Ph.D. Thesis

Exotic ordering and multipole excitations in anisotropic systems

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Introduction

The magnetic properties of Mott insulators – where the insulating state is the consequence of the strong electron correlation – are described by effective models of the local spin (or other) degrees of freedom. The best known example is the Heisenberg model which, despite its simple form, proves to be rather challenging by itself. Nonetheless, depending on the physical properties and structure of the given material, one often needs to add further terms, such as second and third neighbour interactions or plaquette exchange. When the spins are larger, multipole degrees of freedom appear and the possibility of biquadratic or even higher order spin terms becomes a natural option. Additionally, in real materials the relativistic spin-orbit interaction couples the direct space with the spin space leading to the emergence of anisotropies, such as the g-tensor anisotropy and the Dzyaloshinsky-Moriya interaction. Depending on the details of the interactions, the geometry of the lattice and the lengths of the participating spins, various – ordered and disordered – ground states can occur. Some of these can be understood classically, while there are other, more interesting, states of matter which are essentially of quantum mechanical origins.

A typical way of constructing non-magnetic quantum ground state is covering the lattice with valence bonds (a valence bond is a singlet state of a spin pair). Among the two dimensional systems, the Shastry-Sutherland model provides a unique, 'explicit' example of a spin-gapped ground state, where the dimer covering of the lattice is unambiguous [Shastry 1981]. This dimer singlet state is invariant under the discrete lattice translations, therefore, in a broader sense we can think about it as a trivial spin liquid state. An experimental realization of this model is the quasi two-dimensional antiferromagnetic compound: $SrCu_2(BO_3)_2$ [Kageyama 1999]. The zero-field splitting of excitations observed in neutron scattering [Gaulin 2004] and the magnetic field dependence of excitations measured with electron spin resonance [Nojiri 2003] suggested the importance of spin anisotropy.

The quest to discover materials, in which magnetism and ferroelectricity coexists, is fueled by the idea of spintronic devices, in other words, the possibility to control spins by applied voltages, or electric charges by external magnetic field. The concept of ferroelectricity induced by magnetic order is intensively studied nowadays. In such systems the induced ferroelectricity is smaller than in the usual ferroelectric materials, yet the cross-coupling effects are strong due to the sensibility of the magnetic order, and subsequently the induced electric polarization, to the applied magnetic field. In $Ba_2CoGe_2O_7$, as a result of strong easy-plane anisotropy, below 6.7 K the magnetic moments order into a planar antiferromagnetic pattern [Zheludev 2003] which is in fact a multiferroic phase.

The conventional spin wave method provides a systematic way to study the excitation spectrum of ordered magnets. Spin systems with spins $S > 1/2$ – like $Ba_2CoGe_2O_7$ – support tensor interactions and may exhibit unconventional, often non-magnetic orders, such as multipole or nematic order. When one is interested in the dynamical properties of such systems, the conventional spin wave theory, such as the Holstein-Primakoff representation, fails and one needs to introduce generalized bosonic operators related not only to the spin but also to higher order operators. The idea of the extended spin wave has been introduced to study magnetic systems with single-ion anisotropy and/or higher order exchange terms [Onufrieva 1985, Papanicolaou 1984, Papanicolaou 1988], *f*-electron systems [Shiina 2003], as well as for spin systems with orbital degeneracy in terms of flavor waves [Joshi 1999].

Main objectives and techniques

In the thesis I am considering two materials, the frustrated orthogonal dimer system $SrCu_2(BO_3)_2$, and the multiferroic compound $Ba_2CoGe_2O_7$, with the aim to show that simple, but appropriately chosen spin models, discussed in terms of variational approach and generalized spin wave technique, can efficiently describe the physical properties of these compounds.

In order to understand the properties of the experimentally [Kageyama 2000] suggested magnetically disordered ground state of $SrCu_2(BO_3)_2$ I considered a suitable Hamiltonian that contains the possible anisotropy terms such as the Dzyaloshinsky-Moriya (DM) interactions and g-tensor components. On the basis of dimer-factorized variational wave function approach I mapped out the phase diagrams as the function of DM couplings and external magnetic field applied perpendicular and parallel to the $CuBO_3$ layer. The emerging phases were discussed in detail and classified according to the symmetries of the lattice. To give a theoretical explanation on the dynamical properties, I performed a generalized spin wave (bond-wave) calculation to get the excitation spectrum for different field settings, as well as in the momentum space in zero magnetic filed. This approach enabled to discuss the higher excitations which are not reachable with the conventional spin waves or perturbational methods. The zero field splitting of excitations measured in inelastic neutron scattering [Gaulin 2004] have been qualitatively reproduced. Calculating the excitation spectrum for different sets of DM couplings, I studied the effect of anisotropies. Finally, choosing a realistic set of parameters – known from previous works – I have shown that the bond-wave excitations fit extremely well the electron spin resonance [Nojiri 2003] and far infrared spectra [Rõõm 2004].

