1 Introduction

The investigation of quantum phase transitions (QPTs) in systems of correlated electrons is one of the hot topics in modern solid-state physics. QPTs are found in a variety of systems with competing ground states, at a point where the energy scales of the determining interaction mechanisms are in balance. They are zero-temperature transitions, driven by non-thermal control parameters g such as the strength of an external magnetic field, mechanical pressure, or chemical doping. At the quantum critical point (QCP), where the control parameter is at a critical value $g = g_c$, the ground state energy of the infinite lattice system becomes non-analytic. Although not fully established yet, it seems very likely that QPTs are connected to a number of prominent phenomena, such as the occurrence of unconventional superconductivity in the cuprates, pnictides, and heavy-fermion metals [1, 2].

Looking at the phase diagrams of these materials, one often finds that the antiferromagnetic order of the Mott-insulating mother compound can be suppressed by chemical doping, leading to the appearance of a superconducting dome, as was observed in $CePd_2Si_2$ or $La_{2-x}Sr_xCuO_{4+\delta}$ [3, 4]. It is often speculated that a magnetic QCP lies beneath these domes, and that the critical magnetic fluctuations associated with it at least partially constitute the relevant coupling mechanism for the Cooper pairs. However, most experimental methods have only limited access to the superconducting phase, which makes it difficult to prove the existence of the QCP in these materials.

In the heavy-fermion (HF) compounds, the mechanism responsible for the occurrence of superconductivity is not yet fully decoded. Nevertheless, in many cases it seems very plausible that the relevant coupling mechanism for the cooper pairs is given at least in part by critical magnetic fluctuations [5]. The HF systems offer a broad variety of chemical compositions, and are therefore an ideal playground for the understanding of several complex phenomena arising in systems of strongly correlated electrons. The relevant energy scales in these systems are very small. Therefore, a number of different experimental control parameters g can actually be used to tune the systems through the quantum phase transition. This allows to, e.g., study the interplay between quantum criticality and superconductivity or non-Fermi liquid behavior in the vicinity of the QCP.

Also in the cuprates, several experimental and theoretical results point towards the existence of a QCP beneath the superconducting dome, although the connection between superconductivity and the QCP is not as evident as in the HF materials. In particular, the doping dependence of the so-called T^* line and its enclosed "strange metal phase" point towards the regime of optimal doping, suggesting a QCP roughly in the center of the superconducting

dome. In a recent review, S. Sachdev proposed an elaborate scenario in which the competition between spin density wave order and superconductivity leads to a shift of the QCP to lower doping concentrations [6, 7]. The resulting global phase diagram for the hole- and electron doped cuprates consistently explains many experimental results.
In contrast to the complicated situation in the cuprates, pnictides, and heavy-fermion metals, where several degrees of freedom are present, the QPTs in magnetic insulators can be accessed much more directly by means of experiment and theory. Also, while the phase diagrams of heavy-fermion metals or superconductors are in general complex due to several interaction mechanisms, the purely magnetic interactions in magnetic insulators, in particular for the case of low-dimensional spin systems, qualify them as model systems for the study of quantum criticality and give the rare occasion to perform well-controlled calculations of their characteristics and to compare them with experimental data sets of well-characterized sample systems [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18].
Under the aspect of experimental feasibility, the spin properties of organic-based low-dimensional magnets can be fine-tuned by the chemical synthesis. This well-controlled synthesis allows the systematic investigation of the magnetic properties with well-established methods such as neutron scattering, ESR, dc/ac magnetometry, μSR, or NMR. In particular, the high sensitivity of NMR to local hyperfine fields allows to perform detailed studies of, e.g., phase transitions or the local distribution of spin moments [19].

In the scope of this thesis, second-order quantum phase transitions are of interest. For these, the characteristic energy scale Δ of fluctuations above the ground state vanishes with

$$\Delta \propto J\,|g - g_c|^{z\nu} \tag{1.1}$$

as g_c is approached [20]. Here, $z\nu$ is a critical exponent, that is of universal character in several system classes, where it does not depend on most of the microscopic details of the underlying Hamiltonian. [1] With Δ being very small in the vicinity of the QCP, the energy scale of quantum fluctuations, driven by the Heisenberg uncertainty principle, becomes important. While this is in contrast to classical phase transitions, interesting finite-temperature phenomena may occur that are due to the interplay of thermal and quantum fluctuations. Another feature of a second-order quantum phase transition is the divergence of the characteristic length scale ξ, which, e.g., specifies the length scale of the equal time correlations of spin operators. It diverges as

$$\xi^{-1} \propto \Lambda\,|g - g_c|^{\nu}\ , \tag{1.2}$$

where Λ is of the order of the inverse lattice spacing. Combining Eqs. 1.1 and 1.2 gives

$$\Delta \propto \xi^{-z}\ . \tag{1.3}$$

[1] In the case of a Luttinger liquid, the microscopic interactions *are* important for the exponents of the correlation functions.

