition energies, tunnel splitting and first excited librational mode, can be used to determine the rotational potentials of the respective methyl groups. If the shoulder at 15 meV is also interpreted as the libration of the methyl group with the smaller tunnel splitting one derives pure $\cos(3\phi)$ potentials with barrier heights of 38 meV and 47 meV.

Compared to pure TMP these rotational potentials are weaker. Whether there is an influence of charge transfer or whether all changes are solely due to steric effects of the environment requires a mathematical modelling. Such calculations are planned.

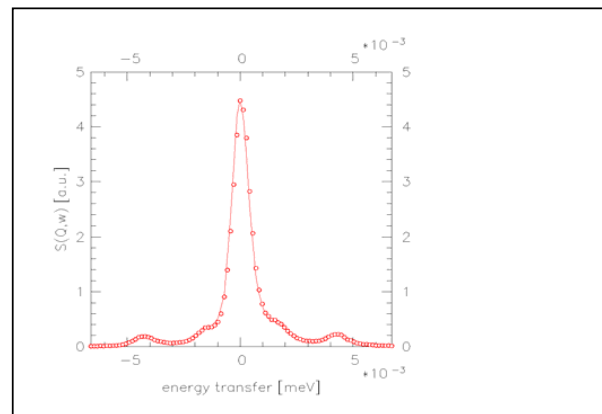
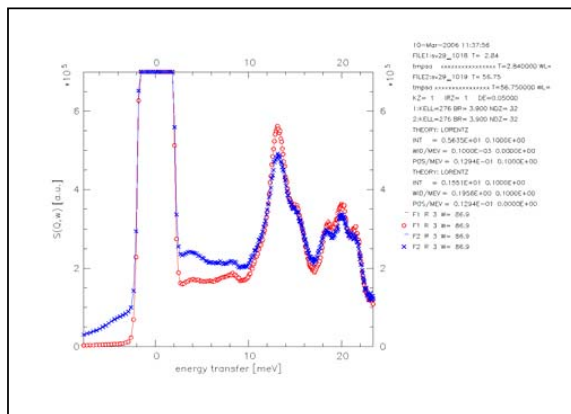


Fig. 1: Spectrum of TMP:SA in the regime of lattice modes. T=2.4K and 50K.

Fig. 2: Spectra of TMP:SA in the regime of tunnel splittings. $T=4.5\text{K}$.

[1] M. Prager, A. Pawlukojc, E. Sobczyk, E. Grech, H. Grimm, J. Phys. Condens. Matter **17**, 5275 (2005)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

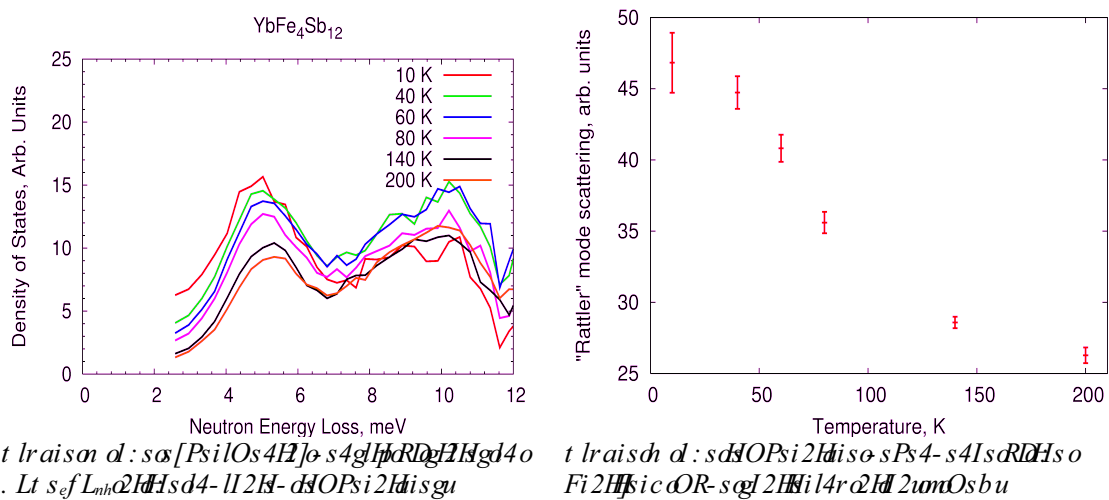
Proposal number:	S29-05-012		
Experiment title:	Präparation und Untersuchung der Eigenschaften von $\text{YbFe}_4\text{Sb}_{12}$		
Dates of experiment:	October 25 th - November 1 st 2005	Date of report:	March 1 st 2006
Experimental team: Names	Addresses		
Hermann Rapp, Günter Frenn, Klaus Vetter, Andreas Dörm	Université de Liège – Dept. de Physique – B5 – B4888 Liège – Belgium Université de Liège – Dept. de Physique – B5 – B4888 Liège – Belgium University of Tennessee, Dept. of Materials Science and Engineering, Knoxville, TN USA Oak Ridge National Laboratory, Oak Ridge, TN, USA		
Local Contact:	Dr. A. Prager		

Abstract

The presence of loosely bound guests, so called “rattlers”, in the cages of filled skutterudites has been shown to yield a strong reduction in the lattice thermal conductivity of these materials, with respect to the unfilled compounds. Several studies of the lattice dynamics in filled skutterudites show that the signature of the “rattler” mode is that of an Einstein oscillator. In particular this signature is observed through heat capacity measurements and inelastic neutron scattering. So far the Einstein oscillator peak in the phonon density of states has been observed in La, Ce, and Ti filled skutterudites by inelastic neutron scattering, [1,2] and in Eu filled skutterudites by nuclear inelastic scattering. [3] The valence state of these filler elements does not change as function of temperature.

The elastic constants of several skutterudites have been reported [1] and the signature of the “rattler” is revealed by a two-level-system contribution to the free energy, where the two-level splitting is the Einstein energy. The shear modulus, I_{44} , in $\text{LaFe}_4\text{Sb}_{12}$, shown on the left of Fig. 1, can be modeled as the sum, full line, of the Varshni behavior, dashed line, observed in CoSb_3 and a contribution from a two-level system [1]. We have measured the elastic constants of $\text{YbFe}_4\text{Sb}_{12}$ as function of temperature between 4 K and 88 K. In $\text{YbFe}_4\text{Sb}_{12}$, a model that supposes that the two-level splitting, $\hbar\omega$, is the Einstein energy, exhibits a strong temperature dependence, must be used in order to fit the experimental data. It has been reported that Yb in $\text{YbFe}_4\text{Sb}_{12}$ may be present in an intermediate valence state between Yb^{2+} and Yb^{3+} , which depends on the temperature. With the characteristic temperature for the Yb valence fluctuation T^* estimated at $\sim 58\text{ K}$ [4], the observed feature at 58 K in the elastic constants is likely to be related to the intermediate valence behavior of the compound.

The goal of this experiment is to carry out a direct measurement of the Yb Einstein oscillator energy, by a determination of the phonon density of states in $\text{YbFe}_4\text{Sb}_{12}$ as a function of temperature, between 158 K and 18 K.



The inelastic scattering by $\text{YbFe}_4\text{Sb}_{12}$ has been measured between 18 and 288 K, and the density of states has been calculated, see Figure 1. The prominent feature in the obtained density of states is the peak at ca. 5 meV that is associated with the Yb “rattler”. Because of the large Yb scattering cross-section, the peak is clearly visible without the subtraction of the acoustic phonon contribution that has to be done in similar experiments.[1,2] It appears that there is no strong dependence of the rattler energy upon temperature and our initial hypothesis is not confirmed by this result. The Bose-factor corrected integral inelastic scattering of the “rattler” mode has been obtained from a fit with a single Gaussian contribution of the peak around 5 meV, and is shown in Figure 2. The observed decrease in this figure clearly demonstrates that the phonon density of states of the material is not constant as a function of temperature, and indicates that it is likely an anharmonicity effect that causes the dramatic softening around 58 K that has been observed by elastic constants measurements.

