Magnetic properties, phase transitions and critical behavior of quasi-two dimensional systems : studies on several layered copper compounds
by Ping Zhou

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University

Abstract:
The reorientation of the sublattice magnetizations from the antiferromagnetic (AF) to the spin-flop (SF) phase is studied by magnetization measurements on new anisotropic Heisenberg quasi-two dimensional antiferromagnets [C6H5(CH2)nNH3]2CuBr4 with n = 1, 2 and 3. The isothermal magnetic phase diagrams along the spin principal axes are obtained, and an analysis from the mean-field theory yields (for the n = 1) J1 = 25.49 K/kB and Jn = 25.45 K/kB for the intralayer perpendicular and parallel exchange components, respectively. A weak antiferromagnetic interlayer interaction and a relatively strong uniaxial anisotropy with the easy axis within the layer are found. Evidence for a possible existence of an intermediate (IN) phase between the AF and SF phase and a comparison for the magnetic phase boundaries between the mean-field calculations and experimental data are presented. Spin-canting effect along the easy and intermediate axes is seen in the isotherms. It is suggested from the results of the isothermal measurements that a competition between the antisymmetric exchange and Zeeman energy above the SF critical field may lead to a "fan" phase which may persist up to a triple point along the intermediate axis while a competition between the inter- and intralayer exchange anisotropies leads to an intermediate phase which can persist up to a tetracritical point along the easy axis. Thermodynamic considerations near the phase boundaries are also discussed. Critical exponent γ and transition temperature Tc were determined by the measurements of a.c. initial susceptibility and critical isothermal magnetization. By employing the static scaling law to analyze the data of isothermal magnetizations near Tc, it was found that at a certain low field and low temperature regions the powder magnetizations are suppressed so that the scaling hypothesis no longer holds.

Zero-field a.c. susceptibility and isothermal magnetization of the quasi-2D systems (alkanediammonium copper tetrahalide series) [NH3(CH2)nNH3]CuX4 where n = 4,5,7 and 10 with X = Cl and Br are also reported. The 3D antiferromagnetic ordering at Tc for the Cl compounds is found. It is shown that the critical susceptibilities decay exponentially as the temperature increases (T > Tc). A power-law divergence in the Br compounds with n = 7 and 10 is seen. This behavior is characteristic of 3D ferromagnetic ordering at Tc. The critical exponent y for the initial susceptibility (T > Tc) has been obtained for these Br compounds. It is found that there is a second (minor) peak below Tc in the Br compounds with n = 5 and 7. The transition associated with this peak may be interpreted as a long range (spontaneous) ordering due to very small spin anisotropies, such as a spin canting effect between the layers. It is seen from the results of isothermal magnetization measurements for these Br compounds that the magnetization is suppressed as the field decreases as compared to the behavior of most 3D ferromagnets. The value of the critical exponent δ estimated from the isothermal data is considerably smaller than that given by the well-studied models. The apparent crossovers are seen in both the initial susceptibility and isothermal magnetization data in which a combination of the spatial- and spin-dimensionality crossovers may be present. To discuss the spin-dimensionality crossover in 2D systems, thermal and field perturbations away from the renormalization-group fixed point are considered in 2D conformal field theory. By applying the c-theorem, general expressions for the effective critical exponents ν , α and δ are obtained in terms of the central charge, the third moment of

energy and spin correlations, temperature and external field. These expressions may be described as critical behavior and crossover phenomena for the 2D systems away from the critical points.

MAGNETIC PROPERTIES, PHASE TRANSITIONS AND CRITICAL BEHAVIOR OF QUASI-TWO DIMENSIONAL SYSTEMS: STUDIES ON SEVERAL LAYERED COPPER COMPOUNDS

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the college of Graduate Studies.

