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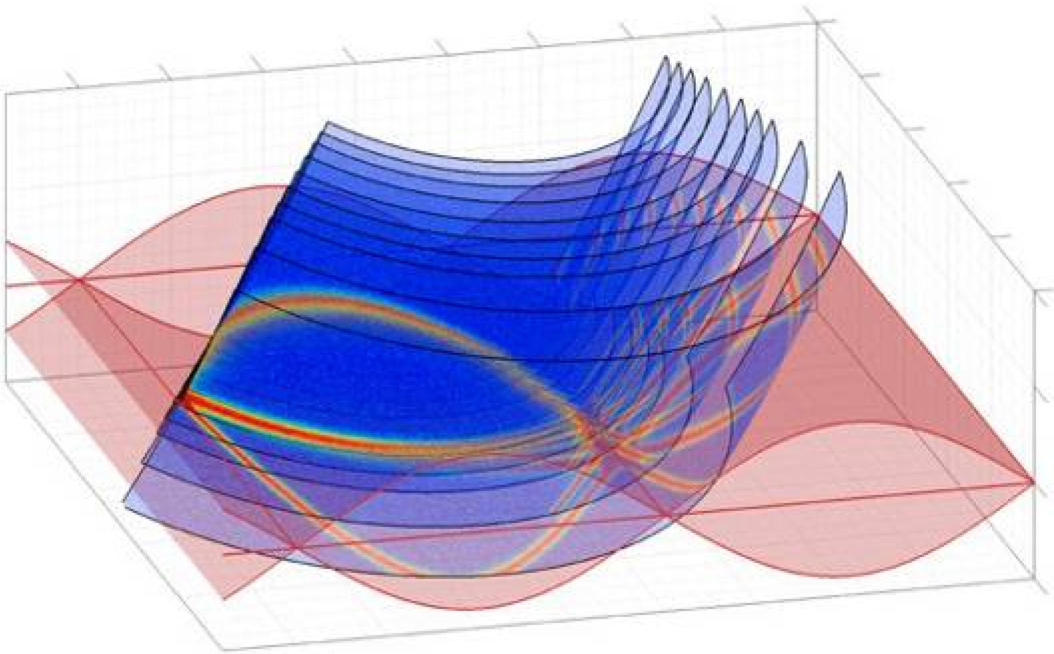

Schweizerische Gesellschaft für Neutronenstreuung
Société Suisse pour la Diffusion des Neutrons
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Neutron Scattering in Switzerland in the 20th Century

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1. Introduction

In two earlier issues of Swiss Neutron News we described the development of neutron diffractometers [1] and neutron spectrometers [2] at the Swiss neutron sources (light-water reactor Saphir 1957–1993, heavy-water reactor Diorit 1960–1977, spallation neutron source SINQ 1996–present) located at Würenlingen/Villigen from the early days up to the present. This information is complemented here by a summary of characteristic scientific and applied results which were obtained with use of the Swiss instruments for neutron scattering in the 20th century.

After the commissioning of the reactor Saphir in the year 1957, an organization called Delegation für Ausbildung und Hochschulforschung (Delegation AF) headed by Walter Hälg was installed at Würenlingen in order to educate students in the field of reactor technology as well as to initiate research with neutrons. Walter Hälg immediately recognized the potential of this new technique for materials research and started to build instruments for neutron scattering experiments. In the year 1972, the Delegation AF was transferred into the Institute for Reactor Technique (ETH Zurich) also headed by Walter Hälg. After his retirement in the year 1984, the neutron scattering activities were continued within the newly founded Laboratory for Neutron Scattering (ETH Zurich) headed by Albert Furrer, which became a joint venture with the Paul Scherrer Institute (PSI) at Villigen in the year 1992. In the nineties neutron scattering studies were also carried out by members of the Abteilung Spallationsneutronenquelle at PSI.

Nearly 1200 papers were published as a result of neutron scattering experiments performed at Würenlingen/Villigen in the 20th century. This was accomplished with a relatively small number of staff members listed in Table 1. The staff members made a special effort to attract young and talented students to start their scientific careers at Würenlingen/Villigen by performing neutron scattering studies in the framework of Ph.D. theses (see Table 2). In addition, many post-doctoral students and guest scientists contributed to the scientific output. From the very beginning in the sixties, a large number of neutron scattering studies were performed in cooperation with a broad national and international user community. In this respect, the user system was introduced at the Swiss neutron sources a long time before it was copied later by most of the neutron scattering centers around the world. The cooperations with Swiss scientists listed in Table 3 were essential to maintain a permanent home base for neutron scattering experiments in Switzerland. More specifically, the strong national user community was able to exert sufficiently strong pressure to change the plans for an early shutdown of the reactor Saphir, to establish the Swiss partnership with the Institut Laue-Langevin (ILL) at Grenoble in the year 1988 as well as to get the green light for the construction of the spallation neutron source SINQ.

In the following sections we try to focus on particular highlights resulting from neutron scattering experiments in the different decades of the 20th century. Our selection is somewhat subjective and by no means complete in terms of a professional review, but it should be regarded as being representative for the particular decade. Of course, given the names, affiliations, and thesis topics listed in Tables 1-3, more complete information can easily be obtained from the web of science.

[1] 50 years of Swiss neutron diffraction instrumentation
P. Fischer, J. Schefer, L. Keller, O. Zaharko, V. Pomjakushin, D. Sheptyakov, N. Aliouane, M. Frontzek, S. L. Holm, K. Lefmann, and M. Christensen, Swiss Neutron News No. 42, August 2013 (http://sgn.web.psi.ch/sgn/snn/snn_42.pdf)

[2] On the history of neutron spectrometers in Switzerland
A. Furrer, Swiss Neutron News No. 43, March 2014 (http://sgn.web.psi.ch/sgn/snn/snn_43.pdf)

Table 1
Staff positions (>3 years) of scientists involved in neutron scattering at Würenlingen/Villigen in the 20th century.

Name	Period	Name	Period
Hälg Walter	1953 - 1984	Zolliker Markus	1991 - 2004
Schneider Toni	1964 - 1969	Medarde Marisa	1992 - present
Truninger Edwin	1964 - 1967	Mesot Joël	1992 - 2008
Fischer Peter	1966 - 2002	Allenspach Peter	1993 - 2004
Bührer Willi	1969 - 1997	Clemens Daniel	1994 - 2002
Furrer Albert	1970 - 2004	Janssen Stefan	1995 - 2004
Benes Josef	1970 - 1982	Keller Lukas	1996 - present
Millhouse Arthur	1971 - 1975	Kohlbrecher Joachim	1996 - present
Tichy Karel	1972 - 1984	Stuhr Uwe	1996 - present
Anderson Ian	1986 - 1991	Roessli Bertrand	1997 - present
Schefer Jürg	1987 - present	Altorfer Felix	1998 - 2002
Böni Peter	1988 - 2000	Zaharko Oksana	1998 - present
Wagner Werner	1990 - 2014	Pomjakushin Vladimir	1999 - present

Table 2
Ph.D. theses in neutron scattering carried out at Würenlingen/Villigen in the 20th century.

Name	Period	Topic
Fischer Peter	1961–1966	Neutron diffraction studies of $MgAl_2O_4$ and $ZnAl_2O_4$
Stoll Erich	1963–1968	Lattice dynamics and electronic properties of Mg
Bührer Willi	1964–1969	Lattice dynamics of copper
Furrer Albert	1965–1970	Lattice dynamics of lead at different temperatures
Waeber Waldemar	1966–1969	Lattice vibrations of gallium
Lutz Ulrich	1966–1970	Lattice dynamics of anthracene
Von Wartburg Werner	1969–1973	Magnetic structure of $Ni_2B_7O_{13}I$
Heer Heinz	1970–1978	Neutron spectroscopic studies of the Ce monopnictides
Meier Guido	1972–1977	Magnetic ordering in the Ce monopnictides
Tellenbach Ulrich	1974–1977	Spin waves in $CsNiCl_3$ and $CsCoCl_3$