References:

1. V. Keppens, D. A. Anzures, B. C. Sales, B. C. Chakoumakos, P. Day, R. Coldea, A. B. Aple, D. A. Gajewski, E. J. Freeman and S. Bennington, *Phys. Rev. B* **39**, 8, L (1998).
2. R. P. Hermann, R. Jin, W. Schweika, F. Granjean, D. A. Anzures, B. C. Sales and G. J. Long, *Phys. Rev. B* **40**, 1d5585 (288d).
3. G. J. Long, R. P. Hermann, F. Granjean, E. Alp, W. Sturhahn, C. E. Johnson, D. E. Brown, and R. Rüffer, *Phys. Rev. B* **32**, 148d82(R) (2885).
4. N. R. Dilley, E. D. Bauer, A. B. Aple, S. Dordevic and D. N. Basov, F. Freibert, T. W. Darling, A. Migliori, B. C. Chakoumakos and B. C. Sales, *Phys. Rev. B* **61**, 4L88–4L14 (2888); and B. C. Chakoumakos, *Phys. Rev. B* **41**, 2H14 (1990).

Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-013		
Experiment title:	Crystal field and phonon density of states in REMnO ₃ (RE=Nd,Pr,Tb,Ho)		
Dates of experiment:	30.11.05-5.12.05 20.1.06-25.1.06	Date of report:	23.5.06
Experimental team:			
Names:	Addresses:		
J. Voigt	Forschungszentrum Jülich		
Local contact:	M. Prager		

We have studied the inelastic neutron scattering from TbMnO₃ powder on the thermal time-of-flight spectrometer SV29. The compound has attracted considerable interest because it exhibits multiferroic behaviour. Antiferromagnetic order and the ferroelectric polarization are intimately connected as evidenced by the polarization flop from the *c*-direction to the *b*-direction in an applied magnetic field of several Tesla [1].

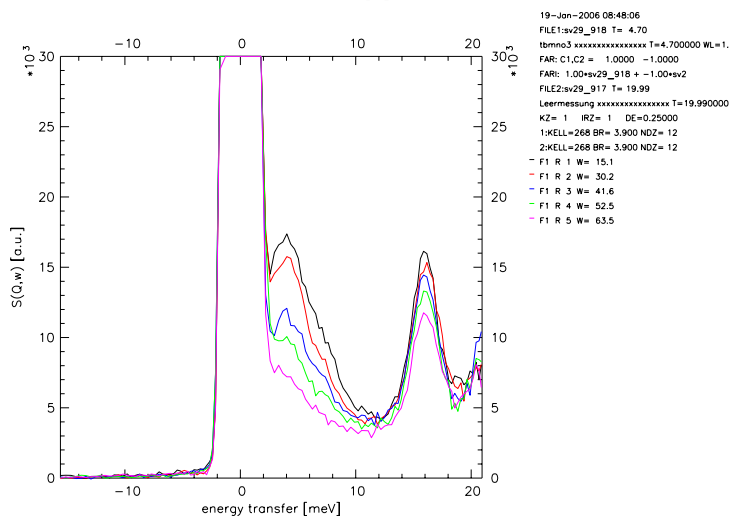


Fig. 1: Spectra integrated over 12 single detectors at 2.5 K as a function of energy transfer. Before $S(Q,\omega)$ calculation, the background from an empty sample container was subtracted and the data was corrected for detector efficiency by a vanadium measurement.

The formation of the ferroelectric polarization at $T_c = 28$ K seems to be coupled to a magnetic reorientation transition from a collinear incommensurate (IC) magnetic structure to a non-collinear. This transition involves also a long range ordering of the Tb^{3+} ions according to a recent neutron diffraction study [2]. The transition temperature is significantly higher than temperature $T_{N,\text{Tb}} = 8$ K, at which the Tb moments order with a different propagation vector as compared to the ordering of the Mn subsystem.

The experiment has been performed on the thermal time-of-flight spectrometer SV29, using a wavelength $\lambda = 1.76$ Å, corresponding to an energy $E_i = 26$ meV. The sample was mounted in a closed cycle cryostat, giving a temperature range from 2.5 K to room temperature. In Fig 1 we present the spectra integrating the signal of 12 neighboring detectors for the whole detector array of 125 detectors at a temperature of 2.5 K. We observe two distinct levels at 4.5 and 17.2 meV. $S(\mathbf{Q},\omega)$ decreases with increasing scattering angle, indicating the Tb^{3+} form factor. Hence we conclude, that both features are crystal field excitations.

We have recorded spectra at temperatures in the different phases. The temperature evolution is shown in Fig 2. As you go from the low temperature Tb ordered phase into the IC non-collinear and ferroelectric phase, the crystal field levels shift to slightly lower energies. Crossing the transition to the IC collinear magnetic and paraelectric structure doesn't lead to significant changes. Unfortunately the statistics of the 50 K data are too poor to establish any changes on entering the paramagnetic state.

References

- [1] T. Kimura *et al.*, PHYSICAL REVIEW B **71**, 224425 (2005).
- [2] M. Kenzelmann *et al.*, PHYSICAL REVIEW LETTERS **95**, 087206 (2005).

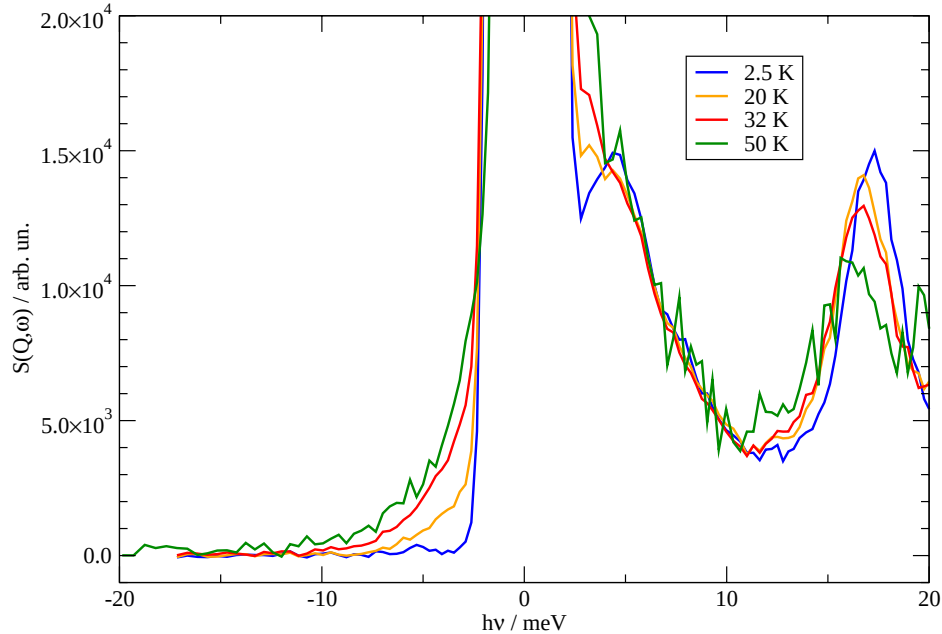


Fig 2: Temperature evolution of $S(\mathbf{Q},\omega)$. The spectra are integrated using always 12 detectors out of the sv29 detector array. The centre of the scattering angle is $2\theta = 30.2^\circ$. A vanadium standard was used to calibrate the detectors. The background subtracted from all spectra was measured at $T = 2.5$ K.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-014		
Experiment title:	INS studies of rotational potentials of methyl groups in the 2,6-dimethylpyrazine:chloranilic acid complex		
Dates of experiment:	24.06.2005, 6 days	Date of report:	25.02.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Molecular alloys have attracted wide interest since mixed systems may show properties unexpectedly different from those of the ingot materials. Among many others the complexes of chloranilic acid CLA with electron donor molecules seem to be interesting from the point of view of materials science.