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ABSTRACT

The reorientation of the sublattice magnetizations from the antiferromagnetic (AF) to the spin-flop (SF) phase is studied by magnetization measurements on new anisotropic Heisenberg quasi-two dimensional antiferromagnets [$C_6H_5(CH_2)_nNH_3]_2CuBr_4$ with n = 1, 2 and 3. The isothermal magnetic phase diagrams along the spin principal axes are obtained, and an analysis from the mean-field theory yields (for the n = 1) $J_\perp = 25.49\ K/k_B$ and $J_\parallel = 25.45\ K/k_B$ for the intralayer perpendicular and parallel exchange components, respectively. A weak antiferromagnetic interlayer interaction and a relatively strong uniaxial anisotropy with the easy axis within the layer are found. Evidence for a possible existence of an intermediate (IN) phase between the AF and SF phase and a comparison for the magnetic phase boundaries between the mean-field calculations and experimental data are presented. Spin-canting effect along the easy and intermediate axes is seen in the isotherms. It is suggested from the results of the isothermal measurements that a competition between the antisymmetric exchange and Zeeman energy above the SF critical field may lead to a "fan" phase which may persist up to a triple point along the intermediate axis while a competition between the inter- and intralayer exchange anisotropies leads to an intermediate phase which can persist up to a tetracritical point along the easy axis. Thermodynamic considerations near the phase boundaries are also discussed. Critical exponent γ and transition temperature T_c were determined by the measurements of a.c. initial susceptibility and critical isothermal magnetization. By employing the static scaling law to analyze the data of isothermal magnetizations near T_c, it was found that at a certain low field and low temperature regions the powder magnetizations are suppressed so that the scaling hypothesis no longer holds.

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CHAPTER I

INTRODUCTION

It is well known that uniaxial antiferromagnets exhibit a bicritical point at a finite magnetic field $\overrightarrow{H}$ parallel to the easy axis. Many of the theoretical predictions, particularly from mean-field theory, renormalization group approach and high-temperature series expansions, concerning the bicritical phase diagram have been confirmed by the experiments. In general, it is expected that weakly anisotropic uniaxial antiferromagnets in a magnetic field $\overrightarrow{H}$ parallel to the easy axis should exhibit a multicritical point at some finite, nonzero value of $\overrightarrow{H}$. The existence of a bicritical or tetracritical point in the uniaxial antiferromagnets is usually determined by the fourth-order spin anisotropy in the Hamiltonian.[1,2] Studies of phase transitions in magnetism have contributed to the understanding of many aspects of other physical systems through the analogy with spin models. A typical example is the study, within mean-field theory, of the supersolid phase in the quantum lattice gas model.[3,4] The supersolid phase introduced in the early 70's is a state in which there coexists both diagonal (crystalline) long-range order and off-diagonal (superfluid) long-range order.[3-8] This phase was first observed experimentally by Rudnick *et al.*[9] and Goodstein *et al.*[10] who showed that a thin film of ^{4}He undergoes a transition from the superfluid phase to the solid phase with no latent heat, implying that there is no first-order phase transition between the superfluid and crystalline states. This model can be represented by the standard boson Hamiltonian in second-quantized form. In this form the Hamiltonian is fully analogous to that of anisotropic Heisenberg spin systems.[3,4,8] We refer here to an anisotropic (biaxial) Heisenberg spin system with two types of exchange interactions, $J(J_x, J_y, J_z)$ and $J'(J'_x, J'_y, J'_z)$. There may exist an intermediate (IN) phase between the spin flop (SF) and antiferromagnetic (AF) phases due to a competition between the interlayer and intralayer exchange anisotropies, which would correspond to the supersolid phase in the quantum lattice gas.

However, the spin system corresponding to the quantum crystal has many aspects which are different from the usual uniaxial antiferromagnets mentioned at the beginning: (a) the system is of biaxial anisotropic form (anisotropic Heisenberg or XYZ-like); (b) the system contains two types of exchange interactions (J and J'); and (c) the spin Hamiltonian contains only linear (Zeeman) and quadratic (exchange) terms. Thus, an important question may remain unresolved: is it possible to confirm this intermediate phase experimentally in quasi-two dimensional spin-1/2 anisotropic Heisenberg antiferromagnets at a finite temperature ? In this work, as a part of the main purpose of this thesis, we strongly suggest that an intermediate phase may exist in the quasi-two dimensional anisotropic Heisenberg systems with strongly ferromagnetic intralayer exchange and weakly antiferromagnetic interlayer exchange. It may be possible to verify this phase in a large variety of layer-type magnetic metallate compounds since a rich variety of nonmagnetic organic cations produce large and variable separation between the magnetic metallate layers. In this thesis, the reorientation of the sublattice magnetizations from the antiferromagnetic to the spin-flop phase is studied by magnetization measurements on new anisotropic Heisenberg quasi-two dimensional antiferromagnets $[C_6H_5(CH_2)NH_3]_2CuBr_4$ (n = 1 and 2). The isothermal magnetic phase diagrams along the spin principal axes are obtained. Evidence for a possible existence of an intermediate phase between the AF and SF phases and a comparison of the magnetic phase boundaries between the mean-field calculations and experimental data are presented.

