Extended ground state manifolds of classical Heisenberg magnets and magnetoelectric selection rules in åkermanites

Ph.D. booklet

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Background

In Mott insulators electron-electron interactions prevent conductance as described by the celebrated Hubbard model [Hubbard, 1963, Gutzwiller, 1963, Kanamori, 1963]. At the limit of large electron-electron repulsion the model is mapped to the *Heisenberg model* [Heisenberg, 1928], where the remaining freedom of the localized electrons are their spins sitting on the lattice. The resulting Heisenberg model has nearest neighbor isotropic, *antiferromagnetic* interactions. Generalization of the Heisenberg model is possible by introducing anisotropic interactions, on-site anisotropies or further neighbor interactions.

Even if we restrict ourselves to the nearest neighbor, isotropic, antiferromagnetic model in the classical approximation, the structure of the lattice may have a dramatic effect on the ground state configuration. In lattices containing triangles the antiferromagnetic interactions cannot be satisfied simultaneously, a phenomenon called *geometric frustration*. Examples of frustrated lattices are the triangular, kagome, face-centered cubic or pyrochlore lattices. One dire consequence of frustration is the large degeneracy of ground states, e.g. for the Ising model on the triangular or kagome lattices the degeneracy is extensive: The ground state entropy scales with the system size. Ground state configurations are related to the minima of the Fourier transform of the interactions as revealed by the the Luttinger-Tisza method [Luttinger and Tisza, 1946, Luttinger, 1951], this set of minima is called the *ground state manifold*. Simple non-frustrated magnets have a ground state manifold consisting of a handful of points and these points are where the magnetic Bragg peaks show up in neutron scattering experiments. In frustrated systems the ground state manifold extends to curves, surfaces or even to the whole Brillouin zone (in the case of the kagome and pyrochlore systems).

The system may walk around on these manifolds and explore the plethora of ground states, and instead of showing magnetic ordering behaves like a *spin liquid* [Balents, 2010, Lacroix et al., 2011, Knolle and Moessner, 2019, Savary and Balents, 2016], without Bragg peaks. This phenomenon was predicted theoretically for a frustrated diamond lattice with first and second neighbor interactions [Bergman et al., 2007] and was found experimentally [Gao et al., 2016] for the compound $MnSc_2S_4$, where the extended ground state manifold was clearly visible by neutron scattering. In pyrochlore magnets frustration leads to the interesting *spin ice* phase [Henley, 2010] as realized by the compounds and $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$. These systems also have extensive ground state manifolds with correlations decaying as a power law with the characteristic *pinch-point singularities*, the hallmark of a correlated paramagnet. Some of the frustrated systems do not order at all, but others may order at very low temperature via the *order by disorder* mechanism, where quantum or thermal fluctuations choose an order. Finally I describe a different application of Heisenberg models in the context of magnetooptics, unrelated to frustration.

In magnetoelectric multiferroic materials the magnetization and electric polarization degrees of freedom are coupled. This coupling manifests itself in the static properties: We can manipulate the electric polarization by the application of external magnetic fields or the magnetization via electric fields. Also at low temperature a magnetic order can induce electric polarization. These cross-correlations show up even in the finite-frequency properties leading to the so-called *electromagnons* [Pimenov et al., 2006, Takahashi et al., 2012, Takahashi et al., 2013, Penc et al., 2012] and to optical anisotropies such as magnetoelectric polarization rotation or non-reciprocal directional dichroism. The latter means that counter-propagating light beams are absorbed differently in a material (in an extreme case the crystal is transparent from one side and completely opaque from the other side). Examples are $Sr_2CoSi_2O_7$ or $Ba_2CoGe_2O_7$ in the family of melilites [Kézsmárki et al., 2014].

Objectives

My thesis consists of two parts: In Chapters 2 and 3 I consider the ground state properties of classical Heisenberg magnets on frustrated lattices, and in Chapter 4 I analyze a simple model to describe the magnetooptical properties of the magnetoelectric multiferroic $Sr_2CoSi_2O_7$.