In $Ba_2CoGe_2O_7$, the 3/2 spin of the cobalt ions allows for quadrupole and octupole degrees of freedom. In the Hamiltonian exchange and single-ion anisotropies, DM coupling and g-tensor anisotropy were included. To study the effects of such terms on the ground state, I mapped out the variational phase diagrams as the function of easy-plane anisotropy and magnetic field at various values of the exchange anisotropy and discussed the properties of the emerging phases, such as magnetization plateaus, superfluid and supersolid states. To give a theoretical description of the high energy excitations observed in THz absorption spectroscopy [Kézsmárki 2011], I performed a multiboson spin wave method which can describe excitations with quadrupole and octupole characteristics along with the usual magnons that appear in the conventional spin wave approach. Calculating the dispersion relation we find that the lower magnetic excitations are in quantitatively good agreement with the neutron scattering experiment [Zheludev 2003], and in addition higher modes appear, one with longitudinal and another with transversal spin fluctuations. Applying finite magnetic field, based on the optical spectroscopy measurements below 12 T, I predicted quantitatively the excitation spectrum which proved to be in good agreement with the high-field measurements up to 33 T. By calculating the dielectric and magnetic dynamic susceptibilities, the nature of the excitations were discussed. In addition, the magnetic field dependence of the magnetic order induced polarization in $Ba_2CoGe_2O_7$ have been considered for a better understanding of the experiments [Murakawa 2010].

The main results of my work are summarized in the following thesis statements.

Thesis statements

1.

I showed that the generalized spin wave method is suitable to quantitatively reproduce the experimentally observed magnetic field dependent excitation spectrum of the orthogonal dimer compound, $SrCu_2(BO_3)_2$. To obtain the correct spectrum one needs to allow for the singlet state to mix with all three triplet components – this goes beyond the usual perturbation approach, where only two states per dimers are kept. Furthermore, the finite-field gap in the perturbational approach is proportional to the intradimer Dzyaloshinsky-Moriya coupling D, while the generalized spin wave method gives a gap proportional to $D^{1/2}$, resulting in a spectrum which is in agreement with the experimental results.[1]

2.

On bipartite lattices with larger spins (S>1/2) the competition of strong single-ion axial anisotropy, the exchange anisotropies, and the off-diagonal exchange support the formation of magnetic supersolid states in finite magnetic field perpendicular to the easy plane. I determined the phase diagram of such an S=3/2 model: When the off-diagonal exchange is zero the phase diagram is characterized by axial antiferromagnetic, ferromagnetic and plateau phases. The supersolid phase emerges in the vicinity of the translational symmetry breaking axial plateau states when the off-diagonal exchange is finite, but smaller than the diagonal one. Between the supersolid and axial phases spin-rotational symmetry breaking superfluid phase is found. When the exchange interaction is isotropic, but the single-ion anisotropy still breaks the SU(2) symmetry, the plateau islands and their supersolid rim are washed away by the superfluid phase.[2]

3.

I pointed out the essential role of the out-of plane Dzyaloshinsky-Moriya interaction for the description of the in-plane magnetic field dependence of the magnetic order induced electric polarization in the multiferroic compound $Ba_2CoGe_2O_7$ at zero temperature. Depending on its direction, one of the two degenerate canted antiferromagnetic states is selected, changing the polarization curve drastically. Furthermore, including an antiferro polarization-polarization term in the Hamiltonian, along with the Dzyaloshinsky-Moriya interaction, can account for the sharp low field (≤ 1 T) decay in the curve of the induced polarization.[3]

4.

I showed that along with the lower lying magnetic excitations, available by the usual Holstein-Primakoff spin wave theory, the high-energy (~1THz) modes observed in $Ba_2CoGe_2O_7$ up to 33 T can be quantitatively reproduced in terms of generalized spin waves. As the Hilbert space of a spin S=3/2 is sufficiently large, these modes exhibit quadrupole and octupole characteristics in a natural way, and the non-centrosymmetric property of $Ba_2CoGe_2O_7$ enables them to be excited by the electric component of the incident light. In the multiferroic ground state the length of the spins is less than 3/2, consequently two of the high-energy modes are longitudinal excitations, in contrast to the usual spin wave method, where the magnons are associated with transverse fluctuations.[4,5]

List of publications

[1] J. Romhányi, K. Totsuka, K. Penc,
Effect of Dzyaloshinskii-Moriya interactions on the phase diagram and magnetic excitations of $SrCu_2(BO_3)_2$
Phys. Rev. B **83**, 024413 (2011)

[2] J. Romhányi, F. Pollmann, K. Penc
Supersolid phase and magnetization plateaus observed in the anisotropic spin-3/2 Heisenberg model on bipartite lattices
Phys. Rev. B **84**, 184427 (2011)

[3] J. Romhányi, M. La jkó, K. Penc
Zero- and finite-temperature mean field study of magnetic field induced electric polarization in $Ba_2CoGe_2O_7$: Effect of the antiferroelectric coupling
Phys. Rev. B **84**, 224419 (2011)

[4] K. Penc, J. Romhányi, T. Room, U. Nagel, Á. Antal, T. Fehér, A. Jánossy, H. Engelkamp, H. Murakawa, Y. Tokura, D. Szaller, S. Bordács, I. Kézsmárki
Spin-stretching modes in non-centrosymmetric magnets: spin-wave excitations in the multiferroic Ba2CoGe2O7
arXiv:1202.3996 (2012)
accepted in Phys. Rev. Lett.

[5] Judit Romhányi and Karlo Penc
Multiboson spin-wave theory for $Ba_2CoGe_2O_7$, a spin-3/2 easy-plane Neel antiferromagnet with strong single-ion anisotropy
arXiv:1205.2196 (2012)
submitted to Phys. Rev. B

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