Name	Period	Topic
Schefer Jürg	1979–1983	Structural studies of metal hydrides
Hälg Beat	1980–1984	Spin dynamics of Ce and U monopnictides
Falk Urs	1981-1984	Magnetic exchange interactions in $CsMn_xMg_{1-x}Br_3$
Stöckli Armin	1983–1987	Dynamics of hydrogen bonds in carboxylic acids
Schmid Beat	1984–1988	Neutron studies of Pr and U trihalogenides and Tb_2Cl_3
Dönni Andreas	1987-1991	Neutron studies of CeX (X=S,Se) and YbX (X=N,P,As,Sb)
Elsenhans Olivier	1987-1991	Crystal-field interaction in RPd_3 (R=Dy,Er,Tm,Yb)
Zolliker Markus	1987-1991	Neutron studies of the shape-memory compounds CuZnAl
Allenspach Peter	1988–1991	Neutron spectroscopic studies of high-T_c superconductors
Rüdlinger Martin	1988–1992	Light induced structural changes in Na nitrosylprussiate
Mesot Joël	1989–1992	Crystal-field interaction in Er based high-T_c compounds
Staub Urs	1989–1993	Crystal-field and exchange effects in high-T_c compounds
Altorfer Felix	1990–1994	Neutron studies of ionic conductors
Guillaume Michel	1991-1994	Neutron studies of high-T_c superconductors
Keller Lukas	1991-1994	Neutron studies of lanthanide and actinide compounds
Roessli Bertrand	1991-1994	Neutron studies of $HoBa_2Cu_4O_8$, Bi_2CuO_4, and $CeGeO_3$
Fauth François	1992–1996	Neutron studies of oriented $HoBa_2Cu_3O_x$ and $ErBa_2Cu_3O_7$
Marti Willi	1992–1995	Neutron studies of $RGaO_3$ (R=La,Pr,Nd) and $NdBa_2Cu_3O_7$
Rosenkranz Stefan	1992–1996	Neutron studies of $RNiO_3$ (R=rare earth)
Henggeler Wolfgang	1993–1996	Neutron studies of magnetic correlations in cuprates
Böttger Grit	1994-1998	Neutron studies of rare-earth based high-T_c compounds
Löffler Jörg	1994–1997	Properties of nanostructured Fe, Co and Ni
Gasser Urs	1995–1999	Magnetic properties of RNi_2B_2C (R=rare earth)
Gutmann Matthias	1995–1999	Local inhomogeneities of high-T_c superconductors
Tixier Sebastien	1997–2000	Structural characterization of metallic multilayers
Semadeni Fabrizio	1997–2000	Spin fluctuations in magnetically ordered systems
Cavadini Nordal	1998–2001	Magnetic correlations in quantum spin systems
Herrmannsdörfer Thilo	1998–2002	Neutron studies of strongly correlated electron systems
Rubio Daniel	1998–2002	Pseudogap and isotope effects in high-T_c compounds
Böhm Martin	1999–2002	Magnetic neutron scattering studies of CuB_2O_4
Schaniel Dominik	1999–2002	Structure of high knowledge content materials
Strässle Thierry	1999–2002	Cooling by the barocaloric effect in rare-earth compounds

Table 3
Cooperations in neutron scattering established with Swiss research institutions in the 20th century.

Organization	Institute	Professors and Senior Scientists
ABB Dättwil	Research Center	P. Brüesch, T. W. Duerig, R. S. Perkins
EPF Lausanne	Applied Physics	F. Lévy
EPF Lausanne	Micro- & Optoelectronics	H. J. Scheel
EPF Lausanne	Physics of Complex Matter	R. Gotthardt
ETH Zurich	Applied Physics	G. Kostorz, B. Schönfeld
ETH Zürich	Cell Biology	K. Mühlethaler
ETH Zurich	Crystallography	Ch. Baerlocher, K. Girgis, F. Laves, A. Niggli, P. Schobinger-Papamantellos, D. Schwarzenbach
ETH Zurich	Physical Chemistry	R. R. Ernst, B. H. Meier
ETH Zurich	Solid State Physics	H. Arend, G. Busch, F. Hulliger, E. Kaldis, W. Känzig, K. Mattenberger, J. Karpinski, H. R. Ott, L. Schlapbach, P. Wachter, O. Vogt
IBM Zurich	Research Center	B. Lüthi, K. A. Müller, A. Segmüller
Univ. Basel	Physics	H. J. Güntherodt, H. Rudin
Univ. Bern	Crystallography	H. B. Bürgi
Univ. Bern	Inorganic Chemistry	S. Decurtins, H. Gamsjäger, H. U. Güdel, K. W. Krämer, A. Ludi
Univ. Fribourg	Physics	L. Schlapbach, A. Züttel
Univ. Geneva	Applied Chemistry	F. Kubel, H. Schmid, P. Tissot
Univ. Geneva	Crystallography	R. Cerny, K. Yvon
Univ. Geneva	Physical Chemistry	H. Bill
Univ. Geneva	Solid State Physics	R. Flükiger, A. Junod, H. G. Purwins, E. Walker
Univ. Lausanne	Crystallography	D. Schwarzenbach
Univ. Zurich	Inorganic Chemistry	J. H. Ammeter
Univ. Zurich	Physics	K. A. Müller, F. Waldner

2. Neutron scattering in the sixties

A prototype two-axis neutron diffractometer was ready for experiments in the year 1960. Fig. 1 is a historical document, displaying the very first measurement on a lead crystal performed by Walter Hälg. At that time the experimental results had to be plotted manually, and calculations had to be done by slide rules (pocket calculators and PC's did not exist). Since auxiliary equipments such as cryostats, furnaces and magnets were initially lacking, the diffraction experiments mainly concentrated on room-temperature investigations to distinguish neighboring elements or ions of the periodic table (e.g. Mg^{2+} and Al^{3+} with equal number of ten electrons) [3] as well as to locate light atoms (e.g. hydrogen) in the presence of heavy atoms [4], thereby demonstrating two outstanding properties of neutrons in contrast to x-rays. In order to demonstrate another important property of the neutron, namely its magnetic moment being an excellent probe to study magnetic phenomena, cooling devices were required. As a first step a liquid-nitrogen cryostat with styrofoam shielding was produced internally by the workshop group. Later a commercial liquid-helium cryostat was purchased, but its operation turned out to be rather expensive, since there was no He gas recovery system. Moreover, liquid helium had to be bought and imported from abroad, often with considerable losses during the transport. Nevertheless, clear evidence for magnetic phase transitions could be provided for several rare-earth compounds

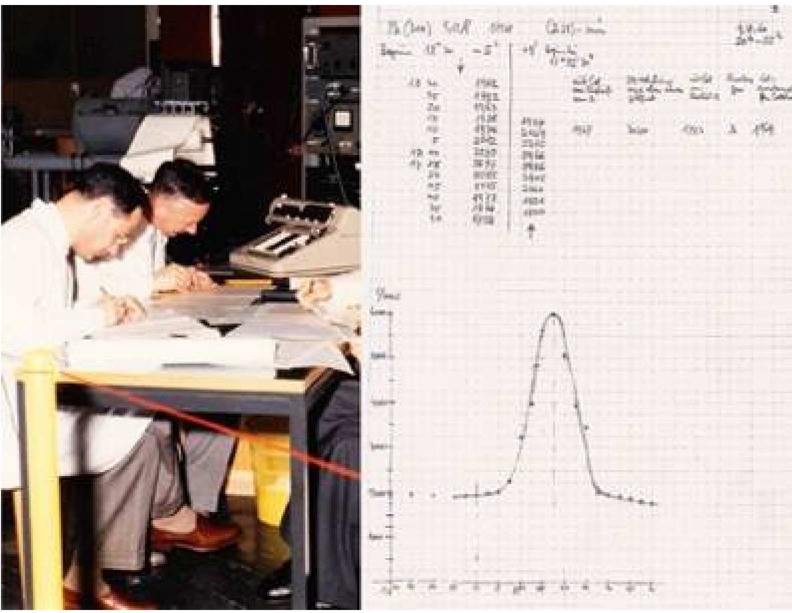


Figure 1
Walter Hälg (right) plots the data of the first neutron diffraction experiment performed for a single crystal of lead at the reactor Saphir (1 MW) in the year 1960 [1.5 Å neutron (200) intensity versus Bragg angle θ in the θ-2θ mode].