The other major part of this thesis contributes to the study of the critical behavior of quasi-2D systems. One of the most fundamental quantities which is used to characterize the nature of magnetic systems near a critical region is the spin-spin correlation function, $\langle S(r)S(0)\rangle$. It does not decay to zero as $r \to \infty$ once long range order exists. Thus, in the critical region ($H_c = 0$), the initial (or staggered) susceptibility of a ferromagnet (or antiferromagnet) is expected to diverge like $\chi \sim (T/T_c - 1)^{-\gamma}$ as $T \to T_c$ ($T > T_c$). Divergent initial susceptibility quite often indicates the onset of an instability with the system starting to order spontaneously. Studies of initial susceptibility may provide direct evidence of anomalies that a system naturally display without involving any field-induced transitions. In the two-dimensional (2D) systems, however, it has been rigorously proven that no long-range order can exist at any nonzero temperature for the ideal (Heisenberg) case [11]. Recently, theoretical studies have shown that even at zero temperature the existence of a long range order in 2D systems may require a certain spin anisotropy.[12-18] Therefore, whether or not there possibly exists a finite "critical" temperature indicated by an infinite initial susceptibility, but no long range order (no phase transitions), has been the subject of many theoretical and experimental studies. Based upon an analysis of the high-temperature susceptibility series (ratio method), Stanley and Kaplan [19] suggested that the combination $M_s = 0$ and $\chi \to \infty$ is possible in 2D Heisenberg systems if the spin correlation function decreases slowly enough with spin separation r specifically like $r^{-\lambda}$ with $0 < \lambda < 2$. Subsequently, a finite critical temperature was conjectured to exist for the 2D XY and planar magnets too.[20-22] Experimentally it has been found that the quasi-2D systems in fact exhibit a finite critical temperature related to a long range order.[23,24] It has been suggested that the experimentally observed long range order is due to a consequence of the presence of a small anisotropy, interlayer coupling or even of the finite size of the sample. Thus, it seems to be difficult to examine the conjecture of Stanley and Kaplan directly since even minute deviations from ideality will cause the behavior near the T_c to be no longer characteristic of the 2D Heisenberg case. The finite T_c and degree of divergence (γ) in the initial susceptibility as $T \rightarrow T_c$ may play the important role in indicating the existence of a phase transition for the various realistic systems.

Zero-field a.c. susceptibility and isothermal magnetization of the quasi-2D systems (alkanediammonium copper tetrahalide series) $[NH_3(CH_2)_nNH_3]CuX_4$ where n = 4, 5, 7 and 10 with X = Cl and Br are reported in this work. The 3D antiferromagnetic ordering for the Cl compounds is found. It is shown that the critical susceptibilities decay exponentially as the temperature increases ($T > T_c$). A power-law divergence in the Br compounds with n = 7 and 10 is seen. This behavior is characteristic of 3D ferromagnetic ordering at T_c. The critical exponent γ for the initial susceptibility ($T > T_c$) has been obtained for these Br compounds. It is found that there is a second (minor) peak below T_c in the Br compounds with n = 5 and 7. The apparent crossovers are seen in both the initial susceptibility and the isothermal magnetization data in which a combination of the spatial- and spin-dimensionality crossovers is present.

In the next chapter, the basic theories will be shortly reviewed. The remainder of that chapter is devoted to an understanding of the basic ideas in this work. Mean-field theory of quasi-2D spin-1/2 anisotropic Heisenberg antiferromagnets will be presented in chapter III. A generalized form of the mean-field approximation for a bilinear spin interaction system is outlined. Following the work of Van Wier *et al.*,[25] the complete solutions of the quasi-2D, anisotropic, Heisenberg antiferromagnets at T=0 are discussed and finite temperature phase diagrams are derived. Liu and Fisher's[3] analysis of a supersolid phase in the quantum lattice gas is directly applied to study of an intermediate phase in the quasi-2D spin-1/2 anisotropic Heisenberg systems. The effect of spin-canting at the transition between the spin-flop and the antiferromagnetic phases are also discussed. The necessary formulae for carrying out a numerical calculation are given. In the chapter IV, experimental studies on the magnetic properties, phase transitions, phase diagrams and critical behavior of the layer compounds $[C_6H_5(CH_2)_nNH_3]_2CuBr_4$ (n = 1, 2 and 3) will be fully reported. Initial susceptibility and isothermal magnetization studies on $[NH_3(CH_2)_nNH_3]CuX$ with n = 4, 5, 7 and 10 for X = Cl_4 and Br_4 are given in chapter V. Spin-dimensionality crossover is also discussed.

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