The frustrated face-centered cubic lattice is one of the most abundant lattices in nature. The classical isotropic Heisenberg model on this lattice up to second neighbor exchanges (the $J_1 - J_2$ model) is well known to the literature. In the ground state (zero temperature) phase diagram of this model four commensurate phases were found [Sólyom, 2007]: One ferromagnet and three kinds of antiferromagnets. I included a third neighbor interaction (the $J_1 - J_2 - J_3$ model) in the hope of finding *incommensurate* phases (spin spirals). I analyzed the phase diagram by the Luttinger-Tisza method and the phase diagram turned out to be surprisingly rich: Three kinds of distinct spin spirals were found with special propagation directions. Furthermore at triple points and special phase boundaries extended (degenerate) ground state manifolds in Fourier space appeared: Three of them were one dimensional and I also found a *surface* at the special point $J_2 = J_1/2 > 0$ and $J_3 = 0$. I thoroughly analyzed all these phases, and at the extended manifolds I constructed families ground states of, among others, aperiodic stacking of independent ferro- or antiferromagnetic planes, and interacting ferromagnetic chains. I explained these degenerate points by covering the lattice with finite motifs and rewriting the Hamiltonian as a complete square of the sums of spins on these motifs.

Founding the two dimensional ground state manifold in the face-centered cubic model at $J_2 = J_1/2 > 0$ and $J_3 = 0$ stimulated the idea of searching for other models with such large degeneracies. I gave a recipe of constructing Heisenberg models on Bravais lattices with codimension-one ground state manifolds (curves in two dimensions and surfaces in three dimensions): These models always contain frustrating interactions. I also analyzed the effect of the thermal order by disorder mechanism on the models generated for the simple cubic and face-centered cubic lattices.

Our experimentalist colleagues found exciting magnetooptical properties (especially non-reciprocal directional dichroism) of the magnetoelectric multiferroic $Sr_2CoSi_2O_7$ in its paramagnetic phase in strong external magnetic fields. In the last part of the thesis I wished to understand these properties. The material is an antiferromagnet with a strong in-plane on-site anisotropy, and can be described by an appropriate quantum Heisenberg model with spin length $S = 3/2$ of the Co^{2+} ions. The induced polarization in these materials is described by spin-quadrupolar operators, thereby the analysis of the Heisenberg model leads to an understanding of the magnetoelectric phenomena. The strength of the anisotropy and the weak correlations in the paramagnetic state motivated to study a single-site model where the exchange interactions are neglected: This simplistic model was able to describe some of the magnetooptical properties. Including the interactions perturbatively justified the success of the single-ion model in retrospect.

Studying the selection rules via group theory led me to the discovery that in materials described by a magnetic group the antiunitary (time-reversed) group elements relate the imaginary and real parts of the transition matrix elements of perturbing operators. In the special case of $Sr_2CoSi_2O_7$ the presence of a two-fold rotation followed by time reversal forces the matrix elements of the magnetization and electric polarization operators to become either real or pure imaginary (in complete agreement with the measurements performed by the group of Sándor Bordács, these experiments motivated the investigation of this problem).

Thesis statements

1. Using the Luttinger-Tisza method I constructed the ground state (zero temperature) phase diagram of the classical isotropic Heisenberg model up to third neighbor interactions of arbitrary sign on the face-centered cubic lattice. I gave a detailed analysis of the commensurate phases: I showed that multiple-$\mathbf{Q}$ orders lead to non-collinear or even non-coplanar orders, and in the case of the Type III antiferromagnet, a chiral ground state. I demonstrated that the introduction of the third neighbor interaction leads to a qualitatively new feature of the model: Incommensurate spin spirals with propagation vectors along special directions in the Brillouin zone appear [1].