These definitions of the occurring singularities are made for the ground state of the system and therefore describe the zero-temperature behavior. However, also at finite temperatures of the order of Kelvin, Δ and ξ depend on g, which allows to probe the QCP in the experiment. In many solid-state samples, in particular magnetic insulators, the density of critical fluctuations is very high and their mass is very small, therefore, the corresponding Bose condensate of excited states sometimes survives even up to room temperature [21], so there is no need to go to nanoKelvin as necessary for cold atomic traps. The Bose-Einstein condensation of hard-core bosons has been related to some phase transitions in quantum magnets which stem from the level crossing of elementary triplet excitations with the ground state at a critical external magnetic field $B = B_c$. Following the pioneering analysis of spin chains [22, 23] and spin ladders [24] in external magnetic fields, magnetic field-driven quantum critical points (QCPs) have been under intense scrutiny for three and quasi-two-dimensional spin $S = 1/2$ dimer systems, i.e. $TlCuCl_3$ [25, 26, 27, 28] and $BaCuSi_2O_6$ [29], for $S = 1/2$ ladder materials $Cu_2(C_5H_12N_2)_2Cl_4$ [16] and $(C_5H_{12}N)_2CuBr_4$ [9, 10], for the $S = 1$ Haldane chain $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ [11], for the coupled chain compound $NiCl_2$-4SC$(NH_2)_2$ (DTN) [12, 13] with $S = 1$, as well as for the effective $S = 1$ system $(CH_3)_2CHNH_3CuCl_3$ [14, 15]. All of these materials feature a gapped zero-field state with the lowest triplet branch condensing as the field is *increased*. In the case of the isotropic, $S = 1/2$ antiferromagnetic Heisenberg chain (AFHC) model, which is of main importance in this thesis, the triplet excitations condense as the *decreasing* magnetic field crosses B_c.
In contrast to thermally-driven phase transitions, the Landau theory of order-parameter fluctuations in the vicinity of the transition cannot be applied in the general case [30, 31]. Since there is not yet an unified theory of quantum criticality, it is crucial to study the QPTs in simple model systems with a well-defined interaction scheme. In a second step, the acquired results can then be applied to systems with more complex interactions.

The isotropic, $S = 1/2$ antiferromagnetic Heisenberg chain model satisfies all the above mentioned criteria. It is one of the main paradigms of quantum many-body physics both from the experimental and theoretical viewpoint. Its importance lies in the fact that, due to its limited number of interaction terms, it is one of the very rare examples in quantum magnetism for which *all* static and dynamic characteristics can be calculated using the tools of modern theoretical physics. The characteristics of many other low-dimensional magnetic systems, which can often be understood in terms of a modification of the AFHC model, are somewhat similar to its characteristics. It was in particular the AFHC model which promoted the development and/or specific application of powerful methods such as the Bethe-Ansatz, density matrix renormalization group (DMRG), or quantum Monte Carlo simulations [32]. On the experimental side, several realizations of the isotropic AFHC model or one of its modifications were synthesized and characterized in the past three decades [33, 34, 35, 36, 37]. With all this at hand, the opportunity for a comprehensive comparison of well-controlled theoretical calculations and experimental results is given. The static characteristics of the

$S = 1/2$ AFHC were successfully compared with experimentally studied features of several quasi-one-dimensional magnetic compounds [32]. For the dynamical properties probed by spectroscopic methods, especially in the vicinity of the quantum critical point, there is still a shortness of experimental data sets and their comparison to calculations. In order to shed more light on this issue, measurements of the static and low-frequency magnetic properties of the metalorganic spin chain compounds copper pyrazine dinitrate (CuPzN) and bisphenazinium copper tetrachloride (PhnCuCl) were performed in the frame of this thesis.
CuPzN is a well-characterized model system for the isotropic $S = 1/2$ AFHC. Due to its relatively small Heisenberg coupling constant $J/k_B = 10.7$ K, the whole magnetic phase diagram, with the external field as a control parameter, can be accessed experimentally. In particular, the regime of the quantum critical point at $B_c = 14.6$ T is amenable by standard laboratory magnets. A long-range ordered phase is found only below 107 mK, which permits an undisturbed study of the correlation functions in the quantum regime at $k_B T \ll J$. The comparison to field- and temperature-dependent numerical and analytical calculations for the $S = 1/2$ AFHC model, which were performed in collaboration with the experimental studies presented in this thesis, gives the rare opportunity for the study of quantum criticality under very well-defined conditions. The results of this successful study can be seen as a reference, against which the results obtained from other low-dimensional spin compounds can be tested.
PhnCuCl is an only recently synthesized metalorganic low-dimensional spin system. Although its magnetic interaction scheme is not fully determined yet, it likely is describable as a modification of the pure AFHC model, and its experimental signatures can therefore well be contrasted against those of the pure $S = 1/2$ AFHC system CuPzN. A characterization of PhnCuCl by means of magnetization and specific heat measurements in a broad range of magnetic fields and temperatures, as well as a series of ^{1}H and ^{35}Cl NMR experiments, are presented in this thesis. Interestingly, both the macroscopic and the local static magnetization are in very good agreement with calculations for the isotropic $S = 1/2$ AFHC model, while the results for the specific heat and the NMR relaxation rate $1/T_1$ deviate from this picture and point towards a distribution of the electronic spectral weight among an increased number of excitation branches.

Chapter 2 of this thesis serves as an introduction to the physics of the AFHC model. The thermodynamic properties and dynamical characteristics are discussed, putting an emphasis on the detection of the latter by means of nuclear magnetic resonance. Several main mechanisms of NMR are discussed in chapter 3, including the splitting of nuclear eigenstates due to static hyperfine fields, the relaxation behavior of the nuclear spin ensemble caused by local fluctuating fields, and the measurement of the corresponding observables in the NMR experiment. The two sample systems investigated in this work are introduced in chapter 4. An overview is given, summarizing existing experimental and theoretical findings from the literature. Chapter 5 deals with the thermodynamical characterization of the sample systems. In particular for PhnCuCl, the magnetization and specific heat data provide an estimate for

the energy scale of the interionic exchange mechanisms. The results of these studies are the prerequisites to address specific questions by means of NMR in chapter 6, where ^{13}C, ^{14}N, ^{1}H, and ^{35}Cl NMR are utilized to study the local static and dynamic electronic properties of both CuPzN and PhnCuCl. A summary of all results presented in this thesis and their discussion is given in chapter 7.