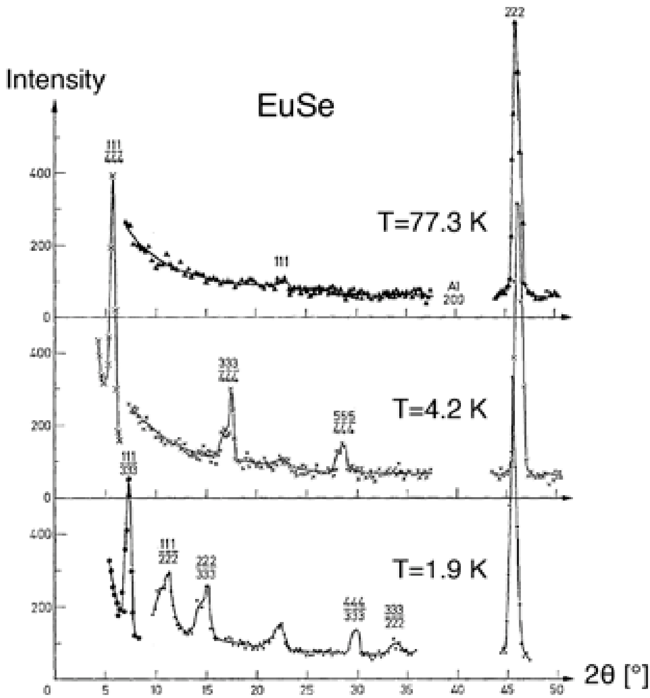
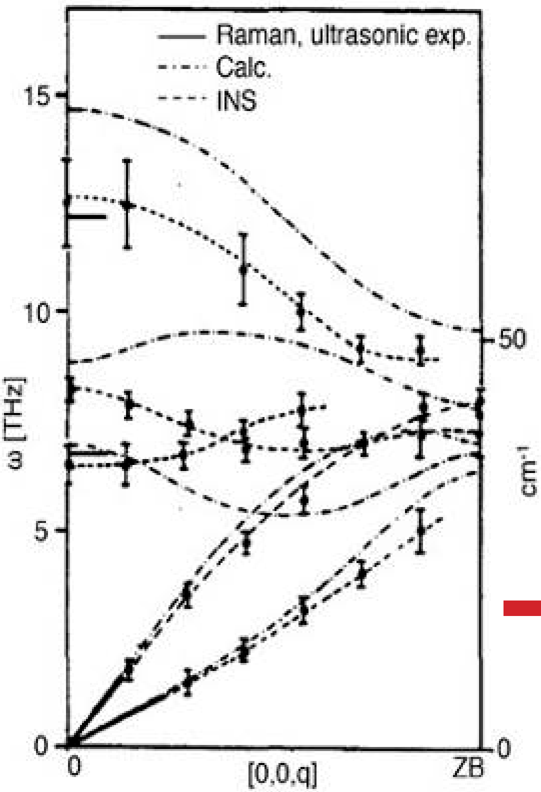


Figure 2

Neutron single crystal [1,1,1] scans of EuSe as a function of temperature (neutron wavelenth λ=1.39 Å). At T=77.3 K only nuclear Bragg peaks with indices (h,h,h) are observed. At T=4.2 K EuSe is antiferromagnetically ordered according to a (++−−)-configuration and propagation vector k=[1/4,1/4,1/4]. At T=1.9 K partial ferromagnetism (k=0) is observed in the intensity increase of the nuclear Bragg peak (1,1,1), whereas the antiferromagnetic moment components are associated with the k vectors [1/3,1/3,1/3] and [1/2,1/2,1/2] (after Ref. 5).

[5] as illustrated for a single crystal of EuSe (with neutron absorbing Eu) in Fig. 2.

Neutron spectroscopic experiments were initially carried out with use of a rotating-crystal time-of-flight spectrometer, later complemented by a triple-axis spectrometer. These instruments allowed to demonstrate another unique property of neutrons, namely to measure excitations at any wavevector in the Brillouin zone, in contrast to optical spectroscopies being confined to the zone center. The aim of the first experiment was to establish the phonon dispersion in a single crystal of copper [6]. In later experiments the phonon dispersion in single crystals of gallium and lead were studied, and finally the mapping of



the phonon dispersion curves in a single crystal of deuterated anthracene could be successfully accomplished as shown in Fig. 3 [7]. The latter study was a remarkable achievement, since at that time only little work on the phonon dispersion in organic molecular compounds was available.

Figure 3
Dispersion curves of deuterated anthracene. Comparison of calculated and measured data (after Ref. 7).

[3] Redetermination of the cation distribution of spinel ($MgAl_2O_4$) by means of neutron diffraction
E. Stoll, P. Fischer, W. Hälg, and G. Maier, J. de Physique 25, 447 (1964)
[4] Neutron diffraction study of $D_3Co(CN)_6$
H. U. Güdel, A. Ludi, P. Fischer, and W. Hälg, J. Chem. Phys. 53, 1917 (1970)
[5] Neutron diffraction evidence for magnetic phase transition in europium selenide
P. Fischer, W. Hälg, W. von Wartburg, P. Schwob, and O. Vogt, Phys. kondens. Materie 9, 249 (1969)
[6] Phonon dispersion in copper
W. Bührer, T. Schneider, and W. Gläser, Solid State Commun. 4, 443 (1966)
[7] Lattice dynamics of deuterated anthracene
U. Lutz and W. Hälg, Solid State Commun. 8, 165 (1970)

3. Neutron scattering in the seventies

In this decade, the instruments for neutron scattering (two diffractometers and two triple-axis spectrometers) were continuously upgraded, and the sample environment included state-of-the-art cryostats, furnaces, and magnets, allowing experiments at the forefront of science to meet the requirements of the steadily growing user community.

The neutron diffraction experiments largely concentrated on the characterization of magnetic ordering phenomena. Among the myriads of samples studied, we mention as an example the compound CeSb which exhibits a remarkably complex magnetic phase diagram with six partially disordered magnetic phases below T_N=16 K [8] as illustrated for the phases I and VI in Fig. 4. The magnetic moments are oriented along the directions <1,0,0>, although the crystal-field interaction favors <1,1,1> as easy directions. This is due to strongly anisotropic exchange interactions which were later established by neutron spectroscopy (see section 4 and Ref. 17).

Consecutively, neutron spectroscopic experiments were carried to determine the crystal-field interaction in these compounds, from which the magnetic properties could be quantitatively reproduced in the mean-field approx-

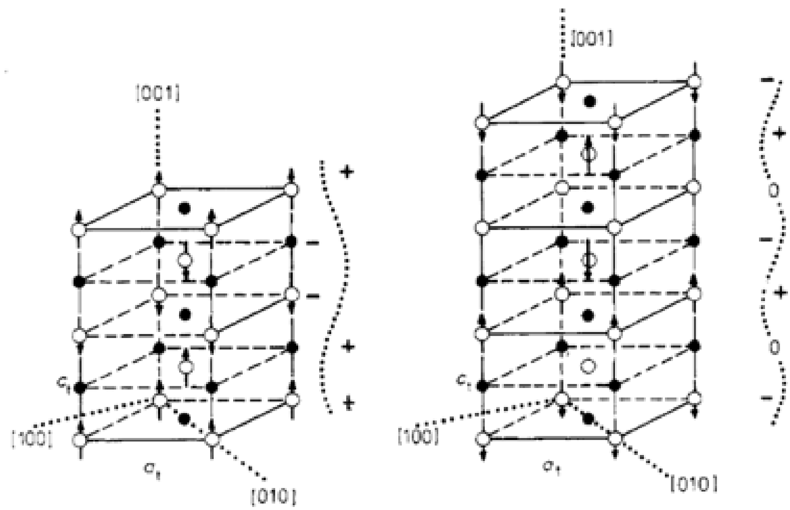


Figure 4
Basic modulated antiferromagnetic structures of CeSb corresponding to Z domains. Left: Phase VI (k = [0,0,1/2], T≤8.9 K). Right: Phase I (k = [0,0,2/3], T=16.0 K). The tetragonal magnetic unit cells are shown. Open and filled circles represent Ce and Sb atoms, respectively. Note the decreasing order from 100% to 67% in the magnetic planes with increasing temperature (after Ref. 8).