The crystal structure of the 1:1 complex of 2,6-DMP and CLA was determined by X-rays at a sample temperature $T=100\text{K}$. The system is monoclinic $P2_1/c$ with $Z=4$ dimeric units in the large unit cell [1]. The 4 dimers are related by symmetry. Thus the complex contains just two equally weighted inequivalent methyl groups. A hydrogen bond links the proton of the CLA to the 2,6-DMP constituent via the nitrogen located between its two methyl groups.

The spectra of DMP:h-CLA and DMP:d-CLA were measured in the regime of phonons using wavelengths $\lambda=1.17\text{\AA}$ and $\lambda=1.76\text{\AA}$. The doublet centered around 12meV (fig. 1) is interpreted as methyl libration split by coupling to lattice modes in agreement with a tunnel splitting of $3.3\mu\text{eV}$ observed with the backscattering spectrometer BSS1 [2]. From the intensity of this tunnelling band it is concluded that the second kind of methyl groups scatters only elastically and must be related with a librational mode at higher energy. The transition at 23meV may be assigned to this mode. Samples to verify the assignment via the isotope effect were not available.

To test whether effects of hydrogen bonding or charge transfer may be visible in the methyl rotational potentials we compare first the rotational potential in the complex to that of pure 2,6-DMP. In this material the rotational potential is found to be much weaker as in the complex [3,4]. Just the opposite happened in the previously studied TMP:CLA where complexation has led to a large reduction of the rotational potentials [5]. This shows that the most important influence must be the geometry of the environment. To identify more subtle effects of charge rearrangement requires a knowledge of the low temperature crystal structure similarly precise as in the case of pure DMP and a similar mathematical treatment of the lattice dynamics.

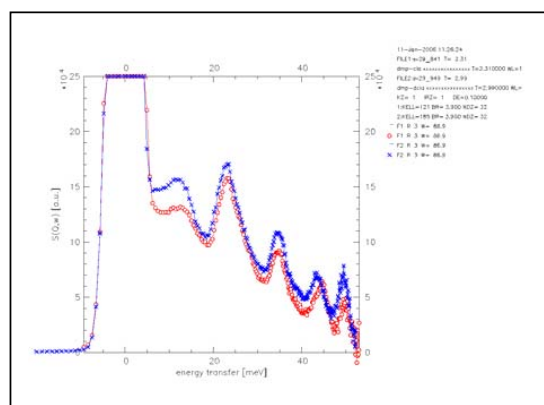
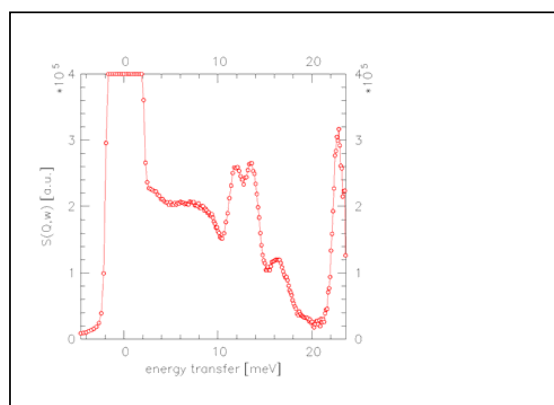


Fig. 1: Spectrum of 2,6-DMP:h-CLA in the regime of lattice modes

Fig. 2: Spectra of 2,6-DMP:h-CLA (ooo) and 2,6-DMP:d-CLA at energies of internal modes.

While no real changes with deuteration were found at low energy transfers $\Delta E < 20 \text{ meV}$ fig. 2 shows that also up to 50 meV there are only minor differences between the materials with protonated and deuterated hydrogen bonds. Only the band at $\sim 43 \text{ meV}$ shows a measurable shift to lower energy with deuteration. In analogy to earlier Gaussian98 calculations this mode could be assigned to C-CH₃ wagging or bending modes. It is obvious that a change of the methyl rotational potential can influence such a mode. This observation is consistent with a reduction of the rotational barrier with in 2,6-DMP:d-CLA deduced from a weakly increased tunnel splitting [5].

- [1] W. Sawka-Dobrowolska, G. Bator, L. Sobczyk, E. Grech, J. Nowicka-Scheibe, A. Pawlukoje, *Struct.Chem.*, in press
- [2] Experimental Report 2005 FRJ2, this volume BSS-05-028
- [3] E. Kaiser-Morris, A. Cousson, W. Paulus, F. Fillaux, *Acta Cryst.* **E57**,o1113(2001)
- [4] B. Nicolai, E. Kaiser, F. Fillaux, G.J. Kearley, A. Cousson, W. Paulus, *Chem. Phys.* **226**,1(1998)
- [5] M. Prager, A. Pawlukoje, E. Sobczyk, E. Grech, H. Grimm, *J. Phys. Condens. Matter* **17**,5275(2005)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S29-05-015		
Experiment title:	Crystal electric field scheme of $R_2\text{PdSi}_3$ ($R = \text{Tb, Er, Tm}$)		
Dates of experiment:	07.12.05-19.12.05 16.01.06-20.01.06	Date of report:	06.06.06
Experimental team: Names	Addresses		
Matthias, Frontzek	TU Dresden, Institut für Festkörperphysik, Zellescher Weg 16; 01062 Dresden		
Local Contact:	Jörg Voigt and Michael Prager		

Experimental report text body

The series $R_2\text{PdSi}_3$ ($R = \text{rare earth metal}$), crystallizing in an AlB_2 derived hexagonal structure, have been found to exhibit strong anisotropic magnetic properties [1] and to show a giant magneto-resistance effect [2]. In the Tb_2PdSi_3 compound low-dimensional magnetism as well as spin-glass like behaviour probably due to geometrical frustration was observed [1]. A spin-glass like transition below the Néel temperature is reported for the Er_2PdSi_3 compound, too [3].

We performed magnetic neutron diffraction studies on $R_2\text{PdSi}_3$ ($R = \text{Tb, Er, Tm}$) single crystals. Due to the crystal electric field (CEF) anisotropy the magnetic moment direction is in the hexagonal plane for Tb_2PdSi_3 ($T_N = 23 \text{ K}$) and along the hexagonal c -axis for Er_2PdSi_3 ($T_N = 7 \text{ K}$) and Tm_2PdSi_3 ($T_N = 1.8 \text{ K}$). The modulation of the magnetic moments is along c^* in the case of Tb_2PdSi_3 , along a^* for Er_2PdSi_3 and along both directions for Tm_2PdSi_3 . The compounds of the isostructural series seem to be strongly influenced by CEF effects and the according magnetocrystalline anisotropy [4]. However, no inelastic neutron scattering experiments have been published so far.

The aim of the experiment was to obtain a first overview of the CEF level scheme of the $R_2\text{PdSi}_3$ compounds. The powder samples ($m \approx 10 \text{ g}$) of $R_2\text{PdSi}_3$ ($R = \text{Y, Tb, Er, Tm}$) were prepared similar to the single crystal growth process.