2. I showed that at triple points and special phase boundaries of the phase diagram of the third neighbor classical isotropic Heisenberg model extended ground state manifolds appear in Fourier space: Three one dimensional manifolds and one two dimensional manifold. At these points I expressed the Hamiltonian as a sum of complete squares of spins over appropriate finite motifs tessellating the lattice. Thereby I explicitly constructed large classes of ground states and explained the degeneracy of the manifolds. These families of exact ground state configurations consist of, among others, frustratingly interacting ferromagnetic chains and randomly stacked ferro- or antiferromagnetic planes [1].

3. I gave a recipe for constructing classical isotropic Heisenberg models on Bravais lattices possessing codimension-one ground state manifolds (i.e. curves in two, and spin spiral surfaces in three dimensions). The models are either fine-tuned or have a few free parameters: In the latter case I showed that varying the parameters allows for topological (Lifshitz) transitions. For the face-centered and simple cubic lattices I calculated the low temperature free energy and demonstrated that the thermal or quantum fluctuations select commensurate phases on the spin spiral surfaces by the order by disorder mechanism [2].

4. I constructed a one-spin model that describes the non-reciprocal directional dichroism of the magnetoelectric multiferroic åkermanite crystal $Sr_2CoSi_2O_7$ in its paramagnetic phase under strong external fields. The model takes into account the external field, the strong in-plane anisotropy, and the electric polarization induced by the metal-ligand hybridization mechanism. Despite its simplicity the model gives the field dependence of the excitation energy correctly. Based on a group theoretical analysis I derived the magnetoelectric selection rules. Promoting the single-ion

model to a lattice and treating interactions perturbatively I also explained the success of the one-ion approach in the paramagnetic phase [3].

5. Ordinary selection rules guarantee that matrix elements of perturbing operators of a symmetric Hamiltonian vanish, provided these operators transform according to certain irreducible representations of the group of the Hamiltonian. I generalized this concept and showed that (in magnetic models of arbitrary spin length and arbitrary magnetic symmetry) the antiunitary symmetry elements of the group of the Hamiltonian connect the real and imaginary parts of matrix elements of operators. As a special case: If a two-fold rotation together with time reversal is a symmetry of the Hamiltonian, and the perturbing operators are even (odd) under this symmetry their matrix elements are real (pure imaginary). Applying this result to the magnetization and polarization operators in the case of $Sr_2CoSi_2O_7$ led to new selection rules as confirmed by the magnetooptical absorption measurements in the paramagnetic [3] and ordered [4] phases.

Publications related to the thesis statements

[1] Péter Balla, Yasir Iqbal, and Karlo Penc

Degenerate manifolds, helimagnets, and multi-$\mathbf{Q}$ chiral phases in the classical Heisenberg antiferromagnet on the face-centered-cubic lattice.

Physical Review Research **2**, 043278 (2020)

[2] Péter Balla, Yasir Iqbal, and Karlo Penc

Affine lattice construction of spiral surfaces in frustrated Heisenberg models

Physical Review B **100**, 140402(R) (2019)

[3] J. Viirok, U. Nagel, T. Rõõm, D. G. Farkas, P. Balla, D. Szaller, V. Kocsis, Y. Tokunaga, Y. Taguchi, Y. Tokura, B. Bernáth, D. L. Kamenskyi, I. Kézsmárki, S. Bordács, and K. Penc

Directional dichroism in the paramagnetic state of multiferroics: A case study of infrared light absorption in $Sr_2CoSi_2O_7$ at high temperatures

Physical Review B **99**, 014410 (2019)

[4] J. Vít, J. Viirok, L. Peedu, T. Rõõm, U. Nagel, V. Kocsis, Y. Tokunaga, Y. Taguchi, Y. Tokura, I. Kézsmárki, P. Balla, K. Penc, J. Romhányi, and S. Bordács

In Situ Electric-Field Control of THz Nonreciprocal Directional Dichroism in the Multiferroic $Ba_2CoGe_2O_7$

Physical Review Letters **127**, 157201 (2021)

Further publication

[5] A. Szilva, P. Balla, O. Eriksson, G. Zaránd, and L. Szunyogh

Universal distribution of magnetic anisotropy of impurities in ordered and disordered nanograins

Physical Review B **91**, 134421 (2015)

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