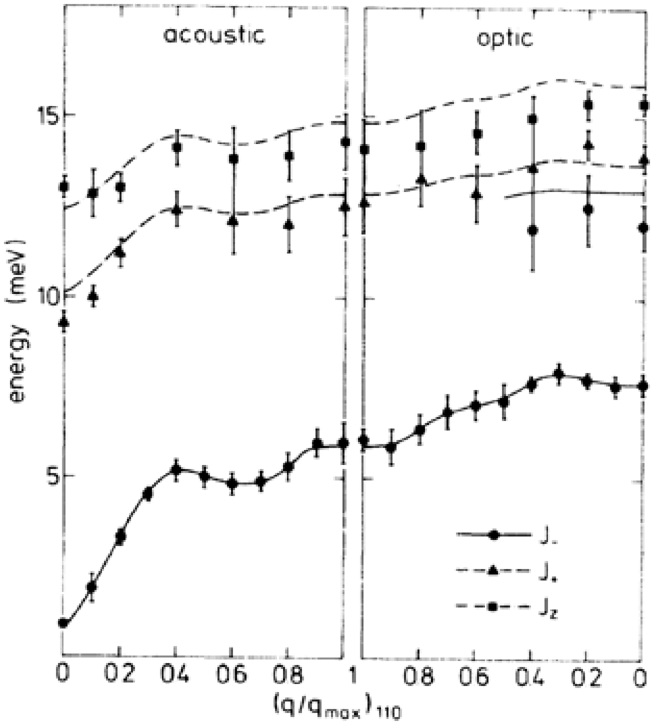


Figure 5
Dispersion of magnetic excitations of $NdAl_2$ at T= 4.2 K for wavevectors along the direction ⟨1,1,0⟩. The lines represent the best fit to a pseudoboson model that includes all ten levels of the Nd^{3+} ground–state multiplet (after Ref. 9).

imation. When single crystals were available, the dispersion of the magnetic excitations could be mapped, yielding additional information on the exchange interaction as exemplified for the compound $NdAl_2$ in Fig. 5 [9].

The Middle East conflict due to the Suez crisis resulted in a worldwide shortage of oil, so that large efforts were undertaken to search for alternative energies. Hydrogen was identified as such a substituent, and neutron scattering was the ideal tool to characterize the proposed hydrogen storage systems. Early neutron diffraction experiments were carried out for the most promising candidates $FeTiD_x$ and $LaNi_5D_x$ [10] to determine the deuterium positions as a function of deuterium pressure. This information turned out to be useful to reconstruct the diffusion paths of the D atoms.

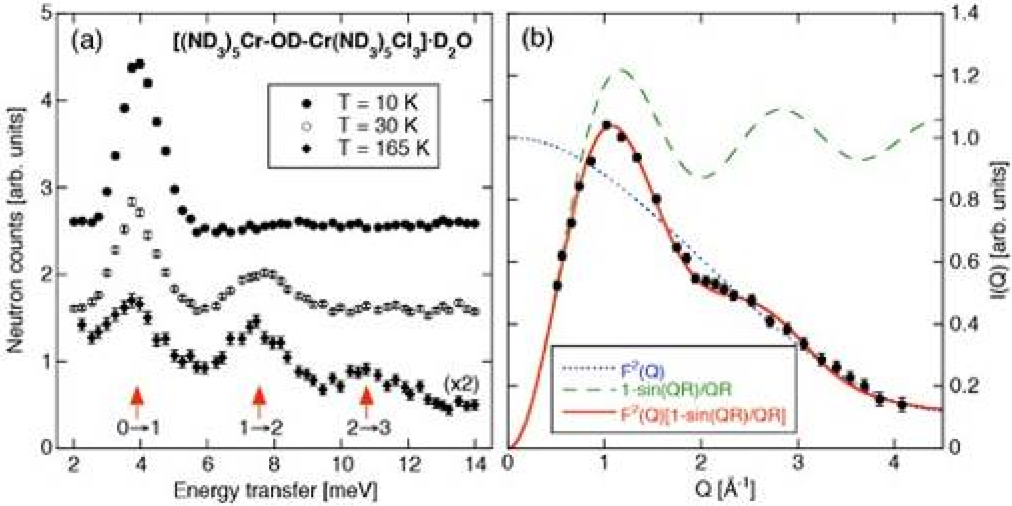


Figure 6

(a) Energy spectra of neutrons scattered from $[(ND_3)_5CrODCr(ND_3)_5]·D_2O$. (b) Q dependence of the intensity of the |0>→|1> transition at T=4.2 K, exhibiting a sinusoidal modulation characteristic of the scattering from magnetic clusters (after Ref. 12).

Other efforts towards technological applications were undertaken in the field of superionic conductivity. The phonon dispersion of several silver halides provided essential information on the conductive behavior [11]. In particular, a very–low-lying dispersionless transverse optic phonon mode as well as strong anharmonic effects were observed, which can be attributed to the movement of the Ag ions.

Neutron spectroscopic experiments were started to study the excitations associated with magnetic clusters embedded in molecular complexes, which was a great challenge due to the small number of atoms taking part of the magnetic scattering process. Nevertheless, the first inelastic neutron scattering experiment was successfully performed for deuterated $[(ND_3)_5CrODCr(ND_3)_5]·D_2O$ [12], in which the weight of the dimeric Cr clusters amounts to only 4 at%. As shown in Fig. 6, three well resolved transitions showed up in the experiments, so that the ground-state exchange splitting of the Cr dimer could be unambiguously determined. The scattering law for magnetic clusters developed in the course of this experiment laid the basis for the many neutron spectroscopic studies of molecular magnets which have been carried out up to the present.

[8] Magnetic phase transitions of CeSb. I. Zero applied magnetic field
P. Fischer, B. Lebech, G. Meier, B. D. Rainford, and O. Vogt, J. Phys. C 11, 345 (1978)
[9] Magnetic excitations in $NdAl_2$
A. Furrer and H. G. Purwins, Phys. Rev. B 16, 2131 (1977)
[10] Neutron scattering investigations of the $LaNi_5$ hydrogen storage system
P. Fischer, A. Furrer, G. Busch, and L. Schlapbach, Helv. Phys. Acta 50, 481 (1977)
[11] Lattice dynamics of silver iodide by neutron scattering
W. Bührer, R. M. Nicklow, and P. Brüesch, Phys. Rev. B 17, 3362 (1978)
[12] Interference effects in neutron scattering from magnetic clusters
A. Furrer and H. U. Güdel, Phys. Rev. Lett. 39, 657 (1977)

4. Neutron scattering in the eighties

The experimental work profitted from the availability of a dilution refrigerator to reach temperatures down to 7 mK as well as of new devices achieving uniaxial and hydrostatic pressures up to 10 GPa. On the instrumental side, the single detector of the powder diffractometer was replaced by a BF_3 based multidetector bank covering an angular range of 80°, and the insertion of a radial oscillating collimator was essential to remove disturbing Bragg peaks originating from the sample surroundings. The triple-axis spectrometers were equiped with large focusing monochromator and analyzer systems. All these measures resulted in intensity gain factors up to two orders of magnitude which permitted new types of experiments.

The research on many topics investigated in the seventies was continued. The structures of novel metal hydrides were determined as exemplified in Fig. 7 for Mg_2FeH_6 with a remarkably high hydrogen density [13]. The study of both magnetic ordering phenomena and magnetic excitation spectra was extended to include more complicated ternary materials. In particular, compounds of com-

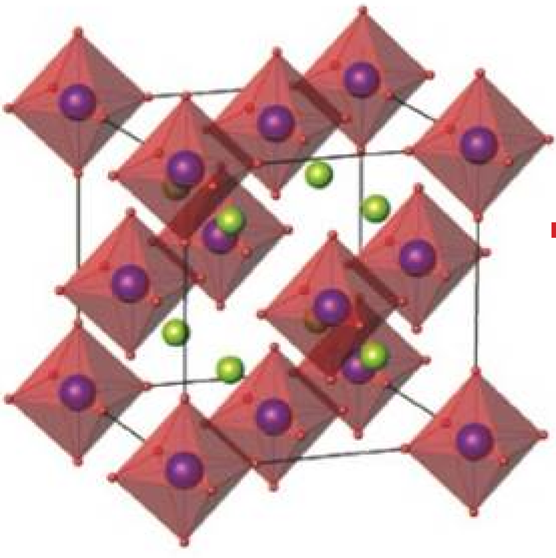


Figure 7
Unit cell of Mg_2FeD_6 with Mg^{2+} ions shown as green spheres and with the characteristic red D_6^- octahedra around central violet Fe^{2+} (after Ref. 13).