The main results for the magnetic ordering compounds are shown in the Figures 1 to 3. For the Tb_2PdSi_3 compound the complete incident energy range of the SV-29 spectrometer was used with additional measurements at incident energies of 6.3 meV and 56.8 meV. Only one CEF transition at around 6.5 meV (Fig. 1) was observed ($T = 2.5 \text{ K}$). The Er_2PdSi_3 and Tm_2PdSi_3 compounds were only measured with an incident energy of 25.3 meV which provides the highest neutron flux at the sample position. Er_2PdSi_3 features two CEF transitions at 3.35 meV and 8.42 meV ($T = 2.5 \text{ K}$) in this energy range (Fig. 2). The measurement on the Tm_2PdSi_3 compound was performed in the standard-orange cryostat which allows lower temperatures than the closed cycle cryostat used for the measurement of the other compounds, since Tm_2PdSi_3 orders below $T = 1.8 \text{ K}$. Similar to Er_2PdSi_3 also in the Tm_2PdSi_3 compound two CEF transitions were observed (Fig. 3). The transition energies are larger with 5.77 meV and 11.28 meV.

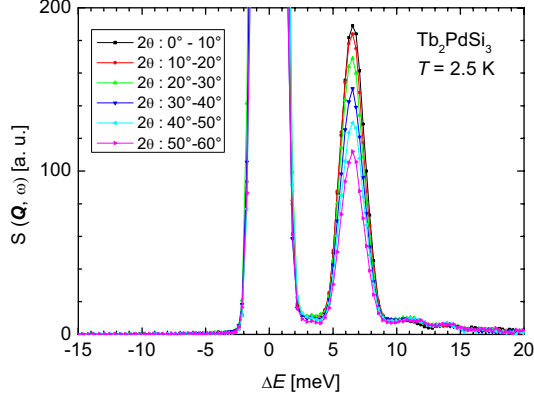


Fig. 1: $S(\mathbf{Q}, \omega)$ of Tb_2PdSi_3 at $T = 2.5$ K; the incident energy was $E = 25.3$ meV.

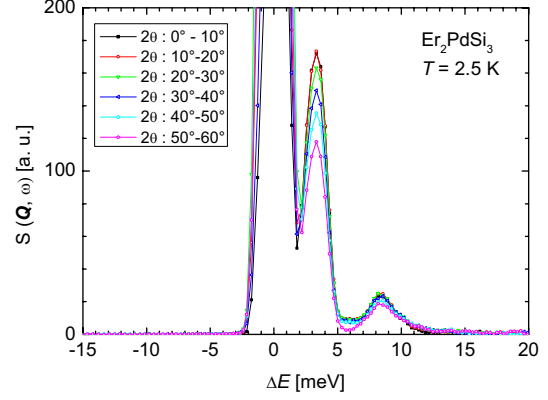


Fig. 2: $S(\mathbf{Q}, \omega)$ of Er_2PdSi_3 at $T = 2.5$ K; the incident energy was $E = 25.3$ meV.

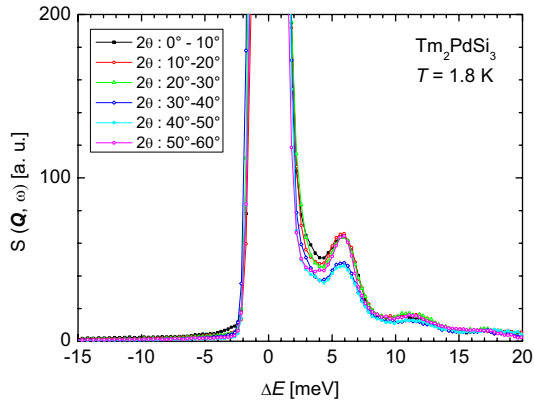


Fig. 3: $S(\mathbf{Q}, \omega)$ of Tm_2PdSi_3 at $T = 1.8$ K; the incident energy was $E = 25.3$ meV.

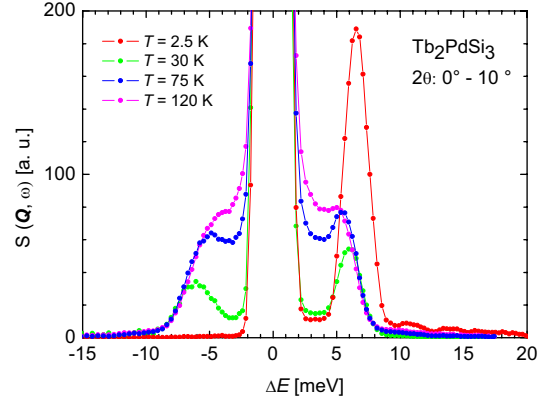


Fig. 4: $S(\mathbf{Q}, \omega)$ of Tb_2PdSi_3 at small scattering angle and at four different temperatures; the data has been modified with the Boltzmann factor (except the $T = 2.5$ K data); incident energy was $E = 25.3$ meV.

The measurements were not only performed at lowest temperature but at 4 different temperatures up to 120 K for each of the three magnetic compounds (temperatures were selected according to characteristic temperatures determined from susceptibility measurements). All investigated compounds exhibit a similar temperature dependent behaviour like the Tb_2PdSi_3 compound. A comparison between different temperatures is shown for the Tb_2PdSi_3 compound in Figure 4. The quasi-elastic line broadens strongly with increasing temperature thus making it difficult to determine the exact energy position of the transition. Still, the crystal field levels seem to decrease in energy with increasing temperature. For the Tb_2PdSi_3 compound no additional transition could be observed. In the cases of the Er_2PdSi_3 and Tm_2PdSi_3 compound one expects to observe the additional transition between the two levels measured at lowest temperature. However, this transition can only be observed in the Er_2PdSi_3 compound. For the Tm_2PdSi_3 compound the energy difference between the two measured levels equals the energy of the first level thus making the transition between the two levels undistinguishable from the transition to the first level. The combination of macroscopic data (e. g. susceptibility, magnetisation) and the measured transitions will lead to a first scheme of the CEF for the $R_2\text{PdSi}_3$ compounds.

References:

- [1] S. Majumdar, E. V. Sampathkumaran, P. L. Paulose, H. Bitterlich, W. Löser, G. Behr, Phys. Rev. B **62** (2000) 14207
- [2] S. Majumdar, H. Bitterlich, G. Behr, W. Löser, P. L. Paulose, E. V. Sampathkumaran, Phys. Rev. B **64** (2001) 012418
- [3] K. K. Iyer, P. L. Paulose, E. V. Sampathkumaran, M. Frontzek, A. Kreyssig, M. Doerr, M. Loewenhaupt, I. Mazilu, G. Behr, W. Löser, Physica B **355** (2005) 158-168
- [4] M. Frontzek, A. Kreyssig, M. Doerr, M. Rotter, G. Behr, W. Löser, I. Mazilu, M. Loewenhaupt, JMMM *accepted for publication*



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-016		
Experiment title:	The study of the quasielastic incoherent neutron scattering from the $K_{1-x}(NH_4)_xSCN$ mixed crystals		
Dates of experiment:	13 days between 21.2. – 20.3.2006	Date of report:	20.5.2006
Experimental team: Names	Addresses		
L. Smirnov I. Natkaniec M. Prager	FSUE SSC RF, Institute of theoretical and experimental physics, Russia JINR, Dubna, Russia Forschungszentrum Jülich, Institut für Festkörperforschung		
Local Contact:	M. Prager		

Experimental report text body

KSCN, potassium thiocyanate, undergoes a phase transition at 413 K from orthorhombic phase with space group $Pbcm-D_{2h}$, $Z=4$ [1], and lattice parameters $a=6.673$, $b=6.715$, $c=7.543$ Å, into a body-centered tetragonal structure with space group $I4/mcm$, $Z=4$ [2] and lattice parameters $a=b=6.70$, $c=7.73$ Å. Similarly NH_4SCN , ammonium thiocyanate, undergoes order-disorder phase transition from a high temperature tetragonal phase I with space group $I4/mcm-D_{4h}$ ¹⁸, $Z=4$, lattice parameters $a=b=6.961$, $c=8.00$ Å to antiferroelectric orthorhombic phase II with space group $Pbcm-D_{2h}$, $Z=4$, lattice parameters $a=6.878$, $b=6.905$, $c=7.912$ Å at 391K [3-4]. Following transition in NH_4SCN appears at 359K from phase II to phase III with a monoclinic crystal structure with space group C_{2h} ⁵, $Z=4$, lattice parameters $a=4.247$, $b=7.146$, $c=13.022$ Å, $\beta=97.8^\circ$ [5].