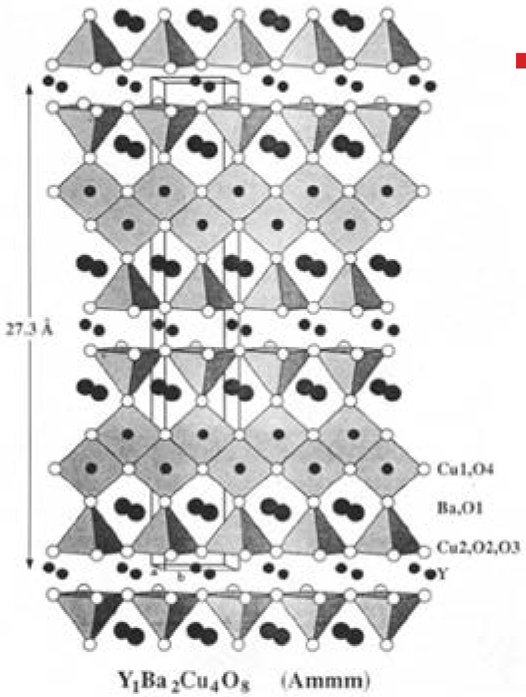


Figure 8
Crystal structure of the 80K superconductor $YBa_2Cu_4O_8$ characterized by double CuO chains (after Ref. 18).

position $Cs_3A_2X_9$ (A=transition metal or rare-earth ion, X=halogen ion) with antiferromagnetically coupled A dimers were intensively investigated due to their interest in fundamental and applied research as novel singlet-triplet systems and new candidates for highly efficient upconversion lasers, respectively. Neutron diffraction experiments gave evidence for spontaneous magnetic order induced by an intratriplet mode in $Cs_3Cr_2I_9$ [14]. On the neutron spectroscopic side, the improved instrumental conditions allowed to observe subtle details of the magnetic excitation spectra, allowing an analysis beyond the conventional Heisenberg model in terms of higher-order and anisotropic exchange interactions [15-17].

However, the highlight of the eighties was the discovery of high-temperature superconductivity in doped La_2CuO_4 by K. A. Müller and G. Bednorz. This set off enormous worldwide efforts to search for other superconducting oxides. Different copper-oxide superconductors of type R_2CuO_{4-x}, $RBa_2Cu_3O_{7-x}$, $RBa_2Cu_4O_{8+x}$, and $R_2Ba_4Cu_7O_{15}$ (R=yttrium or rare-earth) were investigated by neutron diffraction to understand the structural and magnetic properties as a function of doping and pressure. Fig. 8 illustrates the characteristic double CuO chains of $YBa_2Cu_4O_8$ with $T_c=80K$ [18]. It has been realized that the superconducting transition temperature is essentially unchanged upon replacing the Y and La ions by magnetic rare-earth ions, thus neutron spectroscopic experiments to determine the magnetic ground state through the crystal-field interaction turned out to be most useful. However, an unambiguous parametrization of the crystal-field interaction (nine independent parameters are required for orthorhombic symmetry) was not a trivial task, but could successfully be achieved for the first time for the compound $HoBa_2Cu_3O_{7-x}$ [19].

The structure and the dynamics of protons in hydrogen bridges was studied in a series

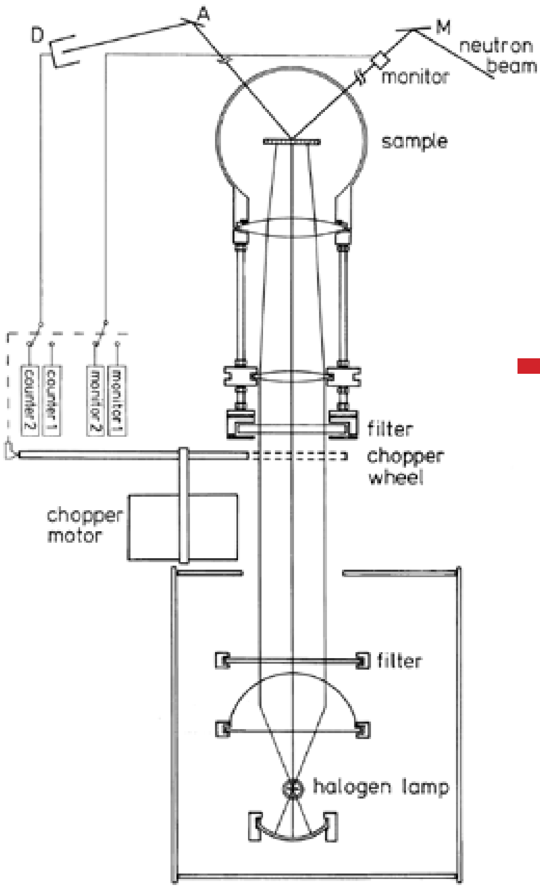


Figure 9
Conceptual design of the instrumental device developed for simultaneous light irradiation and neutron scattering at low temperatures. The light beam is periodically interrupted by a rotating chopper wheel with regularly arranged openings. The neutron count rates are separately stored for the "light" and "dark" experiments by the counters 1 and 2, respectively. The pulsed beam technique is essential to avoid sample heating upon illumination by light (after Ref. 21).

of dimeric carboxylic acids which are frequently used in the production of polymers, pharmaceuticals, solvents, and food additives. It has been suggested that the double proton exchange occurs through a torsional motion of the entire COOH group, but the results obtained by quasielastic neutron scattering unambiguously rejected this view in favor of a translational motion [20].

Inelastic neutron scattering experiments were started to investigate photoeffects on the dynamical properties of chlorophyll molecules embedded in membranes. A special device was developed to allow the simultaneous irradiation of the sample by neutrons and light at low temperatures as shown in Fig. 9 [21]. The illumination by light results in a partial freezing of rotational modes which may be attributed to a possible coupling with particular mechanisms of the photosynthetic process.

The compound NiTi exhibits a thermoelastic martensitic phase transformation at T_m=278 K. After a special thermomechanical

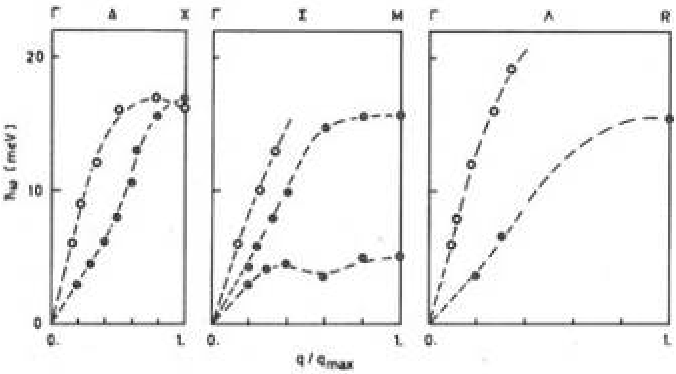


Figure 10
Phonon dispersion curves observed for the shape-memory compound NiTi at T=293 K (after Ref. 22).

treatment the transition is associated with a reversible shape change when the temperature is cycled around T_m. The shape-memory mechanism is reflected in unusual features of the phonon dispersion curves as shown in Fig. 10 [22]. More specifically, the transverse acoustic phonon modes exhibit a convex behavior and a dip along the ⟨1,1,0⟩ direction which are considered as precursor effects of the martensitic phase transition.

[13] Crystal and magnetic structures of ternary metal hydrides: A comprehensive review
K. Yvon and P. Fischer, Hydrogen in intermetallic compounds I, Topics in Applied Physics 63 (Ed. L. Schlapbach, Springer-Verlag, Berlin 1988) p. 87

[14] Spontaneous magnetic order induced by an intratriplet mode in the dimerized singlet-ground-state system $Cs_3Cr_2I_9$, B. Leuenberger, H. U. Güdel, and P. Fischer, Phys. Rev. Lett. 55, 2983 (1985)

[15] Three-spin interaction in $CsMn_{0.28}Mg_{0.72}Br_3$
U. Falk, A. Furrer, H. U. Güdel, and J. K. Kjems, Phys. Rev. Lett. 56, 1956 (1986)

[16] Neutron spectroscopic study of anisotropic exchange in the dimer compound $Cs_3Ho_2Br_9$
A. Furrer, H. U. Güdel, E. R. Krausz, and H. Blank, Phys. Rev. Lett. 64, 68 (1990)

[17] Anisotropic exchange and spin dynamics in the type-I (-IA) antiferromagnets CeAs, CeSb, and USb: A neutron study
B. Hälg and A. Furrer, Phys. Rev. B 34, 6258 (1986)

[18] Low-temperature anomalies and pressure effects of the structure and T_c of the superconductor $YBa_2Cu_4O_8$ (T_c=80 K), E. Kaldis, P. Fischer, A. W. Hewat, E. A. Hewat, J. Karpinski, and S. Rusiecki, Physica C 159, 668 (1989)

[19] Neutron spectroscopic determination of the crystalline electric field in $HoBa_2Cu_3O_{7-x}$
A. Furrer, P. Brüesch, and P. Unternährer, Phys. Rev. B 38, 4616 (1988)

[20] The mechanism of proton dynamics in solid carboxylic acids
B. H. Meier, R. Meyer, R. R. Ernst, A. Stöckli, A. Furrer, W. Hälg, and I. Anderson, Chem. Phys. Lett. 108, 522 (1984)

[21] Light irradiation of matter in neutron scattering experiments
A. Stöckli and A. Furrer, Rev. Phys. Appl. 19, 751 (1984)

[22] Lattice instability in the intermetallic compound NiTi
O. Mercier, P. Brüesch, and W. Bührer, Helv. Phys. Acta 53, 243 (1980)

5. Neutron scattering in the nineties

At the end of 1993 the reactor Saphir was finally shut down, but the regular operation of the spallation neutron source SINQ started only in mid-1998. In order to avoid the threatening neutron gap, a Swiss neutron base was established at the ILL Grenoble from 1995–1998 in the framework of a "collaborating research group", giving exclusive access to the three-axis spectrometer IN3 (100%) and the powder diffractometer D1A (50%). The imposed limited access to Swiss instruments in the mid-nineties allowed the staff members (see Fig. 11) to engage themselves in the organization of the first European Conference on Neutron Scattering in Interlaken (ECNS 1996), which featured a record attendance of more than 700 participants.

Many fascinating results were obtained by both neutron diffraction and neutron spectroscopic experiments on multiferroic systems (e.g. $KNiPO_4$), heavy-fermion superconductors (such as the highly cited compound UM_2Al_3 with M=Pd,Ni [23]), Kondo compounds (e.g. $YbCu_4M$ with M=Au,Pd), and "free-electron"

Figure 11
The organizing committee of the 1st European Conference of Neutron Scattering (ECNS 1996) in Interlaken. Front row (from left to right): J. Duppich, secretary, A. Furrer, secretary, W. Fischer. Back row: J. Mesot, J. Schefer, P. Fischer, H. Heer, P. Allenspach, W. Bührer, P. Böni, W. Wagner, G. Bauer.

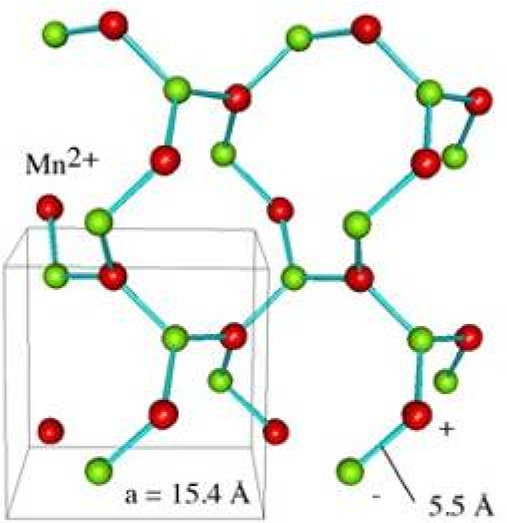


Figure 12
Antiferromagnetic Mn^{2+} ordering (shown by red and green spheres indicating antiparallel moment orientation) in supramolecular $Mn_2FeC_{36}D_{24}N_6O_{12}$ below T_N=13 K. μ_{Mn}=4.6(1) μ_B at T=1.8 K (after Ref. 24).

rare-earth halides (e.g. R_2X_5 with R=Ce,Pr and X=Br,I). Outstanding concerning novelty was the study of three-dimensional chiral, oxalate-bridged supramolecules containing magnetic ions such as Fe^{2+} and Mn^{2+}. This is exemplified in Fig. 12 for $Mn_2FeC_{36}D_{24}N_6O_{12}$ in which three-dimensional antiferromagnetic Mn^{2+} ordering was found below T_N=13 K, whereas iron does not order magnetically [24].

The research on high-temperature superconductors was continued. A systematic neutron diffraction study of the compounds $RBa_2Cu_3O_x$ (R=yttrium and rare earths, x=6 and 7) nicely showed how the apex oxygen position monitors changes of the charge distribution in the copper-oxide planes [25]. Efforts were undertaken to study the coexistence of superconductivity and magnetic ordering in the mK range due to the rare-earth ions [26] as shown in Fig. 13 for both the two-dimensional Dy ordering in $DyBa_2Cu_4O_8$ and the three-dimensional Er ordering in $Er_2Ba_4Cu_7O_{14.9}$. Neutron spectroscopic studies of the crystal-field spectra gave evidence for a superposition of local regions of semiconducting and metallic character [27], thereby confirming the percolative nature of high-temperature superconductivity. In addition, by studying the relaxation rate of crystal-field excitations large oxygen and copper isotope effects on the pseudogap were observed as shown in Fig. 14 [28], giving support for the importance of electron-phonon induced effects in any model for high-temperature superconductivity. The International Science Index (ISI) identified Ref. 28 for the whole field of physics as a so-called Fast Breaking Paper which corresponds to the top 1% of highly cited papers having the largest bimonthly increase of citations in 22 broad fields of science.

As a consequence of the hype with high-temperature superconductors, the neutron scattering studies of the cuprates were extended to other perovskites such as rare-earth based manganates, nickelates, and gallates, which exhibit interesting physical properties as a function of temperature, pres-

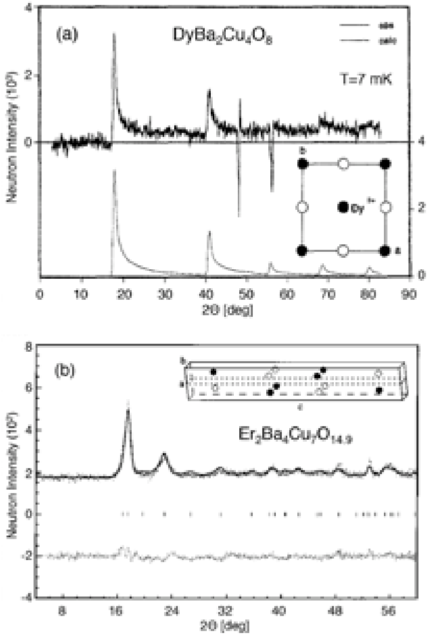


Figure 13

(a) Two-dimensional antiferromagnetic Dy^{3+} ordering in $DyBa_2Cu_4O_8$ at 7 mK and corresponding magnetic difference neutron diffraction pattern (7 mK - 1.2 K) from DMC. The observed points are corrected for paramagnetic diffuse scattering. Filled and open circles indicate antiparallel alignment of the magnetic moments perpendicular to the (a,b) plane. (b) Three-dimensional magnetic Er^{3+} ordering in superconducting $Er_2Ba_4Cu_7O_{14.9}$, corresponding to k=[0,1/2,1/2] and associated magnetic difference neutron diffraction pattern (25 mK - 3 K), measured on D1A at ILL. Black and white spheres indicate antiferromagnetic ordering with the magnetic moments oriented parallel to the b-axis; T_c=89 K and T_N=0.54 K (after Ref. 26).

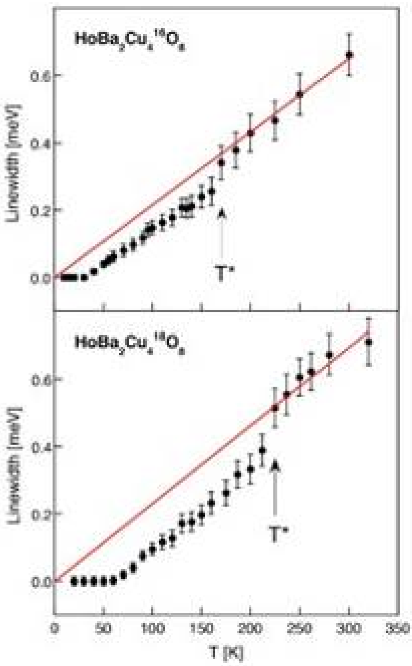


Figure 14

Temperature dependence of the intrinsic linewidth of the lowest ground-state crystal-field transition in $HoBa_2Cu_4{}^{16}O_8$ and $HoBa_2Cu_4{}^{18}O_8$. The lines denote the linewidth in the normal state. T* corresponds to the temperature where the pseudogap opens (after Ref. 28).

sure, and doping. Neutron diffraction experiments revealed essential information on specific interatomic distances and superexchange angles relevant for the understanding of the different types of phase transitions (structural, magnetic, metal-insulator), most prominently present in the rare-earth nickelates. The structural study of the metallization process in $PrNiO_3$ [29] profitted from the