As was shown in [6] KSCN and NH_4SCN can form solid solutions in all concentration region of ammonium. The $K_{1-x}(NH_4)_xSCN$ mixed crystals are obtained in the result of the evaporation of water stoichiometrical solutions of KSCN and NH_4SCN at 323K. KSCN and NH_4SCN are isomorphic at this temperature, ionic radii of these substances are close and this promotes to the formation of solid solutions.

The purpose of the experiment is to determine in the $K_{1-x}(NH_4)_xSCN$ mixed crystals by means of quasielastic incoherent neutron scattering (QENS) the distribution of the barrier to the reorientations of ammonium ions and the energy of the activation in different regimes of concentration. In this first experiment a concentration $x=0.1$ is chosen to avoid to a large degree the interaction between ammonium ions. The spectrometer was used with a wavelength $\lambda=3.52$ Å and a corresponding energy resolution of $\delta E=0.31$ meV.

Fig. 1 shows the spectra measured at sample temperatures from 40K to 110K. A clear quasielastic component is visible. It must be assigned to ammonium reorientational jumps. The data wait for a quantitative analysis based on the random rate distribution model (RRDM) [7]. Beside of the quasielastic component we observe a soft inelastic mode around 3.6 meV of so far unknown origin. Lattice dynamical calculations will help to identify the character of this mode.

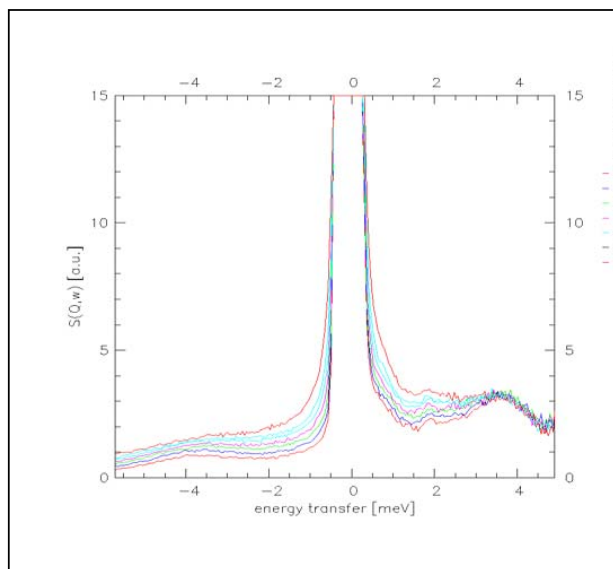


Fig. 1: Spectra of $K_{0.9}(NH_4)_{0.1}SCN$ summed over all Angles. Sample temperature (40-110)K. Data only. $\Lambda=3.52\text{\AA}$.

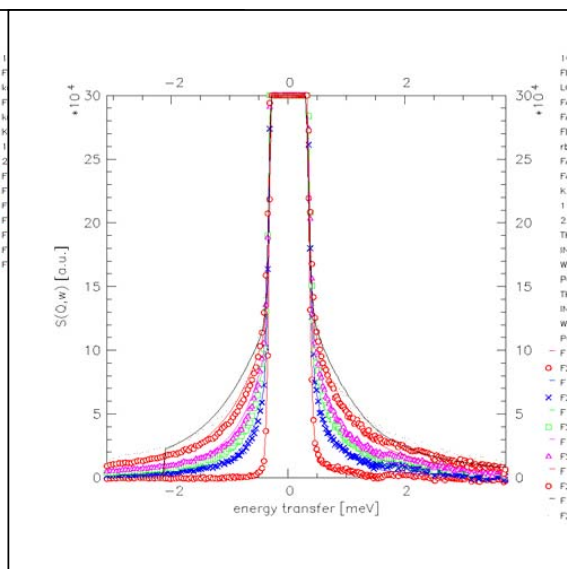


Fig. 2: Spectra of $Rb_{0.9}(NH_4)_{0.1}SCN$ summed over all Angles. Sample temperature (2.4-130)K. Symbols: data, lines: fit. $\Lambda=3.52\text{\AA}$.

Fig. 2 shows the similar measurement for the Rb analogous compound of the same ammonium concentration. Again a quasielastic component is visible which is clearly broader as due to weaker rotational potentials. A fit with a single Lorentzian (solid lines of fig. 2) is feasible with reasonable quality. This could mean that only a single time constant exists or, equivalently, that the potential distribution function is very narrow. However, the line intensity depends on temperature. We may attribute this to a much broader distribution of rotational barrier heights where the higher barriers enter the energy window of the spectrometer with increasing temperature. The data analysis is in progress.

References:

1. H.P.Klug, Z.Kristallogr., 85 (1933) 214.
2. Y.Yamada and T.Watanabe, Bull.Chem.Soc.Jpn., 36 (1963) 1032.
3. W.Klement, Jr. and C.W.F.T.Pistorius, Bull. Chem. Soc. Jpn., 49 (1976) 2148.
4. A.Hamada, S.Yamamoto and Y.Shinnaka, J.Phys.Soc.Jpn., 59 (1990) 954.
5. V.E.Zavodnik, Z.V.Zvonkova, G.S.Zhdanov, E.G.Mirevich, Sov.Phys.-Crystallogr. 17 (1972) 85.
6. I.Natkaniec, L.S.Smirnov, A.I.Solov'ev, Physica B213&214 (1995) 667-668.
7. J. Colmenero, R. Mukhopadhyay, A. Alegria, B. Frick, Phys. Rev. Lett. 80,2350(1998)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	S29-05-017		
Experiment title:	Studies on the Crystal field of TbMn ₂ O ₅		
Dates of experiment:	07.02. – 15.02.2006	Date of report:	01.06.2006
Experimental team: Names	Addresses		
Lieh-Jeng Chang	Nuclear Science and Technology Development Center National Tsing Hwa University 101, Sec. 2, Kuang-Fu Road HsinChu, 30013, Taiwan		
Local Contact:	Dr. Jörg Voigt		

Experimental report text body

Introduction

There is currently a great interest in the materials that exhibit interplay between lattice distortions and electrical and magnetic ordering. Among these materials, magnetoelectrics, in which magnetism and ferroelectricity coexist and are mutually coupled, are being investigated extensively. These materials display phenomena such as the control of electrical polarization by the application of an external magnetic field, providing an additional degree of freedom for the design of new devices.¹ However; compounds showing large magnetoelectric effects are extremely rare. The magnetoelectric TbMn₂O₅ exhibits a profound interplay between electrical polarization and the applied magnetic field. This is demonstrated by two discoveries: the highly reversible switching of electrical polarization using relatively low magnetic fields of 0-2T; and the combined application of electric and magnetic field, which leaves a permanent imprint in the polarization.²

TbMn₂O₅ is an insulator and consist of linked Mn⁴⁺O₆ octahedra and Mn³⁺O₅ pyramids adopting space group *Pbam*. The octahedral share edges to form ribbons parallel to the c axis, adjacent ribbons being linked by pairs of corner-sharing pyramids.¹ The structure at room temperature is orthorhombic. (Fig. 1)³ The reported neutron diffraction measurements on TbMn₂O₅ as a function of temperature and applied field which show unambiguous correlations between dielectric anomalies and changes in the periodicity of the spin structure. First, the onset of ferroelectricity at 38 K is associated with the appearance of incommensurate antiferromagnetic ordering T₁ = 43 K. At T₂ = 33 K, just above the maximum in spontaneous polarization **P**, propagation vector **k** locks into a commensurate value (1/2, 0, 1/4). Remarkably, at T₃ = 24 K, where the dielectric constant **ε** has an upward “jump”, **k** becomes suddenly incommensurate again, a rare example of such a transition on cooling. The low temperature transition (T₄ = 10 K) coincides with a major increase of the Tb ordered moment. The 43 and 24 K transitions are accompanied by clear anomalies in the lattice parameters, particularly along the *b* “polar” axis, and in the atomic displacement parameters.⁴

Experiments

8 grams of TbMn_2O_5 polycrystalline sample have been prepared through conventional solid-state reaction method and characterized by powder x-ray diffraction and magnetization. All the observable peaks on the powder x-ray pattern can be well indexed for showing the sample to be single phase. A broad peak has been observed on the magnetic susceptibility from 50 to 20 K corresponding to the series of transitions mentioned above. Experiments were performed at SV-29, thermal time-of-flight spectrometer, in an orange cryostat for temperature between 2.5 K and 60 K. Neutron wavelength of 1.17 Å and 1.76 Å, which correspond to graphite crystals PG002/PG004 monochromater, were selected for the time-of-flight experiments.