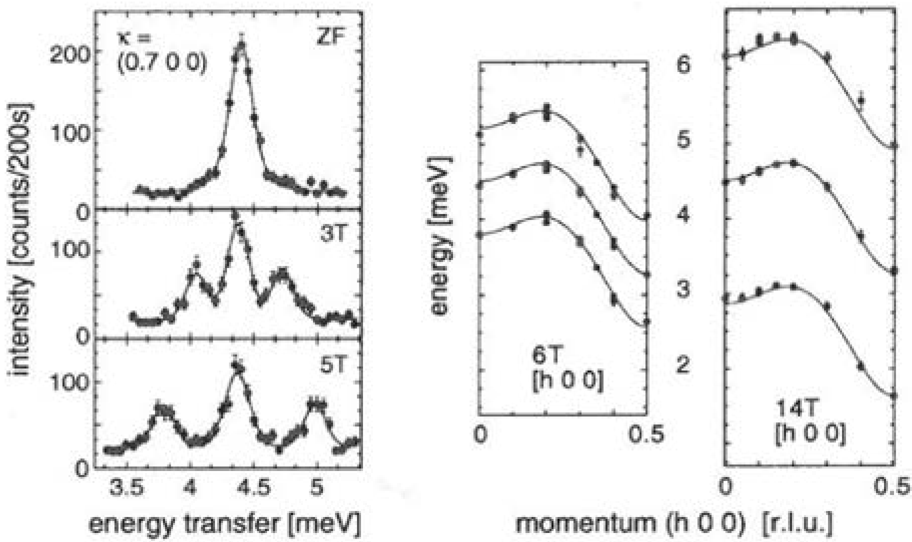


Figure 15
Characteristic field dependence of the magnetic excitation modes in the gapped phase of $KCuCl_3$ at T=2 K. The application of a magnetic field (3T, 5T, 6T, 14T) splits the singlet-triplet transition (ZF) into three modes (after Ref. 32).

development of a zero-matrix pressure cell allowing pressures up to 5 GPa. An interesting oxygen isotope effect was detected for the magnetic structure of the compound $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$; the sample with the isotope ^{16}O is ferromagnetic, while the sample with the isotope ^{18}O displays antiferromagnetic ordering [30]. The pressure-induced structural phase transition observed for the compound $Pr_{1-x}La_xNiO_3$ and the corresponding change of the crystal-field ground state verified by neutron spectroscopy was the basis for the first experimental demonstration of cooling by adiabatic pressure application [31].

Detailed neutron scattering studies of novel quantum spin systems were initiated on the compound series $ACuCl_3$ (A=K, Tl, NH_3) which are characterized by antiferromagnetically coupled copper dimers. The resulting triplet nature of the excitations was confirmed by the observed three-fold splitting of the modes in a magnetic field as shown in Fig. 15 [32].

Investigations on a series of binary metal systems were carried out to determine short-range order effects by diffuse neutron scattering measurements, which provide information on the effective pair potentials. The experimental strategy was to collect a complete set of diffuse scattering data, preferably covering the irreducible part of the Brillouin zone, as exemplified in Fig. 16 for α-brass [33].

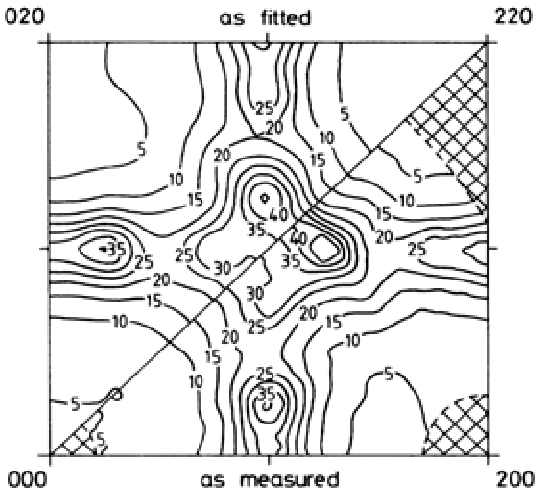


Figure 16
Diffuse elastic scattering observed for α–brass in the reciprocal (001) plane. Experimental results (as measured) are compared with model calculations (as fitted). The lines correspond to diffuse scattering with equal intensity (after Ref. 33).

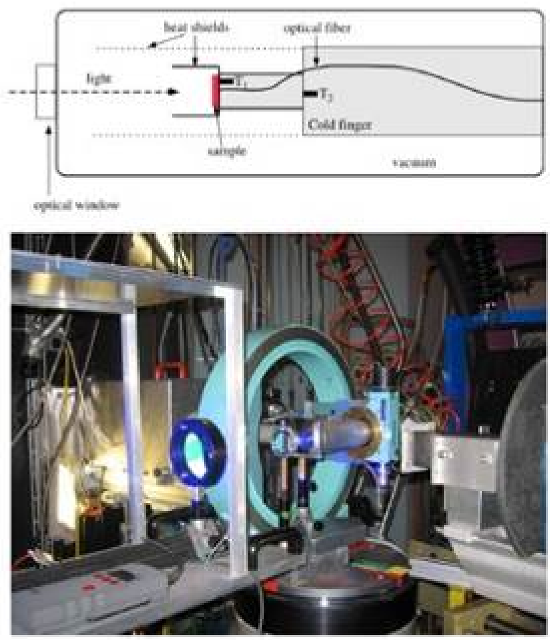


Figure 17
Setup for light irradiation of a single crystal of sodium nitroprusside to create maximum population of its longliving metastable states at low temperatures. These states may be controlled by measuring the transmission by means of the optical fiber connected to a photodiode situated outside the cooling system at room temperature. The photo shows this optical setup mounted on the 4–circle neutron diffractometer TriCS at SINQ.

The application of polarized laser light for 4-circle neutron diffraction measurements on single crystals at low temperatures was successfully developed, starting from a previously discussed experimental setup [21]. With this technique shown in Fig. 17, precise data sets of neutron intensities were collected on a single crystal of sodium nitroprusside

$Na_2Fe(CN)_5NO \cdot 2D_2O$ at 80 K, both in the ground state and in a mixed state of ground state and a long-living excited state [34]. From the derived crystal structures evidence was obtained that the light-induced metastable state differs from the ground state by distinct modifications of the Fe-N-O bond. The system has proven to be a promising material for optical storage on the molecular level.

[23] Neutron diffraction study of the heavy fermion superconductors UM_2Al_3 (M=Pd,Ni)
A. Krimmel, P. Fischer, B. Roessli, H. Maletta, C. Geibel, C. Schank, A. Grauel, A. Loidl, and F. Steglich, Z. Phys. B 86, 161 (1992)

[24] Three-dimensional helical supramolecules - elucidation of magnetic ordering for an antiferromagnetic phase
S. Decurtins, H. W. Schmalle, R. Pellaux, R. Huber, P. Fischer, and B. Ouladdiaf, Adv. Mater. 8, 647-651 (1996)

[25] A systematic low-temperature neutron-diffraction study of the $RBa_2Cu_3O_x$ (R= yttrium and rare-earths, x=6 and 7) compounds
M. Guillaume, P. Allenspach, W. Henggeler, J. Mesot, B. Roessli, U. Staub, P. Fischer, A. Furrer, and V. Trounov
J. Phys.: Condens. Matter 6, 7963-7976 (1994)

[26] Magnetic 2-D and 3-D ordering phenomena in rare-earth based copper-oxide superconductors and related systems
P. Fischer and M. Medarde, Neutron Scattering in Layered Copper-Oxide Superconductors, Physics and Chemistry of Materials with Low-Dimensional Structures, Vol. 20 (Ed. A. Furrer, Kluwer Academic Publishers, Dordrecht 1998) p. 261

[27] Neutron spectroscopic evidence for cluster formation and percolative superconductivity in $ErBa_2Cu_3O_x$
J. Mesot, P. Allenspach, U. Staub, A. Furrer, and H. Mutka, Phys. Rev. Lett. 70, 865 (1993)

[28] Large isotope effect on the pseudogap in the high-temperature superconductor $HoBa_2Cu_xO_8$
D. Rubio-Temprano, J. Mesot, S. Janssen, K. Conder, A. Furrer, H. Mutka, and K. A. Müller, Phys. Rev. Lett. 84, 1990 (2000)

[29] High-pressure neutron-diffraction study of the metallization process in $PrNiO_3$
M. Medarde, J. Mesot, P. Lacorre, S. Rosenkranz, P. Fischer, and K. Gobrecht, Phys. Rev. B 52, 9248 (1995)