Results

Figure 1(A) shows the experimental results taken at different temperatures at $2\theta \sim 30^\circ$ by using wavelength 1.76 Å. The Vanadium and empty can had been used to calibrate and normalize each detector. The first peak at ~ 5 meV shifts to lower energy when the temperatures increase and finally merges to the broad central peak at 60 K. However, no clear shifting was observed for the peaks at ~ 13 , ~ 16 and ~ 18 meV. Fig. 1(B) shows the results of different Qs at 2.5 K. All of these four peaks intensity seems to follow the form factor effect to reduce their intensities at high Q. This shows these four peaks correspond to the magnetic moments. A further analysis on the intensity is necessary to prove this magnetic form factor effect. No obvious energy dispersion is observed in the experimental results.

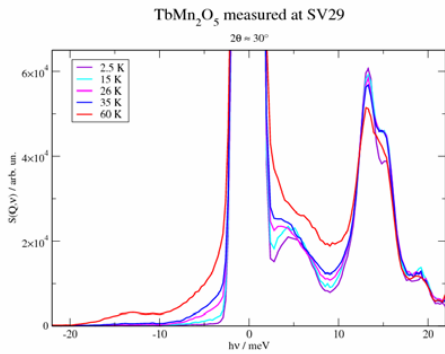


Fig. 1(A) Time-of-flight spectra taken at different temperatures at $2\theta \sim 30^\circ$ by using wavelength 1.76 Å. The Vanadium and empty can had been used to calibrate and normalize each detector.

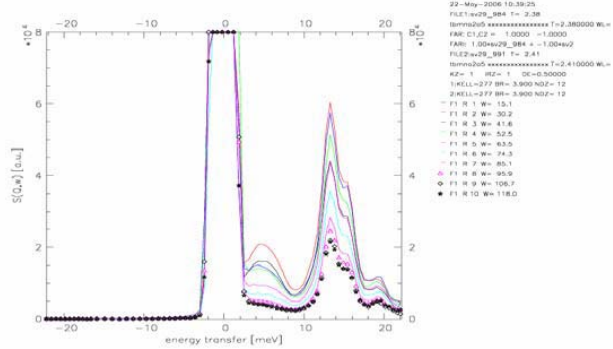


Fig. 1(B) Time-of-flight results of different Qs taken at 2.5 K. All of these four peaks intensity seems to follow the form factor effect to reduce their intensities at high Q.

References:

1. G.R. Blake, et al., Phys. Rev. B **71**, 214402 (1995).
2. N. Hur, et al., Nature (London) **429**, 392 (2004).
3. D. Higashiyama and S. Miyasaka, Phys. Rev. B **72**, 064421 (2005).
4. L.C. Chapon et al., Phys. Rev. Lett **93**, 177402 (2004).



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-05-018		
Experiment title:	Methyl group dynamics in methyl bromide clathrate		
Dates of experiment:	12 days between 26.01. – 15.04.2006	Date of report:	20.05.2006
Experimental team: Names	Addresses		
M. Prager	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Clathrates are characterized by a stable framework of host molecules which form cages which allow to incorporate simple guest molecules. The guest molecules experience a matrix effect in **almost identical environments** and thus show in general well defined spectral lines. Cages of water clathrates are distinguished from many other clathrates by the disorder of hydrogen bonds. This makes on the one hand the data analysis more complex but on the other side more interesting since water cages especially with organic guest molecules may represent model systems of H-bonded hydration shells in biology.

We have recently studied water clathrates with methyl iodide [1] and methyl fluoride [2] guest molecules. While CH₃I was found to mirror the potential surface of the water cages in great detail, disorder and eventually the tendency to form hydrogen bonds mixes such details in case of CH₃F and allows to deduce average potentials and their distribution only.

It can be expected that the other two methyl halide guest molecules with properties in between those of CH₃I and CH₃F may image other details of the clathrate cages. The actual experiment uses methyl bromide as guest molecules. A sample was prepared on site the same way as methyl iodide clathrate by stirring a 1:5.75 molar mixture of CH₃Br and D₂O or H₂O around the final freezing point $T_m \sim 9^\circ\text{C}$. According to literature and our own structure determination [3,4,5] methyl bromide clathrate crystallizes in the cubic I phase.

Fig 1 shows the spectra in the regime of phonons. As in the other clathrates the shoulder at energy transfer $\sim 11\text{meV}$ is taken as a sign of clathrate formation. The raw data of the high resolution measurement (fig. 2) reveals unresolved intensity from almost free rotor transitions at $T_s = 3\text{K}$ and a high rotational mobility of the guest molecules by a quasielastic component. Improved data will be measured at a much better suited cold time-of-flight spectrometer. The isotope effect (figs 3) shows that the strongest vibrational band which shifts by about 1meV to lower energy in the deuterated matrix is likely a host mode. As expected there is almost no change of the methyl rotational dynamics leading to similar high resolution spectra. The data analysis is under work.

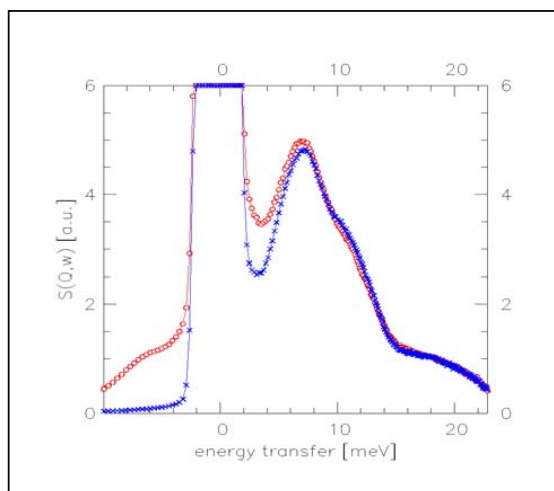


Fig. 1 Spectra of $\text{CH}_3\text{Br} \cdot 5.75\text{H}_2\text{O}$. $\lambda = 1.71 \text{ \AA}$.
Sample temperatures $T_s = 3\text{K}$ (xxx) and 50K (ooo).

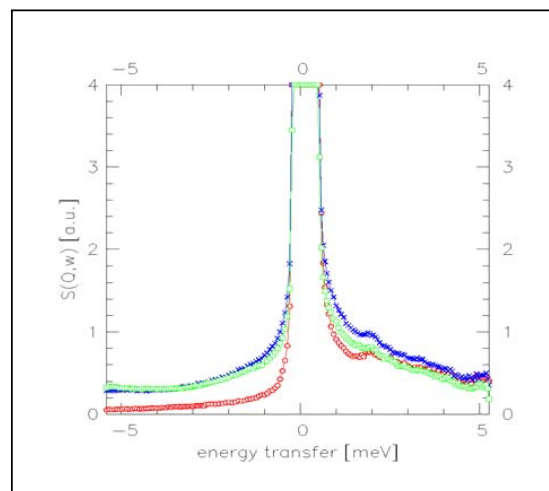


Fig. 2 Spectra of $\text{CH}_3\text{Br} \cdot 5.75\text{H}_2\text{O}$. $\lambda = 3.52 \text{ \AA}$.
 $T_s = 3\text{K}$ (ooo), 60K (xxx) and 80K (□□□□).

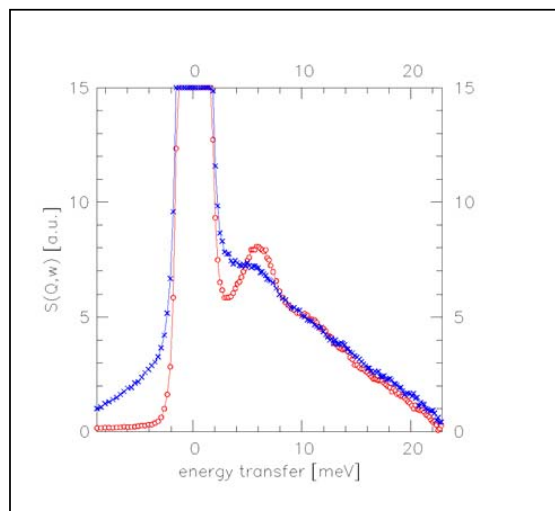


Fig. 3 Spectra of $\text{CH}_3\text{Br} \cdot 5.75\text{D}_2\text{O}$. $\lambda = 1.71 \text{ \AA}$.
Sample temperatures $T_s = 3\text{K}$ (ooo) and 50K (xxx).

- [1] M. Prager, A. Desmedt, A. Buchsteiner, J. Pieper, J. Phys., Condens. Matter 16,7045(2004)
- [2] M. Prager, J. Baumert, W. Press, M. Plazanet, J. Tse, D.D. Klug, PCCP 7,1228(2005)
- [3] A. Jeffryes, in 'Inclusion compounds', Vol. 1, p. 1 of 'Inorganic and physical aspects of inclusion', J.L. Atwood et al eds., Oxford University Press, Oxford 1991
- [4] J.A. Ripmeester, C.I. Ratcliffe, in 'Inclusion compounds', Vol. 4, p. 37 of 'Inorganic and physical aspects of inclusion', J.L. Atwood et al eds., Oxford University Press, Oxford 1991
- [5] This volume, report SV7-05-016



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-06-001		
Experiment title:	Methyl group dynamics in methyl chloride clathrate		
Dates of experiment:	12 days between 26.01. – 15.04.2004	Date of report:	20.05.2006
Experimental team: Names	Addresses		
M. Prager	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Clathrates are characterized by a stable framework of host molecules which form cages which allow to incorporate simple guest molecules. The guest molecules experience a matrix effect in **almost identical environments** and thus show in general well defined spectral lines. Cages of water clathrates are distinguished from many other clathrates by the disorder of hydrogen bonds. This makes on the one hand the data analysis more complex but on the other side more interesting since water cages especially with organic guest molecules may represent model systems of H-bonded hydration shells in biology.

We studied so far water clathrates with methyl iodide [1] and methyl fluoride [2] guest molecules. CH_3I was found to mirror the potential surface of the water cages in great detail. In case of CH_3F a strong tendency to form H-bonds allows leads to a strong averaging of potentials and allows only potential distributions to be obtained. It is expected that the other two methyl halide guest molecules with properties in between those of CH_3I and CH_3F may image other details of the clathrate cages. The actual experiment deals with methyl chloride guest molecules. A sample was prepared on site the same way as methyl iodide clathrate by stirring a 1:5.75 molar mixture of CH_3Cl and D_2O around the freezing point $T_m \sim 19^\circ\text{C}$. According to literature [3,4] methyl chloride clathrate crystallizes in the cubic I phase. Our own structure determination shows, however, that the unit cell is smaller and possibly hexagonal [5]. This has to be confirmed.

Fig 1 shows the inelastic neutron scattering spectra in the regime of phonons. Here the shoulder at energy transfer $\sim 1 \text{ meV}$ is usually taken as a sign of clathrate formation. A high resolution measurement (fig. 2, xxx) reveals the high rotational mobility of the guest molecules by a broad quasielastic component. Rotation is much faster than for $\text{CH}_3\text{Br} \cdot 5.75\text{H}_2\text{O}$ [6]. The inelastic band 2.6 meV observed at $T_S = 3 \text{ K}$ must be attributed to an almost free rotor transition of methyl groups of CH_3Br . Consistent with this assignment there is no isotope effect of this mode with deuteration of the cage. In contrary the strongest vibrational band shifts by about 1 meV to lower energy with deuteration of the host matrix and is likely a mode of the ice cage. The data analysis is under work. Further experiment are under way.

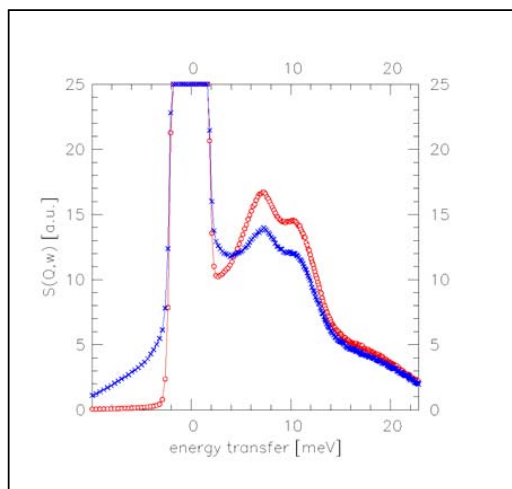


Fig. 1 Spectra of $\text{CH}_3\text{Cl} \cdot 5.75\text{H}_2\text{O}$. $\lambda=1.71\text{\AA}$.
Sample temperatures $T_S=3\text{K}$ (ooo) and 50K (xxx).

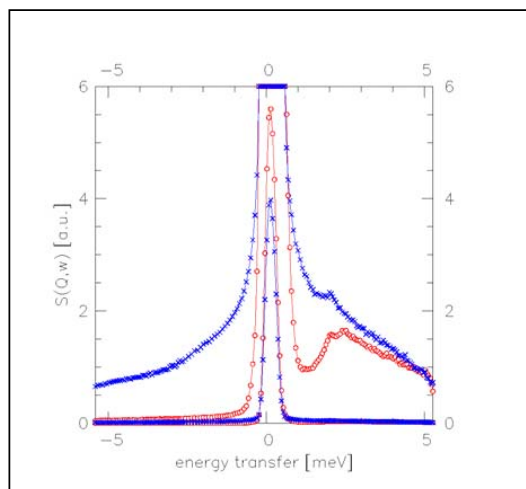


Fig. 2 Spectra of $\text{CH}_3\text{Cl} \cdot 5.75\text{H}_2\text{O}$. $\lambda=3.52\text{\AA}$.
 $T_S=3\text{K}$ (ooo), 60K (xxx).

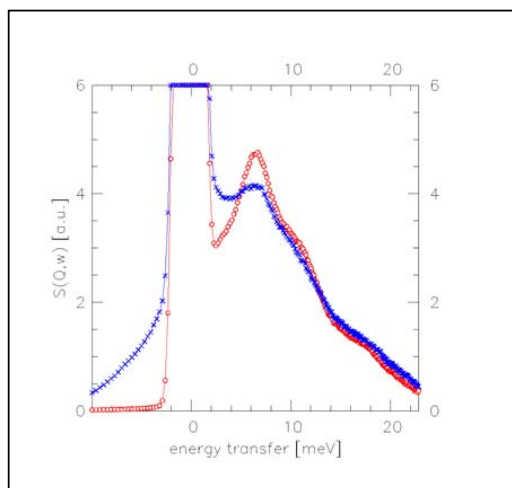


Fig. 3 Spectra of $\text{CH}_3\text{BrCl} \cdot 5.75\text{D}_2\text{O}$. $\lambda=1.71\text{\AA}$.
Sample temperatures $T_S=3\text{K}$ (ooo) and 50K (xxx).