[30] Effect of oxygen isotope substitution on the magnetic structure of $(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3$
M. Balagurov, V. Yu. Pomjakushin, D. V. Sheptyakov, A.L. Aksenov, N.A. Babushkina, L.M. Belova, A. N. Taldenkov, A. V. Inyuskin, P. Fischer, M. Gutmann, L. Keller, O. Yu. Gorbenko, and A. R. Kaul, Phys. Rev. B 60, 383-387 (1999)

[31] Cooling by adiabatic pressure application in $Pr_{1-x}La_xNiO_3$
K. A. Müller, F. Fauth, S. Fischer, M. Koch, A. Furrer, and P. Lacorre, Appl. Phys. Lett. 73, 1056 (1998)

[32] Magnetic excitations in the quantum spin system $KCuCl_3$
N. Cavadini, W. Henggeler, A. Furrer, H.-U. Güdel, K. Krämer, and H. Mutka, Eur. Phys. J. B 7, 519 (1999)

[33] Short-range order in α-brass
L. Reinhard, B. Schönfeld, G. Kostorz, and W. Bührer, Phys. Rev. B 41, 1727 (1990)

[34] Light-induced structural changes in sodium nitroprusside ($Na_2(Fe(CN)_5NO \cdot 2D_2O$) at 80 K
M. Rüdlinger, J. Schefer, G. Chevrier, N. Furer, H.U. Güdel, S. Haussühl, G. Heger, P. Schweiss, T. Vogt, T. Woike, and H. Zöllner, Z. Phys. B 83, 125-130 (1991)

6. A glance into the 21st century

The performance of the spallation neutron source SINQ was gradually improved since its first operation, exceeding a thermal neutron flux of 10^{14} $n\cdot cm^{-2}\cdot s^{-1}$ for the first time in the year 2000. In addition, the instrumental park was continuously extended, including also world-class radiography stations. The real strength of SINQ lies on the cold neutrons rather than on the thermal ones due to the optimum placement of the cold D_2 source in the moderator tank. As a consequence cold neutron instruments at SINQ are often competitive with corresponding instruments at high-flux neutron sources, so that novel classes of neutron scattering experiments become possible which could hardly be carried out with use of the Swiss installations available in the 20th century. Among the many highlights resulting from experiments at SINQ in the new millenium we present below some examples of topics which were already tackled in the nineties, but came to fruition shortly after the year 2000.

The magnetic ground state of CuB_2O_4 is incommensurate at low temperatures and undergoes a continuous phase transition to a noncollinear commensurate antiferromagnetic state at T*≈10 K. Coexistence of long- and short-range magnetic order is observed in both phases which suggests that the association of the Dzyaloshinski-Moriya interaction and anisotropy leads to the formation of a magnetic soliton lattice [35].

Below the ferro-quadrupolar ordering temperature T_Q=6.1 K of HoB_6 high-resolution neutron diffraction measurements on HRPT clearly detected at high scattering angles a structural phase transition from the cubic space group Pm-3m to a rhombohedrally distorted structure with space group R-3m. The corresponding angle α increases from 90 to 90.26 degrees at T=2.1 K which is clearly related to the ferro-quadrupolar ordering of HoB_6 [36].

The vortex lattice in $La_{2-x}Sr_xCuO_4$ was investigated by SANS experiments which revealed a crossover from triangular to square coordination with increasing magnetic field [37]. The existence of an intrinsic square vortex lattice was never observed so far in high-T_c superconductors and is indicative of the coupling of the vortex lattice to a source of anisotropy, such as that provided by a d-wave order parameter or the presence of stripes.

Chiral fluctuations in a noncentrosymmetric crystal of MnSi were observed by using polarized neutron spectrometry, but without disturbing the sample by a magnetic field [38].

Based on the previous work on novel quantum spin systems [32], the first observation of the Bose-Einstein condensation in a magnetic material was reported for $TlCuCl_3$ at a critical magnetic field, where the energy of the lowest triplet component intersects the ground-state singlet, resulting in a field-induced magnetically ordered state [39].

An effort was made to search for the origin of the biquadratic exchange interaction reported for $CsMn_xMg_{1-x}Br_3$ in earlier experiments (see Ref. 15). Among the many possible explanations, exchange striction turned out to be the proper mechanism [40]. This effect is commonly applied in submarine telephony and also explains the permanent hum of a transformer's iron core, as highlighted in Physics Today 57 (issue 8, August 2004, p. 11).

[35] Formation of a magnetic soliton lattice in copper metaborate
B. Roessli, J. Schefer, G. A. Petrakovskii, B. Ouladdiaf, M. Boehm, U. Staub, A. Vorotinov, and L. Bezmaternikh, Phys. Rev. Lett. 86, 1885 (2001)

[36] The cubic to trigonal phase transition in HoB_6 measured on the new powder neutron diffractometer HRPT at SINQ
A. Dönni, P. Fischer, L. Keller, V. Pomjakushin, Y. Nemoto, T. Goto, and S. Kunii, J. Phys. Soc. Japan. 70, Suppl. A, 448 (2001)

[37] Direct evidence for an intrinsic square vortex lattice in the overdoped high-T_c superconductor $La_{1.83}Sr_{0.17}CuO_4$
R. Gilardi, J. Mesot, A. Drew, U. Divakar, S. L. Lee, E. M. Forgan, O. Zaharko, K. Conder, V. K. Aswal, C. D. Dewhurst, R. Cubitt, N. Momono, and M. Oda, Phys. Rev. Lett. 88, 217003 (2002)

[38] Chiral fluctuations in MnSi above the Curie temperature
B. Roessli, P. Böni, W. E. Fischer, and Y. Endoh, Phys. Rev. Lett. 88, 237204 (2002)

[39] Bose-Einstein condensation of the triplet states in the magnetic insulator $TlCuCl_3$
Ch. Rüegg, N. Cavadini, A. Furrer, H.-U. Güdel, K. Krämer, H. Mutka, A. Wildes, K. Habicht, and P. Vorderwisch, Nature 423, 62 (2003)

[40] Origin of higher order magnetic exchange: Evidence for local dimer exchange striction in $CsMn_{0.28}Mg_{0.72}Br_3$ probed by inelastic neutron scattering
Th. Strässle, F. Juranyi, M. Schneider, S. Janssen, A. Furrer, K. W. Krämer, and H. U. Güdel, Phys. Rev. Lett. 92, 257202 (2004)

7. Concluding remarks

The scientific highlights presented in the preceding sections are to a large extent the result of neutron scattering experiments performed at the medium-flux reactors Saphir and Diorit with thermal neutron fluxes around 10^{14} $n\cdot cm^{-2}\cdot s^{-1}$ which is an order of magnitude below the flux of the worldwide leading neutron sources. Nevertheless, the work performed at Würenlingen/Villigen turned out to be absolutely competitive on an international level and repeatedly touched innovative frontiers of condensed-matter science. The reason for these achievements is clear. The neutron source is only the first element of a usable facility, but its power can be dramatically enhanced by optimizing the instrumentation. This was made possible in Switzerland by a reasonably good level of funding and most importantly by clever staff members assisted by expert technicians who persistently tried to incorporate innovative ideas into the instruments with the aim to transport as many useful neutrons as possible to the detector.

The excellent conditions offered at Würenlingen/Villigen attracted a large national user community to perform joint experiments in the fields of crystallography, solid-state physics, chemistry, and materials science, thereby establishing the world's strongest per capita national research community in neutron scattering [41]. There were almost no administrative hurdles in the allocation of beam time, i.e., the users usually got rapid access to the instruments whenever their research programmes required neutron beams. Unfortunately, instruments for soft-matter research could not be provided due to the lack of cold neutrons. Early plans to install a cold-neutron guide hall at the reactor Saphir were given up in favor of the spallation source SINQ which concentrates on cold neutrons and therefore offers experimental possibilities in new fields of research. These new opportunities have been fully exploited by the Swiss user community. Indeed, an expert commission of the European Union made the following statement on the proposal "Access to the Neutron Scattering Facility SINQ" in the year 2001: "Recent scientific highlights listed in the proposal are impressive in both quality and range of topics covered." We therefore realize with pleasure that the tradition of neutron scattering at Würenlingen/Villigen established in the 20th century has been taken over and further developed in the 21st century up to the present.

[41] Analytical report
T. Riste, in Neutron beams and synchrotron radiation facilities (OECD Megascience Forum, Paris 1994), p. 63 (ISBN 92-64-14249-5)