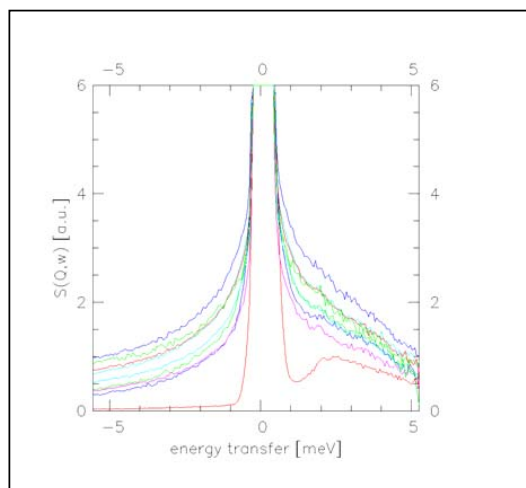


Fig. 4 Spectra of $\text{CH}_3\text{Cl} \cdot 5.75\text{H}_2\text{O}$. $\lambda=3.52\text{\AA}$.
 $T_S=3\text{K}$ and 40K to 120K , most steps 10K .

- [1] M. Prager, A. Desmedt, A. Buchsteiner, J. Pieper, J. Phys.: Condens. Matter 16,7045(2004)
- [2] M. Prager, J. Baumert, W. Press, M. Plazanet, J. Tse, D.D. Klug, PCCP 7,1228(2005)
- [3] A. Jeffryes, in 'Inclusion compounds', Vol. 1, p. 1 of 'Inorganic and physical aspects of inclusion', J.L. Atwood et al eds., Oxford University Press, Oxford 1991
- [4] J.A. Ripmeester, C.I. Ratcliffe, in 'Inclusion compounds', Vol. 4, p. 37 of 'Inorganic and physical aspects of inclusion', J.L. Atwood et al eds., Oxford University Press, Oxford 1991
- [5] This volume, report SV7-06-005
- [6] This volume, report S29-05-018



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	S29-06-002		
Experiment title:	Phase transformations and excitations in collidin, 2,4,6-trimethyl-pyrazin		
Dates of experiment:	10.03. – 15.03.2006	Date of report:	20.05.2006
Experimental team: Names	Addresses		
I. Natkaniec M. Prager	Institut of Nuclear Physics, Krakow, Poland Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

Collidin, 2,4,6-trimethyl-pyridin, shows an unusual structural behaviour with temperature. At a first cooling from the liquid into the solid phase it becomes disordered and remains so down to the lowest temperatures. Only after annealing below the melting point for some time the system gets long range ordered. The crystal structure was determined by single crystal X-ray diffraction [1]. The crystal was grown from the liquid and thereafter cooled down to 180K. The monoclinic space groups $P2_1/c$ with two molecules in the asymmetric unit was found. One of the methyl groups was thought to be disordered.

We used thermal and high resolution neutron spectroscopy to study the dynamic counterpart of the structure. Fig. 1 shows spectra taken on the thermal TOF spectrometer SV29 at various states of the sample. Circles represent the quenched sample. The broad unstructured intensity distribution of the disordered crystal transforms after annealing into a spectrum with characteristic bands (squares). Their temperature evolution is shown at $T=60K$ (triangles) and $T=80K$ (crosses). The assignment of the bands requires a lattice dynamical calculation.

The high resolution spectra show an analogous behaviour (fig. 2). The circles represent again the quenched sample at a temperature $T=4K$. At this temperature quasielastic scattering has died out. The apparent Lorentzian intensity is attributed to rotational tunnelling of methyl groups. Disorder leads to a distribution of rotational potentials and therefore a distribution of tunnel transitions. A model to describe such spectra is available in the literature [2]. It looks that the intensity corresponds to more than 1/3 of the methyl groups found to be disordered in the crystal structure analysis. After annealing a part of the broad intensity distribution has transformed into a clear tunnelling transition (fig. 2, crosses) indicative of the new order. Its low intensity must be related with a symmetry reduction in the ordered phase. At higher temperature (fig. 2, 60K=triangles, 80K=squares) quasielastic scattering is broader than the resolution of the instrument (fig. 2, diamonds) but needs a more elaborate study.

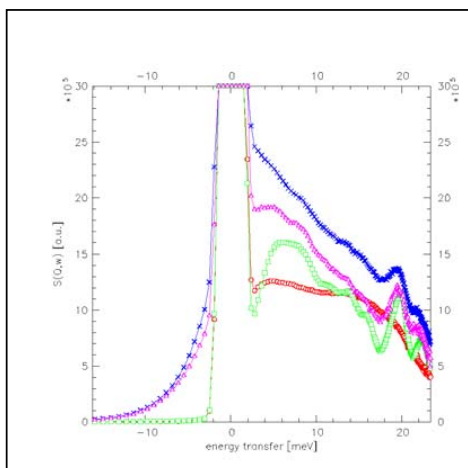


Fig. 1 Spectra of collidin. SV29: $\lambda=1.59\text{\AA}$
ooo: quenched, $T=3\text{K}$; square: annealed, $T=3\text{K}$;
triangle: annealed, 60K ; xxx: annealed, $T=80\text{K}$

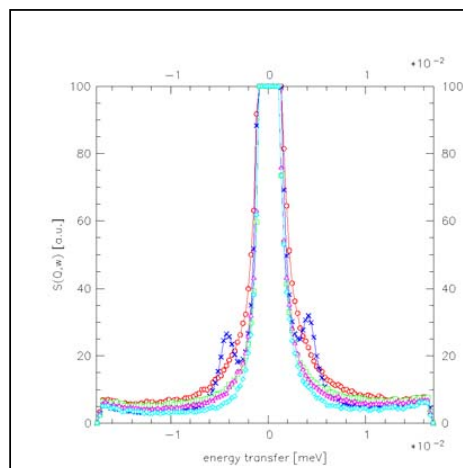


Fig. 1 Spectra of collidin. BSS: $\lambda=6.28\text{\AA}$
ooo: quenched, 4.5K ; xxx: annealed, 4.5K ;
triangle: annealed, 60K ; square: annealed, $T=80\text{K}$;
diamond: resolution

Collidin shows some similarities to other cyclic hydrocarbons. With toluene it shares the phase behaviour: disorder at direct cooling – crystallisation after annealing. The way of data analysis used in case of toluene [4] could be applied here too. There is also some analogy with mesitylene. Structurally the two compounds are closely related due to the symmetric arrangement of methyl groups, electrically collidin has a unique tendency of hydrogen bond formation [1]. Some metastable phases exist in both materials. Tunneling spectroscopy is especially suited to resolve the differences [4,5]. These analogies shall be exploited in the ongoing data analysis of collidin.

- [1] A.D. Bond, J.E. Davies, Acta Cryst. E57, o1141(2001)
- [2] J. Colmenero, R. Mukhopadhyay, A. Alegria, B. Frick, Phys. Rev. Lett. 80,2350(1998)
- [3] A. Moreno, J. Colmenero, A. Alegria, B.Frick, M. Prager, J. Chem. Phys. ,(2001) Toluene
- [4] I. Natkaniecz
- [5] M. Prager, I Natkaniecz, H. Grimm, J. Phys.: Condens. Matter ,(2005)Mesitylene